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A bimetallic nickel-gallium complex catalyzes CO₂ hydrogenation via the intermediacy of an anionic d¹⁰ nickel hydride

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Abstract

Large-scale CO₂ hydrogenation could offer a renewable stream of industrially important C₁ chemicals while reducing CO₂ emissions. Critical to this opportunity is the requirement for inexpensive catalysts based on earth-abundant metals instead of precious metals. We report a nickel-gallium complex featuring a Ni(0) \rightarrow Ga(III) bond that shows remarkable catalytic activity for hydrogenating CO₂ to formate at ambient temperature (3150 turnovers, turnover frequency = 9700 h⁻¹), compared with prior homogeneous Ni-centered catalysts. The Lewis acidic Ga(III) ion plays a pivotal role in stabilizing catalytic intermediates, including a rare anionic d^{10} Ni hydride. Structural and *in-situ* characterization of this reactive intermediate supports a terminal Ni–H moiety, for which the thermodynamic hydride donor strength rivals those of precious metal-hydrides. Collectively, our experimental and computational results demonstrate that modulating a transition metal center via a direct interaction with a Lewis acidic support can be a powerful strategy for promoting new reactivity paradigms in base-metal catalysis.

Introduction

Efficient recycling of CO₂ to industrial chemicals and liquid fuels, such as formic acid or methanol, could generate value-added products from an abundant C1 feedstock while alleviating adverse effects associated with rising CO₂ levels. Although a CO₂-to-fuel scheme would require efficient CO₂ capture and sustainable H₂ production,¹ we focus on the singularly formidable challenge of developing base-metal catalysts for selective CO₂ hydrogenation under mild conditions.²⁻⁵ CO₂ hydrogenation to methanol remains a daunting task; the few known molecular catalysts rely almost exclusively on precious metals (Ru, Ir),⁶⁻ ¹¹ with only a single instance of a base-metal (Co) catalyst.^{6-10,12} Furthermore, base-metal catalysts remain uncommon for the hydrogenation of CO₂ to formate.¹³⁻¹⁷ In the past decade, impressive catalytic performance has been achieved using phosphine-ligated Fe and Co catalysts, which generate formate with turnover numbers (TONs) from 9000 to 59000 with high turnover frequencies (TOFs).¹⁸⁻²⁰

Despite the aforementioned recent advances of Fe and Co catalysts, the progress of Ni-based systems for CO₂ hydrogenation has been limited.²¹⁻²³ The first homogeneous Ni catalyst was reported over 40 years ago: Ni(dppe)₂, where dppe = bis(diphenylphosphino)ethane, produced formate from H₂ and CO₂, albeit with poor activity (TON = 7, TOF = 0.35 h^{-1}).²¹ Recently, a water-soluble Ni bis(diphosphine) catalyst mediated the H₂/CO₂-to-formate reaction in aqueous solution using NaHCO₃ as the base, but the activity remained low (TOF of $0.40(5) \text{ h}^{-1}$ at 80 °C and 34 atm of H₂/CO₂).²³ In related work, a Ni PCP-pincer catalyst generated formate from H₂ and NaHCO₃ with a comparatively impressive TON of 3000 at 150 °C and 54 atm; however, the catalyst was inactive when NaHCO₃ was replaced with CO₂.²⁴

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The dearth of Ni catalysts for CO₂ hydrogenation stems from several inherent limitations. Ni, being more electronegative than Fe and Co, has a lower propensity for binding and activating H₂ to generate Ni-H,²⁵ and once generated, the resulting Ni-H species are typically weak hydride donors. Furthermore, Ni-H complexes which are potent enough hydride donors to react with CO₂ tend to form strong Ni–O bonds which prevent formate liberation.²⁶This lack of strong hydride donors is illustrated by the fact that even for the most hydridic Ni–H reported, ²⁶ [HNi(dmpe)₂]⁺ (dmpe = bis(dimethylphosphino)ethane) with a thermodynamic hydricity ($\Delta G^{\circ}_{H^{-}}$) of 50.7 kcal/mol in CH₃CN, outer-sphere hydride transfer to CO₂ to generate free formate (*c.f.* $\Delta G^{\circ}_{H^{-}}$ = 44 kcal/mol) is thermodynamically unfavorable by \sim 7 kcal/mol in CH₃CN.^{27,28} However, it should be noted that there are several examples of Ni-H complexes which are sufficiently hydridic to react with CO_2 to form η^1 -O formate adducts of Ni.²⁶ In these cases, the more salient issue which precludes catalytic CO₂ hydrogenation is the formation of strong Ni–O bonds which impede formate release and thus prevent catalytic turnover. Catalytic liberation of CO₂ reduction products in these systems can be accomplished in some cases using stoichiometric boranes or silanes to form strong B-O or Si-O bonds which permit Ni-O bond cleavage and drive catalytic turnover. For example, Ni POCOP-pincer complexes can rapidly insert CO₂ into Ni-H bonds and further reduce CO₂ to methoxides using stoichiometric borane.²⁹ The requirement of B-H or Si-H reductants to drive catalysis, however, is a drawback in that the overall transformations lack atom economy.^{29,30}

Circumventing the inherent limitations of Ni in CO₂ hydrogenation would involve stabilizing Ni–H in more reduced charge states and/or lower Ni oxidation states,^{31,32} while still allowing the regeneration of Ni–H from H₂ and base.^{33,34} A highly reduced Ni center could potentially allow for both facile hydride transfer from a Ni–H species to CO₂, along with a decreased propensity for undesirably strong formate binding in the subsequent step.

Specifically, our strategy involves the incorporation of a Lewis acidic Ga(III) metalloligand which acts as a σ -acceptor toward Ni in NiGaL (1).³⁵⁻³⁸ We have previously shown that positioning the supporting Ga(III) ion directly *trans* to the substrate binding site at Ni allows for H₂ binding to form a non-classical H₂ adduct, (η^2 -H₂)NiGaL, under 1 atm H₂ (Fig. 1).^{39,40} In this combined experimental and theoretical study, we show that the Ga(III) support plays a vital role in stabilizing a d^{10} terminal Ni–H species which is strongly hydridic, with an estimated $\Delta G^{\circ}_{H^{-}}$ value of ~31 kcal/mol in CH₃CN that rivals those of precious metal-hydrides and allows for spontaneous reaction with CO₂ to generate and release formate.⁴¹ Taken together, the supporting Ga(III) ion modulates the properties of Ni so as to promote H₂ heterolysis and stabilize a highly reactive Ni–H species, affording a Ni catalyst capable of mediating efficient CO₂ hydrogenation to formate at room temperature.

