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Nickel-catalyzed release of H_2 from formic acid and a new method for the synthesis of zerovalent Ni(PMe₃)₄⁺

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Ni(PMe₃)₄ serves as a catalyst for the release of H₂ and CO₂ from formic acid. The capacity of Ni(PMe₃)₄ to achieve this transformation is linked to the ability of the PMe₃ ligand to induce decarboxylation, as illustrated by the observation that both Ni(py)₄(O₂CH)₂ and Ni(O₂CH)₂·2H₂O react with PMe₃ to afford Ni(PMe₃)₄; the latter transformation also provides a convenient method for the synthesis of a zerovalent nickel compound.

Introduction

The growing demand for energy has prompted much effort in the utilization of fuels that are more sustainable than those based on fossil feedstocks.¹ For example, hydrogen, which can be generated by renewable means, is a promising alternative because it can be used in either a fuel cell or a combustion engine.² A problem with the use of hydrogen as a fuel, however, is that current storage and transportation techniques are inadequate.³ Therefore, much attention has been directed towards discovering both physical and chemical methods to provide hydrogen on demand.⁴ Formic acid, in particular, has garnered interest as a chemical medium for storing H₂ because it is a liquid at room temperature and, as a consequence, is easy to handle and transport.5 The utilization of formic acid as a storage medium for H₂, however, requires effective catalysts to release H2 on demand; indeed, both heterogeneous and homogeneous catalyst systems have been investigated.^{6,7} In particular, there is much interest in the discovery of catalysts that utilize earth abundant nonprecious metals.8,9 Therefore, we describe here the ability of a nickel compound to serve as a catalyst for the release of H₂ from formic acid.

Results and discussion

Zerovalent trimethylphosphine compounds of the class $M(PMe_3)_n$ are known for a variety of transition metals, *e.g.* $Mo(PMe_3)_6$, $W(PMe_3)_6$, $Fe(PMe_3)_5$, $Os(PMe_3)_5$, $Co(PMe_3)_4$,

well-known to be highly reactive due to the strong σ -donor and weak π -acceptor character of PMe₃, which results in metal centers that are classified as "electron rich". For example, $Ni(PMe_3)_4$ ¹¹⁻¹³ exhibits diverse reactivity, which includes ligand exchange and Si-H, O-H, S-H, C-S, S-S, and C-halogen bond cleavage transformations.¹⁴ In view of such reactivity, we have examined the ability of $Ni(PMe_3)_4$ to serve as a catalyst for the release of H₂ from formic acid. Significantly, Ni(PMe₃)₄ does indeed catalyze this transformation (Scheme 1)^{15,16} and can decarboxylate formic acid at 80 °C with a turnover number (TON) of 70 and an initial turnover frequency (TOF) of 1.7 h^{-1} . This activity is, however, modest in comparison to other nonprecious metal catalysts; for example, [{P(CH₂CH₂PPh₂)₃}- $FeH(H_2)$ [BPh₄] possesses a TOF of 335 h⁻¹,^{8a,17,18} $[\kappa^3\mathchar`-C_5H_3N(CH_2PBu^t_2)_2]\mbox{Fe}(CO)H_2$ has a TOF of 520 $h^{-1},\mbox{8b}$ $[HN(CH_2CH_2PPr_2)_2]Fe(CO)(O_2CH)H$ achieves a TOF of 196728 h^{-1} , s^g and a bis(imino)pyridine aluminum complex, [^{Ph}I₂P]AlH(THF), has a TOF of 5200 h⁻¹.^{8d} The only other example of a nickel compound, namely $[\kappa^3-C_6H_3(CH_2PBu_2^t)_2]$ NiH, that has recently been reported to release H₂ from formic acid has an initial TOF of 240 h^{-1} .^{8c,19} However, Ni(PMe₃)₄ can achieve the catalytic conversion in absence of a base, whereas $[\kappa^3-C_6H_3(CH_2PBu_2^t)_2]$ NiH requires the presence of an amine (either Et₃N or OctNH₂) to achieve catalysis.^{8c}

 $Ni(PMe_3)_4$, $Pd(PMe_3)_4$, and $Pt(PMe_3)_4$.¹⁰ Such compounds are

The essential features of the mechanism of the catalytic cycle are proposed to involve (i) formation of a nickel formate species, (ii) decarboxylation of the nickel formate to afford a nickel hydride intermediate, and (iii) release of H_2 . For

