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Application of POCOP Pincer Nickel Complexes to the Catalytic Hydroboration of Carbon Dioxide

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Abstract: The reduction of CO_2 is of great importance. In this paper, different types of bis(phosphinite) (POCOP) pincer nickel complexes, [2,6-$(R_2PO)_2C_6H_3$]NiX (R = ^{t}Bu, ^{i}Pr, Ph; X = SH, N_3, NCS), were applied to the catalytic hydroboration of CO_2 with catecholborane (HBcat). It was found that pincer complexes with ^{t}Bu$_2$P or ^{i}Pr$_2$P phosphine arms are active catalysts for this reaction in which CO_2 was successfully reduced to a methanol derivative (CH_3OBcat) with a maximum turnover frequency of 1908 h^{-1} at room temperature under an atmospheric pressure of CO_2. However, complexes with phenyl-substituted phosphine arms failed to catalyze this reaction—the catalysts decomposed under the catalytic conditions. Complexes with ^{i}Pr$_2$P phosphine arms are more active catalysts compared with the corresponding complexes with ^{t}Bu$_2$P phosphine arms. For complexes with the same phosphine arms, the catalytic activity follows the series of mercapto complex (X = SH) $\approx$ azido complex (X = N_3) >> isothiocyanato complex (X = NCS). It is believed that all of these catalytic active complexes are catalyst precursors which generate the nickel hydride complex [2,6-$(R_2PO)_2C_6H_3$]NiH in situ, and the nickel hydride complex is the active species to catalyze this reaction.

Keywords: nickel catalyst; hydroboration; carbon dioxide; catecholborane; pincer complex; mercapto complex; azido complex; isothiocyanato complex

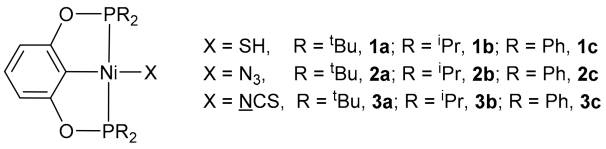
1. Introduction

The development of effective chemical processes that catalytically convert carbon dioxide to valuable compounds has received a great deal of attention recently [1–6]. Of the various chemical transformations investigated, catalytic reduction of CO_2 to methanol (MeOH) is of particular interest because the latter is a very important commodity chemical and can be used as a type of clean fuel. Over the last 20 years, great efforts have been made to reduce CO_2 to MeOH or its derivatives [5–13]. Specifically, significant progress or breakthroughs have been achieved in metal catalyzed homogeneous conversion of CO_2 to MeOH [14–29].

As an earth-abundant cost-effective late transition metal, nickel has been extensively used to catalyze a variety of chemical transformations since the last century. Nowadays, homogeneous nickel catalysis is becoming more and more important in modern synthetic chemistry because of the diverse novel catalytic reactivities of nickel complexes [30–32].

We have been interested in the chemistry of transition metal complexes bearing bis(phosphinite) (POCOP) pincer ligands [14,15,26,27,33–38]. Recently, we applied some POCOP pincer nickel thiolato complexes, [2,6-$(R_2PO)_2C_6H_3$]NiY (R = ^{t}Bu, ^{i}Pr; Y = SC_6H_4-*p*-OCH_3, SC_6H_4-*p*-CH_3, SPh, SC_6H_4-*p*-CF_3, SCH_2Ph), to the catalytic reduction of CO_2 with catecholborane (HBcat) [27]. Carbon dioxide was effectively reduced to CH_3OBcat under very mild conditions, and turnover frequencies (TOFs) up