Results and discussion

Catalysis

Under ambient conditions (1 atm 1:1 H₂/CO₂, 293 K), complex **1** catalyzes CO₂ hydrogenation to formate in 91% yield (0.36 mol% catalyst loading; Table 1, entry 1). A stoichiometric base is necessary for formate production, and high yields were obtained using Verkade's proazaphosphatrane, 2,8,9-triisopropyl-2,5,8,9-tetraaza-1- phosphabicyclo[3,3,3]undecane (abbrev. as Vkd).^{42,43} Catalyst performance was further optimized by increasing the H₂/CO₂ pressure to 34 atm and decreasing the catalyst loading by ten-fold to 0.03 mol%, which gave near quantitative generation of formate (Table 1, entries 2-3). The corresponding kinetic plot in Figure 2 shows that catalyst **1** attained 3150 formate turnovers in ~40 minutes with an initial TOF of 9700 h⁻¹. The high activity of **1** sharply contrasts that of prior Ni homogeneous catalysts (Table S3).^{21,23}

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A strong base is necessary for catalysis mediated by 1 based on trials with bases of varying strengths (p K_a of conjugate acid in CH₃CN): Vkd (33.6),⁴² *t*-butyl tetramethyl guanidine (abbrev. tBuTMG, 26.5),⁴⁴ and triethylamine (18.8).⁴⁵ Under identical conditions (1 mM 1, 34 atm 1:1 H₂/CO₂, 293 K), reactions with tBuTMG resulted in a lower yield of formate (80%) and a 30-fold decrease in the maximum rate (Table 1, *c*,*f*: entries 2 and 4). Moreover, an induction period of ca. 3 h was observed for tBuTMG (Fig. 2 inset, SI Fig. S9). Of relevance, an initial induction period was also reported for CO₂ hydrogenation catalyzed by HCo(dmpe)₂ using a base of comparable strength to tBuTMG.^{18,46} With NEt₃, an even weaker base, no formate was generated (entry 5). Presumably, NEt₃ is not sufficiently basic to deprotonate the H₂ adduct, (η^2 -H₂)NiGaL, precluding formation of the catalytically active Ni–H species (Fig. 1).

The striking effect of the supporting Ga(III) ion is appreciated by comparing 1 with the isostructural Ni-only congener, NiLH₃ (2).^{39,47} Basically, no formate was generated using 2 as the catalyst (entries 6-7). Adding GaCl₃ as a co-catalyst with 2 also did not yield any formate (entry 8). Altogether, the catalytic results suggest that an intact Ni \rightarrow Ga interaction (*vide infra*) within our ligand framework provides the requisite tuning effect at Ni to enable catalysis.

Isolating catalytic intermediates

Because of the remarkable CO₂ hydrogenation activity by **1** relative to known Ni homogeneous catalysts, we sought to elucidate the role of the supporting Ga(III) ion in promoting catalysis. Previously, the H₂ adduct, $(\eta^2$ -H₂)NiGaL, was characterized *in situ* using various NMR techniques. In this work, we targeted two later stage intermediates: the Ni(0) anionic hydride and the Ni(0) anionic formate adduct, which is formed after hydride transfer to CO₂ (Fig. 1). The anionic Ni(0) hydride, [VkdH][HNiGaL] ([VkdH][**3**]), was generated *in situ* by subjecting a THF-d₈ solution of **1** to 3-5 equiv. of Vkd and 1 atm of H₂. The ³¹P NMR spectrum displayed two new resonances at 76 and -12 ppm in a 3:1 ratio for the ion-paired [HNiGaL]⁻ and [VkdH]⁺ fragments, respectively (Fig. S10). The single ³¹P signal of **3** is consistent with retention of *C*₃ symmetry, while the hydride resonance in the ¹H NMR spectrum appears as a broad peak at -6.4 ppm with no discernible coupling even at low temperatures (Fig. S11-12). Of note, the ³¹P NMR spectrum of a close analogue, [K(THF)_x][**3**], resolves nicely into a doublet with ²*J*_{P-H} of 31.6 Hz (Fig. S16). Based on the spectroscopic data, we propose that the hydride ligand is terminally bound to the Ni center and resides in the apical pocket *trans* to the Ga(III) ion. In support, density functional theory (DFT) calculations predicted the terminal hydride to be more stable than the bridged Ni(μ -H)Ga isomer (Fig. S25, Table S6).

To validate the proposed structure of **3**, the bis(triphenylphosphine)iminium (PPN) analogue was independently prepared and investigated by single-crystal X-ray diffraction. The hydride species was synthesized by adding 1.1 equiv. nBuLi to **1**, presumably via an *in situ* Ni alkyl species that undergoes β -hydride elimination.²⁶ Subsequent salt exchange with [PPN][tetrakis[3,5-bis(trifluoromethyl)phenyl]borate] ([BArF]⁻) afforded [PPN][**3**]. Of note, the chemical shifts of the hydride and the phosphines in [PPN][**3**] are nearly identical to those of [VkdH][**3**], implying that [PPN][**3**] is a reasonable model of the catalytically relevant species (Fig. S15). From a THF/pentane solution of [PPN][**3**], bright-yellow single crystals were obtained that were suitable for X-ray diffraction. The structural characterization of [PPN][**3**] (Fig. 3) is noteworthy because anionic d^{10} hydride complexes are very rare.⁴⁸ The only other mononuclear anionic Ni(0) hydride is [Na(THF)₄][HNi(CO)₃], which is unstable at room temperature.⁴⁹ Moreover, **3** has catalytic utility in that it can be generated from H₂ and

base, which is in sharp contrast to the synthesis of [Na(THF)₄][HNi(CO)₃] where stoichiometric NaHAl(*i*-Bu)₃ is employed.