HCO₂H
$$\xrightarrow{\text{Ni}(\text{PMe}_3)_4}$$
 H₂ + CO₂
Scheme 1



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example, one possible sequence, as illustrated in Scheme 2, involves oxidative addition of formic acid to give a five-coordinate formate-hydride, namely Ni(PMe₃)₃(O₂CH)H,²⁰ which exists in equilibrium with four-coordinate Ni(PMe₃)₂(O₂CH)H.^{21,22} Subsequent elimination of CO2 forms a dihydride intermediate, Ni(PMe₃)₂H₂,^{23,24} which releases H₂ by either reductive elimination or by reaction with formic acid. Support for one step in this type of mechanism is provided by Darensbourg's proposal that Ni(PCy₃)₂(O₂CH)H undergoes exchange with ¹³CO₂ by a mechanism that involves decarboxylation and the formation of an unstable dihydride intermediate, $Ni(PCy_3)_2H_2$.^{25,26} In addition to the possibility of H₂ release occurring via $Ni(PMe_3)_2H_2$, it is also possible that the release occurs via five-coordinate Ni(PMe₃)₃H₂, which is anticipated to be in equilibrium with Ni(PMe₃)₂H₂.^{21,27} Density functional theory calculations illustrate that the proposed four-coordinate square-planar²⁸ and five-coordinate²⁹ trigonal bipyramidal intermediates (Fig. 1) are thermodynamically accessible from $Ni(PMe_3)_4$ and HCO_2H (Table 1) and thereby provide support for the pathways illustrated in Scheme 2.





Fig. 1 Geometry optimized structures of proposed intermediates for decarboxylation of formic acid (methyl group hydrogen atoms are omitted for clarity).

Table 1 ΔG values of intermediates (kcal mol⁻¹) relative to Ni(PMe₃)₄ + $\frac{1}{2}$ (HCO₂H)₂ in the gas phase

	<i>x</i> = 3	<i>x</i> = 2
Ni $(PMe_3)_x(O_2CH)H + (4 - x) PMe_3$ Ni $(PMe_3)_xH_2 + CO_2 + (4 - x) PMe_3$	-3.4 8.6	-12.3

In view of the proposal that the catalytic mechanism for the release of H₂ from formic acid involves decarboxylation of a formate intermediate, we sought to examine if coordination of PMe₃ to a well-defined nickel formate complex could induce the transformation. Significantly, we observed that addition of PMe₃ to the pyridine complex, Ni(py)₄(O₂CH)₂,³⁰ results in the release of CO₂ and H₂ at room temperature, with the accompanying formation of Ni(PMe₃)₄ (Scheme 3). Furthermore, PMe₃ also reacts with a suspension of Ni(O₂CH)₂·2H₂O (which, in the solid state, features an extended structure with bridging formate ligands)³¹ in benzene to release CO₂ and H₂ at 60 °C and form Ni(PMe₃)₄ (Scheme 3).^{32,33}

The ability of PMe₃ to induce the room temperature decarboxylation of a nickel formate species is of considerable significance in view of the fact that the reverse reaction, *i.e.* the insertion of CO₂ into a M–H bond, is more commonly observed.³⁴ However, despite the fact that many metal-hydride compounds insert CO₂ to afford a formate species, there are several ¹³CO₂ isotopic exchange studies that provide evidence for the occurrence of the reverse transformation, as illustrated by experiments involving $[M(CO)_5(O_2CH)]^-$ (M = Cr, Mo, W)^{34a} and Ni(PCy₃)₂(O₂CH)H.²⁵ Furthermore, some metal formate compounds, *e.g.* Re(PMe₃)₄(CO)(O₂CH),^{34c} M(dppp)(CO)₃(O₂CH) (M = Mn, Re),³⁵ CpRe(NO)(PPh₃)(O₂CH),³⁶ Fe(dmpe)₂(O₂CH)₂^{34f} CpMo(PMe₃)₂(CO)(O₂CH)^{8f} and $[P^{R_2}OCOP^{R_2}]Ni(O_2CH),^{34m,n}$ are known to dissociate CO₂ at either elevated temperatures or upon removal of the CO₂ atmosphere.