to 2400 h^{-1} were observed. Although POCOP pincer nickel hydrides are also good catalysts for this reaction under the same conditions [14–16], the catalytic activity of the nickel thiolato complexes are better than that of the corresponding nickel hydride complexes. It was concluded that the thiolato complexes may work as pre-catalysts with the in situ generated nickel hydride complexes being the real active species. The superior catalytic activity of the thiolato complexes may be due to some in situ generated thiolato species that act as co-catalysts. To confirm this speculation, we initiated a more extensive study for this hydroboration reaction. In this paper, we used different types of POCOP pincer ligated nickel complexes with different phosphine arms and different auxiliary ligands, [2,6-$(R_2PO)_2C_6H_3$]NiX (Scheme 1), to catalyze this reaction under the same conditions. It was found that pincer complexes with $^tBu_2P$ or $^iPr_2P$ arms are active catalysts and CO_2 was reduced to CH_3OBcat at room temperature under an atmospheric pressure of CO_2. Turnover frequencies up to 1908 h^{-1} were observed. Complexes with $^iPr_2P$ arms are more active catalysts compared with the corresponding complexes with $^tBu_2P$ arms. For complexes with the same phosphine arms, the catalytic activity follows the series of mercapto complex (X = SH) ≈ azido complex (X = N_3) >> isothiocyanato complex (X = NCS). The results are consistent with the speculation that these different types of pincer nickel complexes are catalyst precursors and the in situ generated pincer nickel hydrides are the actual active species to catalyze the hydroboration of carbon dioxide with catecholborane.

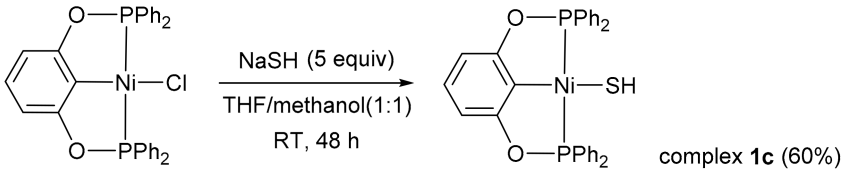


Scheme 1. The nickel complexes used for the catalytic hydroboration of CO_2 with HBcat.

2. Results and Discussion

2.1. Synthesis and Characterization of the Ni Catalysts

Complexes **1a** [37], **1b** [38], **2a–c** [35] and **3a–c** [35] were synthesized as described in the literatures. Complex **1c** has never been reported before and was synthesized by the reaction between [2,6-$(Ph_2PO)_2C_6H_3$]NiCl and NaSH in THF/methanol at room temperature (Scheme 2). As a new complex, **1c** was fully characterized by nuclear magnetic resonance spectroscopy (NMR), Fourier Transform infrared spectroscopy (FTIR), X-ray crystallography and elemental analysis.



Scheme 2. Synthesis of complex **1c**.

Complex **1c** is an air-sensitive orange solid and is soluble in toluene and dichloromethane. The ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra of **1c** were in good agreement with the structure depicted in Scheme 2. Complex **1c** showed the expected spectra characteristics for a POCOP pincer ligated nickel complex [14–16,27,33–42]. Similar to other reported transition metal mercapto complexes [37,38,43–45], the ^1H NMR resonance of the –SH proton of **1c** appeared in a relatively high-field (−0.76 ppm) as a triplet. An H–P coupling constant of 19.7 Hz was observed. The $^{31}P\{^1H\}$ NMR spectrum of **1c** displayed one singlet, implying an identical chemical environment for the two phosphine arms in solutions. The FTIR spectrum of **1c** displayed a weak absorption at 2546 cm^{-1} which was attributed to the S–H stretching vibration.

Single crystals of **1c** used for X-ray diffraction analysis were obtained by recrystallization in *n*-hexane/CH_2Cl_2 solution at −10 °C. The identity of the crystals was affirmed by $^{31}P\{^1H\}$ NMR spectroscopy. The diffraction experiment was carried out at 103 K using a Bruker SMART6000 CCD diffractometer (Bruker Corporation, Karlsruhe, Germany). The molecular structure of **1c** is shown in Figure 1 and the selected bond lengths and angles are also provided.