In comparison with NiGaL (1), [PPN][3] has subtle structural differences that are instructive to consider. One effect of the hydride donor is that the Ni–Ga bond contracts slightly from 2.3789(8) in 1 to 2.3549(7) Å in [PPN][3] (Fig. 3, Table S5).³⁹ Hence, the dative Ni–Ga interaction remains intact upon the introduction of a *trans* hydride. Perhaps the most informative parameter is the position of the Ni and Ga centers relative to their respective P₃ and N₃ donor sets. In [PPN][3], both Ni and Ga are displaced further above the P₃- and N₃-planes by 0.07 Å and 0.17 Å, respectively, than in 1. Intriguingly, the displacement of Ga is more than double that of Ni upon introduction of the hydride ligand despite the fact that the hydride only interacts directly with Ni. This striking structural feature underscores the cooperativity of the Ni-Ga unit, as both metals reposition to accommodate the incoming hydride ligand. A complementary interpretation is that a strong Ni–Ga dative interaction assists in stabilizing the electron-rich, anionic Ni–H moiety.

Next, we sought to characterize the anionic Ni formate intermediate, $[(HCO_2)NiGaL]^-$ (4), which appears in the catalytic cycle following hydride transfer to CO₂ (Fig. 1). The formate species, [VkdH][4], was generated *in situ* by exposure of [VkdH][3] to CO₂ (1 atm) or by addition of excess (~4 equiv.) $[VkdH][HCO_2]$ to **1**. A diagnostic ¹H NMR resonance at 8.68 ppm is assigned to the proton of the coordinated formate (*c.f.* 8.79 ppm for free [VkdH][formate], Fig. S20). This intermediate was also isolated as the PPN ion-pair by exposing [PPN][3] to CO₂. The solid-state structure of the resulting complex, $[PPN][(HCO_2)NiGaL]$ ([PPN][4]), shows an η^1 -*O* formate ligand and an intact Ni–Ga bond of 2.3789(5) Å, which is essentially identical to that of **1** (Fig. 3, Table S5).

Understanding the Ni(0) hydride intermediate (3)

To gain additional insight into the nature of the Ni(0)–H bond, we undertook a complementary experimental and theoretical investigation of [HNiGaL]⁻. By IR spectroscopy, a KBr pellet of [PPN][**3**] displayed a broad band of medium intensity at 1696 cm⁻¹, which shifted to 1226 cm⁻¹ upon deuteration (Fig. S26). The Ni–H vibrational frequency was further confirmed by a closely matched value of 1697 cm⁻¹ from DFT calculations (Fig. S27). Of note, this frequency value is extremely low for terminal hydrides of Ni, and nearly ties with CpNi(IMes)H (1695 cm⁻¹) for the lowest Ni–H stretching frequency.^{26,50}

Another useful parameter for comparing the reactivity of metal hydride complexes is the thermodynamic hydricity ($\Delta G^{\circ}_{H^{-}}$), or the free energy needed to cleave a M–H bond to generate a hydride ion.^{41,51} The $\Delta G^{\circ}_{H^{-}}$ of [HNiGaL]⁻ was experimentally determined by measuring the H₂ heterolysis equilibrium with NiGaL and Vkd base [equation (1)], in conjunction with the known pK_a of VkdH⁺ [equation (2)] and the H₂ heterolysis constant [known in CH₃CN, equation (3)], as shown below.^{27,41}

	$[HNiGaL]^{-} \rightleftharpoons NiGaL + H^{-}$	$\Delta G^{\circ}_{\mathrm{H}^{-}} = \Delta G^{\circ}_{1} + \Delta G^{\circ}_{2} + \Delta G^{\circ}_{3}$
(3)	$H_2 \rightleftharpoons H^+ + H^-$	$\Delta G^{\circ}_3 = +76 \text{ kcal/mol}$
(2)	$Vkd + H^+ \rightleftharpoons VkdH^+$	$\Delta G^{\circ}_2 = -1.364(\mathrm{p}K_\mathrm{a})$
(1)	$[HNiGaL]^{-} + VkdH^{+} \rightleftharpoons NiGaL + H_2 + Vkd$	$\Delta G^{\circ}_{1} = -\operatorname{RTln}(K_{eq})$

As hydricity values are typically measured in CH₃CN since ΔG°_{3} is known [equation (3)], one caveat to estimating the absolute hydricity of [HNiGaL]⁻ is that K_{eq} of equation (1) was measured in THF due to complications arising from poor solubility of NiGaL in CH₃CN and competitive binding between H₂ and CH₃CN (see SI). K_{eq} of equation (1) was measured to be 0.16 in THF based on two independent trials employing different base concentrations. If K_{eq} of equation (1) is comparable in THF and CH₃CN solvents, one can estimate $\Delta G^{\circ}_{H^-} \approx$

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31.3(5) kcal/mol for [HNiGaL]⁻ in CH₃CN. Alternatively, one can rigorously measure the difference in $\Delta G^{\circ}_{H^-}$ values between [HNiGaL]⁻ and H₂ in THF [equations (1)-(2)]. This difference, or $\Delta G^{\circ}_{H^-}(3) - \Delta G^{\circ}_{H^-}(H_2)$, is -37.1(6) kcal/mol in THF, and of interest, is comparable to $\Delta G^{\circ}_{H^-}(3) - \Delta G^{\circ}_{H^-}(H_2)$ in CH₃CN of -45 kcal/mol, using the *estimated* $\Delta G^{\circ}_{H^-}(3)$ of 31 kcal/mol.