With respect to the mechanism of the PMe₃ induced decarboxylation, a plausible sequence involves the initial coordination of PMe₃ to afford a four-coordinate adduct, Ni(PMe₃)₂(O₂CH)₂. Two decarboxylation events would sequentially form Ni(PMe₃)₂(O₂CH)H and Ni(PMe₃)₂H₂, of which the latter would be expected to release H₂ in the presence of PMe₃ to form Ni(PMe₃)₄, as illustrated in Scheme 4. Precedent for this mechanism is provided by the observations that (i) the tricyclohexylphosphine counterpart, Ni(PCy₃)₂(O₂CH)H, is a known compound and (ii) Ni(PCy₃)₂(O₂CH)H undergoes facile reversible decarboxylation to generate Ni(PCy₃)₂H₂ (*vide supra*).²⁵ Density functional theory calculations also indicate that





this pathway is feasible. For example, decarboxylation of $Ni(PMe_3)_2(O_2CH)_2$ is thermodynamically (ΔG) downhill by 2.4 kcal mol⁻¹, while decarboxylation of Ni(PMe_3)_2(O_2CH)H is only uphill by 13.0 kcal mol⁻¹; subsequent dissociation of H₂ and formation of Ni(PMe_3)₄ from Ni(PMe_3)₂H₂ is downhill by 7.7 kcal mol⁻¹ (Scheme 4).³⁷

Finally, in addition to the PMe₃ induced decarboxylation of formate being of mechanistic interest, it is also of synthetic relevance since it provides a very useful method for obtaining $Ni(PMe_3)_4$, which was first reported in 1970 by Tolman¹² and by Klein and Schmidbaur.13 Specifically, Tolman described the synthesis of Ni(PMe₃)₄ by the reaction of bis(1,5-cyclooctadiene)nickel(0), Ni(COD)₂, with PMe₃,¹² while Klein and Schmidbaur described syntheses that involved (i) reduction of Ni(II) salts by PMe₃ in basic aqueous solution and (ii) the reaction of (Me₃P)₂NiCl₂ with aqueous-alcoholic solutions of either KOH or NaOSiMe₃;¹³ in both of the latter cases, Me₃PO is formed as a byproduct, while the reactions with KOH and NaOSiMe₃ are also accompanied by the formation of NiX₂ (X = OH, OSiMe₃). Although a variety of other syntheses of $Ni(PMe_3)_4$ have subsequently been reported, including (i) the reaction of Ni(PMe₃)₂Me₂ with PMe₃,³⁸ (ii) the reduction of $NiCl_2$ by Na(Hg) in the presence of PMe_3 ,³⁹ and (iii) the cocondensation of nickel atoms with PMe3 via metal-vapor synthesis techniques,⁴⁰ the direct synthesis from $Ni(O_2CH)_2 \cdot 2H_2O$ offers several advantages. For example, the byproducts $(CO_2,$ H₂ and H₂O) are easy to remove, whereas other methods generate byproducts, e.g. Me₃PO, NiX₂ (X = OH, OSiMe₃), NaCl, and Hg, that require additional steps for their removal. Furthermore, the direct synthesis from Ni(O₂CH)₂·2H₂O (i) obviates the need to prepare starting materials such as Ni(PMe₃)₂Me₂ or Ni(COD)₂,⁴¹ (ii) does not require the use of mercury and an alkali metal reductant, and (iii) does not require highly specialized metal-vapor synthesis equipment.

Conclusions

In summary, Ni(PMe₃)₄ has been shown to catalyze the conversion of formic acid to H_2 and CO_2 *via* a mechanism that is proposed to involve the decarboxylation of a nickel formate intermediate, followed by elimination of H_2 from a nickel dihydride species. The capacity of Ni(PMe₃)₄ to achieve this transformation is linked to the ability of PMe₃ to induce decarboxylation, as illustrated by the observation that both $Ni(py)_4(O_2CH)_2$ and $Ni(O_2CH)_2 \cdot 2H_2O$ react with PMe₃ to afford $Ni(PMe_3)_4$. The latter transformation also provides a convenient method for the synthesis of a zerovalent nickel compound.