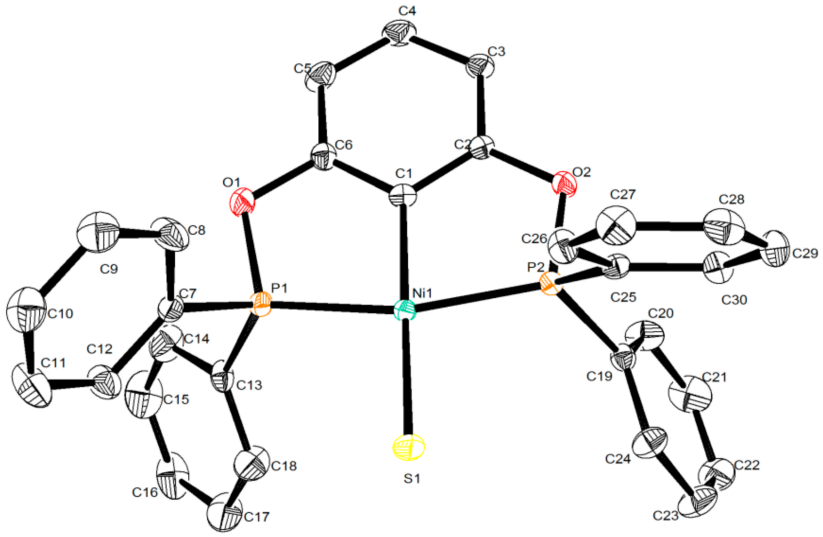


Figure 1. Thermal ellipsoid plots of complex **1c** at the 50% probability level (hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg): Ni1–C1, 1.890(2); Ni1–P1, 2.1389(8); Ni1–P2, 2.1456(8); Ni1–S1, 2.1852(7); P1–Ni1–P2, 164.13(3); S1–Ni1–C1, 177.33(8); P1–Ni1–S1, 98.78(3); P2–Ni1–S1, 97.00(3).

As shown in Figure 1, the square-planar geometry for the Ni center of **1c** is distorted; this is quite common for POCOP pincer nickel complexes [14–16,27,33–42]. Both the C_{ipso}–Ni and Ni–S bond lengths in complex **1c** are comparable to those of the related pincer nickel mercapto complexes with $^tBu_2P$ or $^iPr_2P$ arms [37,38]. This indicates that the C_{ipso}–Ni and Ni–S bond strengths are not considerably affected by the substituents on the phosphine arms.

2.2. Catalytic Hydroboration of CO_2 with HBcat

In order to check the catalytic activities, a NMR tube reaction was carried out for each of the nickel complexes. Typically, the nickel complex (0.01 mmol) was mixed with HBcat (0.3 mmol) in C_6D_6 (0.5 mL) in a NMR tube under a N_2 atmosphere. Carbon dioxide was then introduced and the reaction was monitored by NMR spectra at room temperature. For complexes **1a**, **1b**, **2a**, **2b** and **3b**, the ^{11}B NMR spectra showed that HBcat was completely or partly consumed in 30 min. CH_3OBcat and catBOBcat were formed as evidenced by the two singlets at 23.6 and 22.6 ppm [14,26,27,46,47] in the ^{11}B NMR spectra (see Figure 2 for example, the representative ^{11}B NMR spectra for the interactions of the nickel complexes with HBcat under CO_2). The formation of CH_3OBcat was also confirmed by the singlet at 3.36 ppm [14,26,27,46] in the ^1H NMR spectra. Similar to the hydroboration of CO_2 with HBcat using the related nickel thiolato complexes as the catalysts [27], the $^{31}P\{^1H\}$ NMR spectra were too complex to be understood—many unidentified species were shown. For complex **3a**, no reaction was observed after 60 min at temperatures up to 60 °C as evidenced by the $^{31}P\{^1H\}$ NMR spectra. For complexes **1c**, **2c** and **3c**, black precipitate developed in 10 min and the $^{31}P\{^1H\}$ NMR spectra showed that the original nickel complexes decomposed completely; neither CH_3OBcat nor catBOBcat were detected by the NMR spectra.