To further test the assumption that measuring K_{eq} of equation (1) in THF can lead to meaningful comparisons with $\Delta G^{\circ}_{H^{-}}$ values obtained wholly in CH₃CN, we probed the hydride-transfer equilibrium between 1 and HCo(dmpe)₂ (known $\Delta G^{\circ}_{H} = 36$ kcal/mol in CH₃CN). No hydride transfer to NiGaL was detected in THF over 10 days, suggesting that the $\Delta G^{\circ}_{H^{-}}$ value of [HNiGaL]⁻ is <33 kcal/mol (Fig. S33). In the reverse direction, essentially full consumption of [HNiGaL]⁻ and [Co(dmpe)₂]⁺ to give (CH₃CN)NiGaL and HCo(dmpe)₂ was observed within 3 days in 3:1 CH₃CN:THF, confirming that the lack of hydride transfer between HCo(dmpe)₂ and NiGaL was due to the greater thermodynamic stability of HCo(dmpe)₂ relative to [HNiGaL]⁻ rather than sluggish hydride transfer kinetics. Additionally, DFT studies of isodesmic hydride transfer between [HNiGaL] and [Ni(dmpe)₂]²⁺ in CH₃CN predicted a hydricity of 28-31 kcal/mol for [HNiGaL]⁻ that matches the experimental estimate (Table S11).³⁴ The importance of Ga(III) for stabilizing the anionic Ni-H is, perhaps, underscored by our inability to synthetically generate the $[H-NiLH_3]^$ analogue. We also note that we have not observed H₂ binding to NiLH₃ even at high pressure and low temperature (34 atm H₂, 193K) and have not observed H₂ deprotonation to give a $[H-NiLH_3]^-$ analogue using excess strong base (Vkd base or potassium tert-butoxide).

For comparison, $[\text{HNi}(\text{diphosphine})_2]^+$ complexes have hydricity values that range from 50 to 68 kcal/mol.⁴¹ With a considerably lower $\Delta G^\circ_{\text{H}^-}$ value (31 kcal/mol), $[\text{HNiGaL}]^$ is, by a wide margin, the strongest hydride donor of any Ni–H reported to date. The exceptional hydricity of $[\text{HNiGaL}]^-$ can be attributed to its anionic charge and the zero-valent

oxidation state of Ni, which is distinct from the cationic Ni(II) hydrides in the literature.²⁶ Notably, [HNiGaL]⁻ is among the strongest hydride donors of any first-row metal (*c.f.* HCo(P₄N₂), $\Delta G^{\circ}_{H^-} = 31.8$ kcal/mol),⁵² and is even on par with some of the more hydridic precious metal complexes, (e.g. HRh(diphosphine)₂, $\Delta G^{\circ}_{H^-} = 26-34$ kcal/mol).⁴¹ Of relevance to catalysis, the low $\Delta G^{\circ}_{H^-}$ of [HNiGaL]⁻ would allow for direct outer-sphere hydride transfer to CO₂ with a driving force of ~13 kcal/mol.²⁸ It should be noted, however, that the driving force in catalysis is likely greater for the conversion of [VkdH][**3**] and CO₂ to [VkdH][**4**] due to enthalpic contributions from subsequent Ni–O bond formation in the formate adduct after initial hydride transfer (*vide infra*).

Perhaps, the most unexpected feature of **3** is its stability as an anionic d¹⁰ hydride.⁴⁸ A simple bonding analysis between a d^{10} metal and H⁻ would require the M–H σ -antibonding orbital to be fully populated. Natural orbitals obtained from complete active space self-consistent field (CASSCF)⁵³ calculations, however, revealed a distinctly different bonding scheme. While the five Ni 3*d* orbitals are indeed doubly occupied, consistent with Ni(0), they show essentially no bonding to the hydride. Rather, the natural orbital involved in Ni–H σ -bonding has both metal contributions [29% Ni, primarily $4p_z$; 10% Ga] and substantial hydridic character [51% H(1*s*)] (Fig. 4, Table S13).

We further propose that the Ni \rightarrow Ga interaction is critical for stabilizing the Ni(0)–H bond because of the symbiotic nature of two σ -bonding interactions: (1) donation of hydride to Ni, via H(1s) \rightarrow Ni(4p_z/4s), and (2) donation from Ni to Ga, via Ni(3d_{z2}) \rightarrow Ga(4p_z/4s). This stabilization of the Ni(0)–H by Ga(III) can be interpreted as an *inverse trans influence* exerted by the Ga metalloligand,⁵⁴ which acts as a σ -acceptor^{55,56} toward Ni and strengthens the Ni–H bond directly *trans* to it ("pull-pull"). In support, a natural bond orbital analysis shows that the Ni \rightarrow Ga stabilization energy increases by 10 kcal/mol from NiGaL (1) to [HNiGaL]⁻(3) (Fig. S35, Table S14).⁵⁷

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Mechanistic insights

A simple catalytic cycle is proposed (Fig. 1): (1) H₂ binding to NiGaL forms (η^2 -H₂)NiGaL, (2) deprotonation by base generates [HNiGaL]⁻, (3) hydride transfer to CO₂ forms [(η^1 -HCO₂)NiGaL]⁻, and (4) liberation of formate regenerates NiGaL. This catalytic mechanism is commonly proposed, albeit typically with M(H)₂⁺ and a neutral M–H as the catalytic intermediates instead of M(η^2 -H₂) and the anionic M–H proposed here.³

The feasibility of the proposed mechanism is further demonstrated by complementary reactivity studies. Initial binding of H₂ is favored as 1 showed no propensity to bind CO₂ even under 34 atm. Deprotonation of (η^2 -H₂)NiGaL to generate [HNiGaL]⁻ occurred readily in the presence of H₂ (1 atm) and excess Vkd (Fig. S10-11). Of interest, the pK_a^{THF} of (η^2 -H₂)NiGaL was measured to be 27.5(2) via the proton-transfer equilibrium between (η^2 -H₂)NiGaL and Vkd in the overall H₂ heterolysis reaction [equation (1), Table S9]. This supports the hypothesis that a strong base is necessary to form the active species, [HNiGaL]⁻. For comparison, the pK_a^{THF} of H₂ is estimated to be 49,⁵⁸ which means that the acidity of H₂ increases by 21 pK_a units upon binding to NiGaL. This drastic increase in the acidity of H₂ upon binding to Ni, which allows for deprotonation to give the catalytically relevant anionic hydride, is not observed for NiLH₃, rendering it essentially catalytically inactive (*vide supra*). Finally, the reaction between [VkdH][HNiGaL] and CO₂ (1 atm) was observed to form [VkdH][(HCO₂)NiGaL] (Fig. S22). Additionally, isotopic labelling studies confirmed that formate was derived from D₂ and ¹³CO₂ (Fig. S38).

Monitoring the Ni speciation during catalysis also provided unique insights. Throughout catalysis, the observed catalyst resting state is the formate species, [VkdH][4] (Fig. S36). From [VkdH][4], regeneration of the catalytically active [VkdH][3] was observed to occur upon the addition of H₂ (1 atm) in the presence of Vkd (Fig. S37). The buildup of the formate complex during catalysis suggests the rate-limiting step is the liberation of $[VkdH][HCO_2]$ to regenerate NiGaL. In highly active Fe and Co pincer systems with TONs of ~10⁴, formate dissociation is also sluggish, and substoichiometric Li⁺ additives are needed to promote formate loss and drive catalytic turnover.^{19,20} In the present system, no additives were used. Presumably, formate extrusion is enhanced by the overall anionic charge of the Ni formate intermediate and the weaker Ni(0)–OCHO bond.

Conclusion

In summary, we have shown that a Lewis acidic Ga(III) supporting ion can interact with Ni to enable direct CO₂ hydrogenation to formate at ambient temperature with excellent yields. The high formate turnovers (3150) and TOF (9700 h⁻¹) are unprecedented for Ni and respectable compared to state-of-the-art homogeneous first-row metal catalysts (i.e. Fe, Co). The Ga(III) support plays a pivotal role in stabilizing the unusual anionic [HNiGaL]⁻ species, which is by far the strongest Ni–H donor reported to date ($\Delta G^{\circ}_{H^{-}} \approx 31$ kcal/mol) and on par with the most hydridic first-row and many precious metal hydrides. The significance of the Lewis acidic Ga(III) support is further emphasized via comparison to NiLH₃, which is essentially inactive for CO₂ hydrogenation due to its inability to bind and activate H₂ toward deprotonation to stabilize an analogous anionic hydride. Future studies will further elucidate the catalytic mechanism and detail the roles of the Ga(III) supporting ion therein, as well as investigate the influence of other group 13 Lewis acidic supports on Ni-catalyzed CO₂ hydrogenation.

Experimental Section

High-pressure catalytic reactions

 CO_2 hydrogenation reactions at 34 atm of ~1:1 H₂/CO₂ were performed in PEEK high-pressure NMR spectroscopy tubes designed and built at Pacific Northwest National

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Laboratory, as reported previously.⁵⁹ In a typical catalytic experiment (0.25 mM NiGaL (1), 800 mM Vkd base), a stock solution of 1 (11.8 mg, 14.6 μ mol) in 1 mL THF-d₈ was prepared. A 0.875 M solution of Vkd (168.3 mg, 560 μ mol) in 640 μ L THF-d₈ was also prepared. From these stock solutions, a catalyst mixture stock solution was prepared (700 μ L of 800 mM Vkd, 0.25 mM NiGaL). Note that preparations were adjusted accordingly to afford other concentrations of NiGaL (or NiLH₃) and/or other bases, including tBuTMG and NEt₃. Lastly, 300 μ L of the reaction solution was added to two different PEEK NMR spectroscopy cells.

The PEEK cell was sealed and connected to a purged high-pressure line equipped with a vacuum pump and an ISCO syringe pump. The headspace was degassed by opening the PEEK cell to static vacuum (3×10 s). Gas was delivered to the cell from an ISCO syringe pump running constantly at 34 atm (i.e. continuous gas feed). The contents of the PEEK cells were mixed using a vortex mixer for approximately 3 minutes until the pressure stabilized. After stabilization, the cell was inserted into the NMR spectrometer periodically to acquire data over time. The contents of the PEEK cell were mixed using a vortex mixer when NMR data was not being collected to promote optimal gas-liquid mixing throughout catalysis. The concentration of formate was determined by integrating the formate resonance relative to the residual HDO resonance in the CoCl₂ in D₂O capillary standard. Synthesis of $[N(P(C_6H_5)_3)_2][HNiGa(N(o-(NCH_2P'Pr_2)C_6H_4)_3)]$ (abbrev. as [PPN][3])

A stirring solution of NiGaL (114.1 mg, 138 μ mol) in 8 mL THF was cooled to -78° C over 15 minutes. To this solution, 62.4 μ L (156 μ mol) of *n*-BuLi solution (2.5 M in hexanes) was added, and the color rapidly changed from deep-red to red-yellow. This solution was allowed to warm to room temperature over the course of 12 h. Subsequent salt exchange was performed by adding solid bis(triphenylphosphine)iminium tetrakis[3,5-

bis(trifluoromethyl)phenyl]borate ([PPN][BArF₂₄], 415 mg, 283 µmol), and the solution was concentrated *in vacuo*, resulting in the precipitation of solids. Et₂O was added until the total volume was ~20 mL and the mixture was stirred vigorously for 3 h, affording a bright yellow precipitate. This precipitate was washed with Et₂O (2 x10 mL) to give [PPN][**3**] as a bright yellow powder (101 mg, 731 µmol, 40% yield). Single crystals of [PPN][**3**] suitable for X-ray diffraction were grown by layering a THF solution with pentane. Additionally, the analogous deuteride complex, [PPN][**3**(D)], was synthesized *in situ* by overnight exposure of [PPN][**3**] (10 mg, 7.4 µmol) to D₂ (4 atm) in THF-d₈ in a J. Young NMR tube.