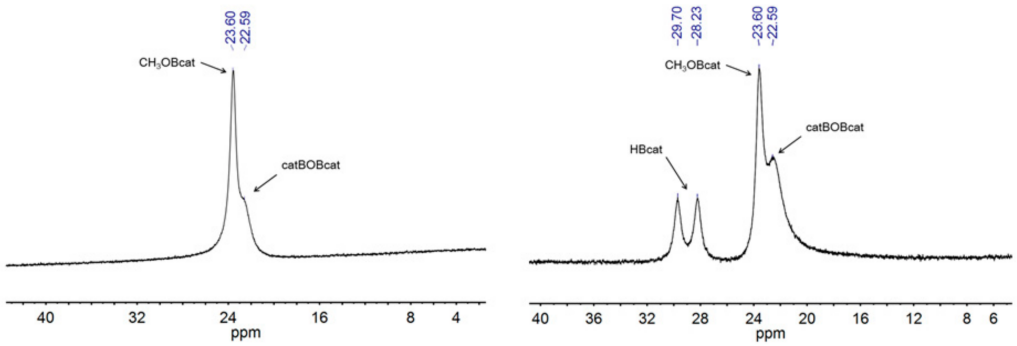


Figure 2. ^{11}B NMR spectra for the interactions of the nickel complexes (0.01 mmol) with HBcat (0.3 mmol) in benzene-d_6 (0.5 mL) under a CO_2 atmosphere at room temperature. The spectra were recorded 30 min after carbon dioxide was introduced into the NMR tube. (**left**, interaction of complex **1b** with HBcat; **right**, interaction of complex **3b** with HBcat).

The above NMR tube reactions indicate that complexes **1a**, **1b**, **2a**, **2b** and **3b** are active catalysts for the hydroboration of CO_2 with HBcat under mild conditions (Scheme 3).

$$CO_2\ (1\ atm)\ +\ 3\ HBcat \xrightarrow[C_6D_6,\ RT]{0.2\%\ [Ni]} CH_3OBcat\ +\ catBOBcat$$

[Ni] = **1a**, **1b**, **2a**, **2b** or **3b**

Scheme 3. Catalytic hydroboration of CO_2 with HBcat.

Flask reactions were carried out to further evaluate the catalytic activities of these complexes. Typically, the nickel complex (0.01 mmol), HBcat (5 mmol) and $C_6(CH_3)_6$ (0.02 mmol, internal standard) were dissolved in benzene-d_6 (4 mL) under a nitrogen atmosphere. The solution was stirred at room temperature and CO_2 was bubbled through the solution at the same time. The reaction was stopped after a large amount of white precipitate developed. The reaction mixture was filtered and the clear liquid was analyzed by NMR spectroscopy. When complexes **3a** and **3b** were used as the catalysts, no white precipitate developed and the reaction was stopped after 2 h.

The isolated white precipitate was confirmed to be catBOBcat [14,26,27,46,47]. The ^{11}B NMR spectra of the clear reaction solutions indicated that HBcat was completely (for the reactions catalyzed **1a**, **1b**, **2a** or **2b**) or partly (for the reaction catalyzed by **3b**) converted to CH_3OBcat and catBOBcat. No product was detected for the reaction catalyzed by **3a**. Based on the ^{1}H NMR integrations of the CH_3OBcat methyl resonance (3.36 ppm) and the $C_6(CH_3)_6$ methyl resonance (2.11 ppm), turnover number (TON) was calculated for each of the reactions. Table 1 summarizes the results of the above catalytic reactions. A representative ^{1}H NMR spectrum of the clear reaction solution that was used to determine the TON value is shown in Figure 3.

Table 1. Turnover number (TON) and turnover frequency (TOF) obtained from the catalytic hydroboration of CO_2 with HBcat catalyzed by [2,6-$(R_2PO)_2C_6H_3$]NiX complexes [1].

Catalyst	X	R	Time (min)	Conversion (%)	TON	TOF (h^{-1})
1a	SH	^{t}Bu	30	100	450 ± 19	900 ± 38
1b	SH	^{i}Pr	15	100	465 ± 15	1860 ± 60
2a	N_3	^{t}Bu	30	100	480 ± 11	960 ± 22
2b	N_3	^{i}Pr	15	100	477 ± 12	1908 ± 48
3a	NCS	^{t}Bu	120	0	0	0
3b	NCS	^{i}Pr	120	68	325 ± 17	163 ± 9

[1] Conditions: 0.01 mmol of catalyst, 5.0 mmol of HBcat, 0.02 mmol of $C_6(CH_3)_6$ (internal standard); 4 mL of benzene-d_6, 1 atm of CO_2, room temperature; TONs (based on HBcat) were calculated from the ^{1}H NMR spectra and averaged from two to three independent experiments; conversions were based on the ^{11}B NMR spectra.