¹H{³¹P} NMR (ppm, THF-d₈, 400 MHz): 7.62 (t, *J*=7.4 Hz, PPN, 6H), 7.56 (d, *J*=7.7 Hz, PPN, 12H), 7.44 (t, *J*=7.5 Hz, PPN, 12H), 7.12 (d, *J*=7.4 Hz, aryl, 3H), 6.56 (t, *J*=7.5 Hz, aryl, 3H), 6.14 (d, *J*=7.9 Hz, aryl, 3H), 5.94 (t, *J*=7.3 Hz, aryl, 3H), 2.60 (br, $CH_2P(^{i}Pr)_2$, 6H), 1.77 (br, $CH(CH_3)_2$, 3H), 1.56 (br, $C'H(CH_3)_2$, 3H), 1.05–0.60 (br, $CH(CH_3)_2$, 36H), –6.45 (br, Ni*H*, 1H, T₁(min)≤0.84(4) s at 233K). ³¹P{¹H} NMR (ppm, THF-d₈, 162 MHz): 75.3 (s, 3P, HNiGaL⁻), 21.0 (s, 2P, PPN). IR (KBr pellet, cm⁻¹): v(Ni–H) 1696 [1226 for **3**(D)]. Anal. calcd for [PPN][**3**], [C₃₆H₃₀NP₂][C₃₉H₆₁N₄P₃NiGa] (%): C, 66.93; H, 6.82; N, 5.20. Anal. calcd for [PPN][**3**·O₂] (%): C, 65.38; H, 6.66; N, 5.08. Found: C, 65.24; H, 6.90; N, 4.86. Elemental analysis consistently showed a low carbon percentage that could be consistent with oxidation by one equivalent of O₂.

Computational methods

Density functional theory (DFT) and *ab initio* wave function calculations were performed for anionic complexes **3** and **4**. Geometries were fully optimized in the gas phase using Gaussian 09 software⁶⁰ and the M06-L⁶¹ local functional with def2-series basis sets,⁶² denoted as M06-L/DEF2 (see SI for details). Vibrational frequency calculations were performed to confirm the stationary point nature of the structures. Solvation effects were considered by performing single-point calculations for all stationary points using the SMD solvation model.⁶³ Isodesmic hydride transfer reactions were modeled by DFT using several different functionals to benchmark the hydricity of **3** relative to those of other previously reported M-H (see Tables S10-11).³³ Complex **3** was further investigated by *ab initio* calculations using the complete active space self-consistent field (CASSCF)⁵³ method. CASSCF calculations were performed on the M06-L/DEF2 optimized structures using the MOLCAS-8.1 package⁶⁴ with relativistic basis sets of atomic natural orbitals types, i.e. ANO-RCC-VDZ were used for N, P, C, H atoms,⁶⁵ and ANO-RCC-VTZ were used for Ni and Ga atoms. The Ni→Ga dative bond was also interrogated by calculating the donor-acceptor stabilization energies for **3** based on natural bond orbital (NBO) analysis.⁵⁷

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:

Additional data for catalysis studies, synthesis of **4**, spectroscopic characterization, computational studies, and hydricity measurements. XYZ files for DFT-optimized geometries. (PDF)

Crystallographic data for [PPN][3] and [PPN][4] (CIF)

(These cif files have been deposited to the Cambridge CCDC 1553935-1553936).

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Notes

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Figure 1. General catalytic scheme for H₂/CO₂ to formate by NiGaL (1). A key step is the base-assisted H₂ heterolysis of (η^2 -H₂)NiGaL to form the anionic Ni hydride intermediate, [HNiGaL]⁻.



Figure 2. Formate turnovers versus time plots for CO_2 hydrogenation reactions catalyzed by **1** and **2** (0.25 mM catalyst, 800 mM Vkd, 1:1 H₂/CO₂) of 34 atm, 293 K, avg. of two trials for each; see Table 1, entries 3 and 7). Inset shows the kinetic plots for **1** (1 or 4 mM) with various bases (Vkd, tBuTMG, and NEt₃; see Table 1, entries 2, 4, and 5). Full kinetic profiles of all trials are shown in Figures S5-S9.



Figure 3. Solid-state structures of [PPN][HNiGaL] ([PPN][**3**], left) and [PPN][(HCO₂)NiGaL] ([PPN][**4**], right) displayed with 50% thermal ellipsoids. The PPN cation and H atoms, except for those on or interacting with the apical ligands, were omitted for clarity. A non-classical hydrogen-bonding interaction, O(formate)---HC(methine), is shown in **4** (light gray line). Relevant structural parameters of [PPN][**3**] and [PPN][**4**] are shown in Tables S4-S5.



Figure 4. Selected natural orbitals obtained from a CASSCF calculation of [HNiGaL]⁻ (**3**). Occupation numbers (shown in parentheses) indicate that these six orbitals are doubly occupied. Refer to Figure S34 and Table S13 for additional details.

Key



NiGaL (1)



NiLH₃ (2)

Table 1. Catalytic CO₂ hydrogenation to formate using NiGaL (1) or NiLH₃ (2) with various bases. Reaction conditions: catalyst (0.25 to 4 mM), 800 mM base, $1:1 \text{ H}_2/\text{CO}_2$ (1 or 34 atm), 0.30 mL THF-d₈ solution, 293 K.^{*a*}

	catalyst	[catalyst]	base	P(H ₂ /CO ₂)	theor. actual		%	$\mathbf{TOF}(\mathbf{h}^{-1})$	
entry		(mM)		(atm)	TON	TON ^b	yield ^c	initial ^d	overall ^e
1^f	1	2.9	Vkd	1	275	250	91	67	41
2	1	1	Vkd	34	800	800	quant.	3680	2130
3	1	0.25	Vkd	34	3200	3150	99	9700	6900
4	1	1	tBuTMG	34	800	640	80	120 ^g	74
5 ^{<i>h</i>}	1	4	NEt ₃	34	200	0	0	<i>N.A.</i>	N.A.
6 <i>f</i>	2	2.9	Vkd	1	275	0.8	0.3	0.14^{i}	0.04
7	2	0.25	Vkd	34	3200	0	0	<i>N.A.</i>	N.A.
8	$2 + GaCl_3$	0.25	Vkd	34	3200	0	0	<i>N.A</i> .	<i>N.A.</i>

^{*a*} Conditions apply to all entries unless otherwise noted. TON, % yield, and TOF are reported as averages of two trials. See SI Table S2 for details. ^{*b*}TON based on ¹H NMR integration of HCO_2^- relative to an internal capillary standard. ^{*c*}% yield based on TON/maximum TON, which closely matched ¹H NMR integration of HCO_2^- relative to $H(base)^+$. ^{*d*}Initial TOF is the initial linear slope of the formate turnovers vs. time plot (initial ~40 min at 1 atm, or 6-10 min at 34 atm). ^{*e*}Overall TOF = turnovers/time for >90% of final yield achieved. ^{*f*}0.40 mL volume for 1 atm runs. ^{*g*}An induction period was observed. Initial TOF defined from ~3.5 h to 7.5 h over which turnovers/time is linear (after induction period). ^{*h*}Single run in 0.75 mL THF in a high-pressure vessel. No HCO_2^- was detected after 150 h at 323 K. ^{*i*}Initial TOF determined for the first time point that HCO_2^- was observed (~3.5 h).

Refer	ences
(1) (2) J. G.; H Ragsda	Olah, G. A.; Prakash, G. K. S.; Goeppert, A. J. Am. Chem. Soc. 2011 , <i>133</i> , 12881-12 Appel, A. M.; Bercaw, J. E.; Bocarsly, A. B.; Dobbek, H.; DuBois, D. L.; Dupuis, M Fujita, E.; Hille, R.; Kenis, P. J. A.; Kerfeld, C. A.; Morris, R. H.; Peden, C. H. F.; Port ale, S. W.; Rauchfuss, T. B.; Reek, J. N. H.; Seefeldt, L. C.; Thauer, R. K.; Waldrop, C
(3)	<i>Rev.</i> 2013 , <i>113</i> , 6621-6658. Wang, WH.; Himeda, Y.; Muckerman, J. T.; Manbeck, G. F.; Fujita, E. <i>Chem. Rev.</i> 2036.12073
(4) 55 729	Klankermayer, J.; Wesselbaum, S.; Beydoun, K.; Leitner, W. Angew. Chem. Int. Ed. 96-7343
(5) (6) 51 749	Aresta, M.; Dibenedetto, A. <i>Dalton Trans.</i> 2007 , 2975-2992. Wesselbaum, S.; vom Stein, T.; Klankermayer, J.; Leitner, W. <i>Angew. Chem. Int. Ed</i>
 (7) v.; Eng (8) (9) Soc. 20 	 Wesselbaum, S.; Moha, V.; Meuresch, M.; Brosinski, S.; Thenert, K. M.; Kothe, J.; Sglert, U.; Holscher, M.; Klankermayer, J.; Leitner, W. <i>Chem. Sci.</i> 2015, <i>6</i>, 693-704. Huff, C. A.; Sanford, M. S. <i>J. Am. Chem. Soc.</i> 2011, <i>133</i>, 18122-18125. Kothandaraman, J.; Goeppert, A.; Czaun, M.; Olah, G. A.; Prakash, G. K. S. <i>J. Am.</i> 0016, <i>138</i>, 778-781.
(10) (11) <i>Eur. J.</i>	Rezayee, N. M.; Huff, C. A.; Sanford, M. S. <i>J. Am. Chem. Soc.</i> 2015 , <i>137</i> , 1028-103 Sordakis, K.; Tsurusaki, A.; Iguchi, M.; Kawanami, H.; Himeda, Y.; Laurenczy, G. 2016 , <i>22</i> , 15605-15608.
(12) 2017 , .	Schneidewind, J.; Adam, R.; Baumann, W.; Jackstell, R.; Beller, M. Angew. Chem. 1 56, 1890-1893.
(13) Lauren	Federsel, C.; Boddien, A.; Jackstell, R.; Jennerjahn, R.; Dyson, P. J.; Scopelliti, R.; hczy, G.; Beller, M. Angew. Chem. Int. Ed. 2010 , 49, 9777-9780.
(14) Angew	Langer, R.; Diskin-Posner, Y.; Leitus, G.; Shimon, L. J. W.; Ben-David, Y.; Milstein . Chem. Int. Ed. 2011, 50, 9948-9952.
(15) M. <i>J. A</i>	Ziebart, C.; Federsel, C.; Anbarasan, P.; Jackstell, R.; Baumann, W.; Spannenberg, A Im. Chem. Soc. 2012 , <i>134</i> , 20701-20704.
(16) 75.	Federsel, C.; Ziebart, C.; Jackstell, R.; Baumann, W.; Beller, M. Chem. Eur. J. 2012,
(17) (18) 11533-	Zell, T.; Milstein, D. Acc. Chem. Res. 2015, 48, 1979-1994. Jeletic, M. S.; Mock, M. T.; Appel, A. M.; Linehan, J. C. J. Am. Chem. Soc. 2013, 12
(19) Hazari	Zhang, Y.; MacIntosh, A. D.; Wong, J. L.; Bielinski, E. A.; Williard, P. G.; Mercado, N.; Bernskoetter, W. H. <i>Chem. Sci.</i> 2015 , <i>6</i> , 4291-4299.
 (20) (21) (22) (23) 3089-3 	Spentzos, A. Z.; Barnes, C. L.; Bernskoetter, W. H. <i>Inorg. Chem.</i> 2016 , <i>55</i> , 8225-823 Inoue, Y.; Izumida, H.; Sasaki, Y.; Hashimoto, H. <i>Chem. Lett.</i> 1976 , <i>5</i> , 863-864. Tai, CC.; Chang, T.; Roller, B.; Jessop, P. G. <i>Inorg. Chem.</i> 2003 , <i>42</i> , 7340-7341. Burgess, S. A.; Kendall, A. J.; Tyler, D. R.; Linehan, J. C.; Appel, A. M. <i>ACS Catal.</i> 096.
(24) 65-69.	Enthaler, S.; Brück, A.; Kammer, A.; Junge, H.; Irran, E.; Gülak, S. ChemCatChem 2
(25) (26) (27) 1925.	Harman, W. H.; Peters, J. C. J. Am. Chem. Soc. 2012 , <i>134</i> , 5080-5082. Eberhardt, N. A.; Guan, H. Chem. Rev. 2016 , <i>116</i> , 8373-8426. Curtis, C. J.; Miedaner, A.; Ellis, W. W.; DuBois, D. L. J. Am. Chem. Soc. 2002 , <i>124</i>