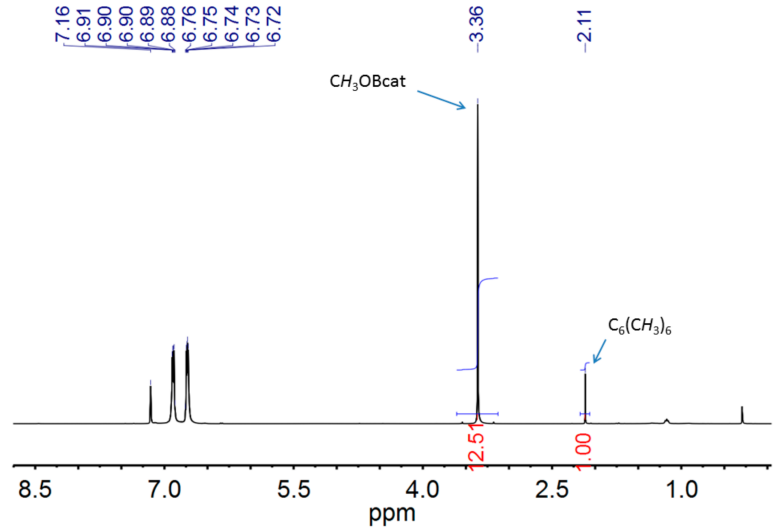


Figure 3. ^{1}H NMR spectrum for the hydroboration of CO_2 with HBcat catalyzed by complex **1a** in benzene-d_6.

It can be seen from Table 1 that the mercapto and azido complexes have quite similar activities in catalyzing the hydroboration of CO_2 with HBcat and the catalytic activities are comparable to those of the corresponding palladium [26] and nickel [27] thiolato complexes reported previously. Complexes with isopropyl-substituted phosphine arms are more active than the corresponding complexes with *tert*-butyl substituted phosphine arms. This is in good agreement with the previous observation for the hydroboration of CO_2 with HBcat using the related nickel thiolato complexes as the catalysts [26,27]. Isothiocyanato complexes are far less active than the corresponding mercapto and azido complexes.

We previously reported that POCOP pincer ligated nickel mercapto complexes with $^{t}Bu_2P$ or $^{i}Pr_2P$ arms (**1a** and **1b**) can interact with HBcat at room temperature to generate POCOP pincer nickel hydride species [38]. In order to obtain more information, we checked the interactions of the other complexes (**1c**, **2a**–**c** and **3a**–**c**) with HBcat. The nickel complexes were treated with an excess amount of HBcat in C_6D_6 at room temperature in a sealed NMR tube and the reactions were monitored by NMR. For the interaction of **2a** or **2b** with HBcat, the hydride species [2,6-$(R_2PO)_2C_6H_3$]NiH [48] was detected by the $^{31}P\{^{1}H\}$ NMR spectra in 20 min. For the interaction of **3b** with HBcat, the hydride species was also observed in 2 h. However, no reaction was detected for the interaction of **3a** with HBcat after 24 h. When **1c**, **2c** or **3c** was treated with HBcat, black precipitate developed in 20 min and the original complex decomposed partly as evidenced by the $^{31}P\{^{1}H\}$ NMR spectra.

It should be noted that POCOP pincer nickel hydride species with entirely phenyl substituted phosphine arms cannot be synthesized because of the instability of this type of hydride complexes [48]. Therefore, the hydride species were not likely formed for the interaction of **1c**, **2c** or **3c** with HBcat.