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(28)DuBois, D. L.; Berning, D. E. Appl. Organomet. Chem. 2000, 14, 860-862. (29)Chakraborty, S.; Zhang, J.; Krause, J. A.; Guan, H. J. Am. Chem. Soc. 2010, 132, 8872-8873. (30)A Ni dicarbene catalyst: Lu, Z.; Williams, T. J. ACS Catal. 2016, 6670-6673. (31)Zimmermann, P.; Limberg, C. J. Am. Chem. Soc. 2017, 139, 4233-4242. (32) Yoo, C.; Lee, Y. Angew. Chem. Int. Ed. 2017, 56, 9502-9506. (33)Mondal, B.; Neese, F.; Ye, S. Inorg. Chem. 2016, 55, 5438-5444. (34)Qi, X.-J.; Fu, Y.; Liu, L.; Guo, Q.-X. Organometallics 2007, 26, 4197-4203. Rudd, P. A.; Liu, S.; Gagliardi, L.; Young, V. G.; Lu, C. C. J. Am. Chem. Soc. 2011, 133, (35) 20724-20727. (36)Bouhadir, G.; Bourissou, D. Chem Soc Rev 2016, 45, 1065-1079, and references therein. See refs. 37-38 for recent examples of bifunctional catalysts with a sigma acceptor ligand at the metal. Takaya, J.; Iwasawa, N. J. Am. Chem. Soc. 2017, 139, 6074-6077. (37)(38)You, D.; Gabbaï, F. P. J. Am. Chem. Soc. 2017, 139, 6843-6846. (39) Cammarota, R. C.; Lu, C. C. J. Am. Chem. Soc. 2015, 137, 12486-12489. (40)Cammarota, R. C.; Clouston, L. J.; Lu, C. C. Coord. Chem. Rev. 2017, 334, 100-111. Wiedner, E. S.; Chambers, M. B.; Pitman, C. L.; Bullock, R. M.; Miller, A. J. M.; Appel, A. (41) M. Chem. Rev. 2016, 116, 8655-8692. Kisanga, P. B.; Verkade, J. G.; Schwesinger, R. J. Org. Chem. 2000, 65, 5431-5432. (42)Wróblewski, A. E.; Pinkas, J.; Verkade, J. G. Main Group Chem. 1995, 1, 69-79. (43) (44) Zall, C. M.; Linehan, J. C.; Appel, A. M. ACS Catal. 2015, 5, 5301-5305. Kaljurand, I.; Kütt, A.; Sooväli, L.; Rodima, T.; Mäemets, V.; Leito, I.; Koppel, I. A. J. Org. (45) Chem. 2005, 70, 1019-1028. Jeletic, M. S.; Helm, M. L.; Hulley, E. B.; Mock, M. T.; Appel, A. M.; Linehan, J. C. ACS (46) Catal. 2014, 4, 3755-3762. Clouston, L. J.; Siedschlag, R. B.; Rudd, P. A.; Planas, N.; Hu, S.; Miller, A. D.; Gagliardi, (47)L.; Lu, C. C. J. Am. Chem. Soc. 2013, 135, 13142-13148. Darensbourg, M. Y.; Ash, C. E. In Adv. Organomet. Chem.; Stone, F. G. A., West, R., Eds.; (48)Academic Press, Inc.: San Diego, CA, 1987. (49) Kleimann, W.; Pörschke, K.-R.; Wilke, G. Chem. Ber. 1985, 118, 323-331. Abernethy, C. D.; Baker, R. J.; Cole, M. L.; Davies, A. J.; Jones, C. Transition Met. Chem. (50)2003, 28, 296-299. Berning, D. E.; Noll, B. C.; DuBois, D. L. J. Am. Chem. Soc. 1999, 121, 11432-11447. (51)Wiedner, E. S.; Appel, A. M.; DuBois, D. L.; Bullock, R. M. Inorg. Chem. 2013, 52, 14391-(52) 14403. Roos, B. O.; Taylor, P. R. Chem. Phys. 1980, 48, 157-173. (53) (54)Vollmer, M. V.; Xie, J.; Lu, C. C. J. Am. Chem. Soc. 2017, 139, 6570-6573. (55)Parkin, G. Organometallics 2006, 25, 4744-4747. (56)Amgoune, A.; Bourissou, D. Chem. Commun. 2011, 47, 859-871. Weinhold, F.; Landis, C. R. Chem. Edu. Res. Pract. 2001, 2, 91-104. (57) (58)Abdur-Rashid, K.; Fong, T. P.; Greaves, B.; Gusev, D. G.; Hinman, J. G.; Landau, S. E.; Lough, A. J.; Morris, R. H. J. Am. Chem. Soc. 2000, 122, 9155-9171. Yonker, C. R.; Linehan, J. C. J. Organomet. Chem. 2002, 650, 249-257. (59) (60) Frisch, M.; Trucks, G.; Schlegel, H.; Scuseria, G.; Robb, M.; Cheeseman, J.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G., Gaussian 09, revision D. 01. Gaussian, Inc., Wallingford CT: 2009. (61) Zhao, Y.; Truhlar, D. G. J. Chem. Phys. 2006, 125, 194101. (62)Weigend, F.; Ahlrichs, R. PCCP 2005, 7, 3297-3305. (63) Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. J. Phys. Chem. B 2009, 113, 6378-6396.

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(64) Aquilante, F.; Autschbach, J.; Carlson, R. K.; Chibotaru, L. F.; Delcey, M. G.; De Vico, L.;
Ferré, N.; Frutos, L. M.; Gagliardi, L.; Garavelli, M. *J. Comput. Chem.* 2016, *37*, 506-541.
(65) Roos, B. O.; Lindh, R.; Malmqvist, P.-Å.; Veryazov, V.; Widmark, P.-O. *J. Phys. Chem. A* 2004, *108*, 2851-2858.





Figure 1

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Figure 4 71x61mm (300 x 300 DPI)











TOC graphic

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