The above experimental results are consistent with the speculation that these different types of pincer nickel complexes are pre-catalysts for the hydroboration of CO_2 with HBcat and the in situ generated pincer nickel hydrides are the actual active species to catalyze this reaction. Any POCOP pincer nickel complexes that can generate POCOP pincer nickel hydrides under the catalytic conditions are active catalysts for the hydroboration of CO_2 with catecholborane. The easier the hydride species can be generated, the more active the catalyst. For the hydroboration of carbon dioxide with HBcat using pure nickel hydrides as the catalysts, less bulky substituents on the phosphine arms make the catalysts less active because of the formation of an inactive complex outside the catalytic cycle [14–16]. However, for the hydroboration of CO_2 with HBcat using a pre-catalyst, such as POCOP pincer ligated nickel thiolato, mercapto, azido or isothiocyanato complex, the catalytic activity is also dependent on the ease or the difficulty to generate the active hydride species. Smaller substituents on the phosphine arms make it easier to generate the active hydride species, although other issues, such as the electronic

nature of the substituents on the phosphine arms [39,49,50] and the bond disassociation energy of the Ni–S or Ni–N bond [34,35], may also play important roles. On the other hand, the in situ generated other species, such as thiolato, azido and isothiosyanato species, may act as co-catalysts for this hydroboration reaction.

3. Materials and Methods

3.1. General Information

All manipulations were performed under an inert gas atmosphere. Solvents were degassed and dried before use. C_6D_6 was distilled from sodium and benzophenone before use. A Bruker Advance 400 MHz spectrometer (Swiss Bruker Corporation, Faellanden, Switzerland) was used for the NMR studies. For ^{1}H and ^{13}C NMR spectra, the residual solvent resonances were used to calibrate the chemical shift values internally. For ^{31}P and ^{11}B NMR spectra, H_3PO_4 (85%) and $BF_3{\cdot}Et_2O$ were used, respectively, to reference the chemical shift (δ 0) externally. Complexes [2,6-$(Ph_2PO)_2C_6H_3$]NiCl] [51], **1a** [37], **1b** [38], **2a–c** [35] and **3a–c** [35] were prepared as described in the literatures.

3.2. Synthesis of [2,6-$(Ph_2PO)_2C_6H_3$]NiSH (**1c**)

THF (10 mL) and MeOH (10 mL) were added to a flask containing [2,6-$(Ph_2PO)_2C_6H_3$]NiCl (572 mg, 1 mmol) and NaSH (280 mg, 5 mmol). The flask was then sealed and the resulting mixture in the flask was stirred at room temperature. After 48 h, the reaction was stopped and the volatiles were removed under vacuum. The residue was extracted with toluene and filtered through a pad of Celite. Complex **1c** was obtained as an orange solid (341 mg, 60% yield) after the solvent of the combined extractions were removed under vacuum. ^{1}H NMR (400 MHz, benzene-d_6, δ): 8.03–8.08 (m, 8H, Ar*H*), 7.01 (t, 1H, Ar*H*, $J_{H–H}$ = 6.9 Hz), 6.94–7.00 (m, 12H, Ar*H*), 6.83 (d, 2H, Ar*H*, $J_{H–H}$ = 6.9 Hz), −0.76 (t, 1H, S*H*, $J_{H–P}$ = 19.7 Hz). ^{13}C{^{1}H} NMR (101 MHz, benzene-d_6, δ): 167.0 (t, Ar*C*, $J_{C–P}$ = 11.4 Hz), 135.5 (s, Ar*C*), 133.6 (t, Ar*C*, $J_{C–P}$ = 24.0 Hz), 132.6 (t, Ar*C*, $J_{C–P}$ = 7.2 Hz), 131.6 (s, Ar*C*), 129.6 (s, Ar*C*), 128.9 (t, Ar*C*, $J_{C–P}$ = 5.8 Hz), 106.7 (t, Ar*C*, $J_{C–P}$ = 7.2 Hz). ^{31}P{^{1}H} NMR (162 MHz, benzene-d_6, δ): 152.9 (s). Selected data from FTIR (KBr disc, cm^{-1}): 2546 (w), 1435 (s), 1106 (m), 838 (s). Anal. Calcd for $C_{30}H_{24}NiO_2P_2S$: C, 63.30; H, 4.25. Found: C, 63.07; H, 4.11.

3.3. X-ray Structure Determination of [2,6-$(Ph_2PO)_2C_6H_3$]NiSH (**1c**)

Single crystals of **1c** used for X-ray diffraction analysis were obtained from *n*-hexane/CH_2Cl_2 solution at −10 °C. The identities of the resulting crystals were confirmed by ^{31}P{^{1}H} NMR spectroscopy before the X-ray diffraction analysis. The intensity data were collected at 103 K on a Bruker SMART6000 CCD diffractometer. A graphite-monochromated Mo Kα radiation (λ= 0.71073 Å) was used for the data collection. Details for the data processing and structure refinement were similar to our previously reported procedures [37]. A summary of crystallographic data and structure refinement for complex **1c** is provided in Table 2.

CCDC 1869263 contains the supplementary crystallographic data for complex **1c**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre (The Cambridge Structural Database, Cambridge, UK).

3.4. Procedure for the Catalytic Hydroboration of CO_2

Flask experiments for the catalytic hydroboration of carbon dioxide were carried out at room temperature under an atmospheric pressure of carbon dioxide in benzene-d_6 with a catalyst-to-substrate ratio of 1:500. The nickel catalyst (0.01 mmol), HBcat (5.00 mmol), hexamethylbenzene (0.02 mmol) and benzene-d_6 (4 mL) were mixed in a flame-dried 50 mL Schlenk flask under N_2. Then CO_2 was bubbled through the solution until a large amount of white precipitate developed. The mixture was stirred for an additional 2 min. The resulting white precipitate was then allowed to settle, and 0.6 mL of the clear liquid was transferred under nitrogen into a NMR tube. ^{11}B and ^{1}H NMR spectra were

then recorded. The TON numbers were calculated based on the ^{1}H NMR integrations of the CH_3OBcat methyl resonance at 3.36 ppm and the $C_6(CH_3)_6$ (internal standard) methyl resonance at 2.11 ppm. The conversions were calculated from the ^{11}B NMR spectra.

Table 2. Summary of crystal data and structure refinement for complex **1c**.

Empirical formula	$C_{30}H_{24}NiO_2P_2S$	Volume, Å^3	2582.0(3)
Formula weight	569.20	Z	4
Temp, K	103(2)	d_{calc}, g cm^{-3}	1.464
Crystal system	Monoclinic	λ, Å	0.71073
Space group	P 1 21/c 1	μ, mm^{-1}	0.983
a, Å	14.9995(10)	No. of data collected	29,194
b, Å	9.9798(5)	No. of unique data	10,374
c, Å	17.2488(12)	R_{int}	0.0895
α (°)	90	Goodness-of-fit on F^2	1.003
β (°)	90.195(3)	R_1, wR_2 ($I > 2\sigma(I)$)	0.0583, 0.1182
γ (°)	90	R_1, wR_2 (all data)	0.1111, 0.1411

4. Conclusions

In summary, we have applied three different types of POCOP pincer nickel complexes (i.e., mercapto complex, azido complex and isothiosyanato complex) to the catalytic hydroboration of carbon dioxide with catecholborane. CO_2 was successfully reduced to a methanol derivative (CH_3OBcat) under an atmospheric pressure of CO_2 at room temperature with TOFs up to 1908 h^{-1}. It was found that pincer complexes with isopropyl-substituted phosphine arms are more active than the corresponding complexes with *tert*-butyl substituted phosphine arms. Complexes with phenyl-substituted phosphine arms decomposed under the catalytic conditions and failed to catalyze the reactions. Of the three types of complexes, the isothiosyanato complex is far less active than the corresponding mercapto and azido complexes. It is concluded that all of these catalytically active complexes are catalyst precursors which generate the nickel hydride complex [2,6-$(R_2PO)_2C_6H_3$]NiH in situ under the catalytic conditions, and the nickel hydride complex is the active species to catalyze this reaction.

Author Contributions: Conceptualization, J.Z.; Methodology, J.Z.; Validation, J.Z. and X.C.; Investigation, J.C., T.L., B.C. and Y.D.; Resources, J.Z. and X.C.; Data curation, X.C.; Writing—Original Draft Preparation, J.C, T.L. and B.C.; Writing—Review and Editing, J.Z.; Visualization, J.Z.; Supervision, J.Z. and X.C.; Project Administration, J.Z. and X.C.; Funding Acquisition, J.Z. and X.C.

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Conflicts of Interest: The authors declare no conflict of interest. The funder had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

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