Experimental section

General considerations

All manipulations were performed using a combination of glovebox, high vacuum and Schlenk techniques under a nitrogen or argon atmosphere.⁴² Solvents were purified and degassed by standard procedures. NMR spectra were measured on Bruker 300 DRX and Bruker Avance 500 DMX spectrometers. ¹H NMR spectra are reported in ppm relative to SiMe₄ ($\delta = 0$) and were referenced internally with respect to the protio solvent impurity $(\delta = 7.16 \text{ for } C_6 D_5 H)$.⁴³ ¹³C NMR spectra are reported in ppm relative to SiMe₄ ($\delta = 0$) and were referenced internally with respect to the solvent (δ = 128.06 for C₆D₆).^{43 31}P NMR chemical shifts are reported in ppm relative to 85% H_3PO_4 ($\delta = 0$) and were referenced electronically by using the ¹H resonance frequency of SiMe4.44 Chemicals were obtained from Sigma-Aldrich [formic acid and mesitylene], Alfa Aesar [Ni(O₂CH)₂·2H₂O] and Cambridge Isotope Laboratories $[H^{13}CO_2H]$, and used as supplied. Ni(py)₄(O₂CH)₂ was obtained by the literature method.³⁰

Computational details

Calculations were carried out using DFT as implemented in the Jaguar 8.9 (release 15) suite of *ab initio* quantum chemistry programs.⁴⁵ Geometry optimizations were performed with the B3LYP density functional using the 6-31G**++ (H, C, O, P) and LACVP (Ni) basis sets, which were also used to determine Gibbs free energy values at 1 atm and 298.15 K. The energies of the optimized structures in the gas phase were also reevaluated by additional single point calculations on each optimized geometry using the cc-pVTZ(-f)++ correlation consistent triple- ζ (H, C, O, P) and LAV3P (Ni) basis sets. Cartesian coordinates and energies of the geometry optimized structures are provided in the ESI.[†]

Synthesis of Ni(PMe₃)₄ from Ni(O₂CH)₂·2H₂O

A green suspension of Ni(O_2 CH)₂·2H₂O (500 mg, 2.71 mmol) in benzene (*ca.* 30 mL) was cooled to -196 °C and treated with PMe₃ (2.0 mL, 20 mmol) *via* vapor transfer. The mixture was heated overnight at 60 °C under a nitrogen atmosphere that was open to a bubbler. Over this period, the mixture became bright yellow and produced an orange oily deposit. The volatile components were removed *in vacuo*, and the residue was extracted into pentane (*ca.* 30 mL). The solvent was removed from the pentane extract *in vacuo* to give Ni(PMe₃)₄ as a yellow powder (639 mg, 65% yield), which was identified by ¹H, ³¹P{¹H} and ¹³C{¹H} NMR spectroscopy.⁴⁰

Synthesis of Ni(PMe₃)₄ from Ni(py)₄(O₂CH)₂

A green suspension of $Ni(py)_4(O_2CH)_2$ (150 mg, 0.322 mmol) in benzene (*ca.* 5 mL) was cooled to -196 °C and treated with PMe₃ (0.20 mL, 2.0 mmol) *via* vapor transfer. The mixture was stirred overnight at room temperature in a sealed ampoule. Over this period, the mixture became bright yellow and produced an orange oily deposit. The volatile components were removed *in vacuo*, and the residue was extracted into pentane (*ca.* 6 mL). The solvent was removed from the pentane extract *in vacuo* to give Ni(PMe₃)₄ as a yellow powder (51 mg, 44% yield) which was identified by ¹H, ³¹P{¹H} and ¹³C{¹H} NMR spectroscopy.⁴⁰

Decarboxylation of formic acid catalyzed by Ni(PMe₃)₄

Formic acid (5.0 µL, 0.13 mmol) was added to a solution of $Ni(PMe_3)_4$ (5.0 mg, 0.014 mmol) in C_6D_6 (ca. 0.7 mL) containing mesitylene (3.0 µL, 0.022 mmol) as an internal standard. The sample was examined by NMR spectroscopy, thereby demonstrating the immediate formation of a species tentatively identified as $[Ni(PMe_3)_4H]^+$ [¹H NMR (C₆D₆): -17.76 [s, 1H, NiH], 0.88 [s, 36H, Ni(PMe₃)₄]. ${}^{31}P{}^{1}H$ NMR (C₆D₆): -20.11 [s]].⁴⁶ The mixture was then heated to 80 °C and monitored by ¹H and ³¹P{¹H} NMR spectroscopy. Most of the formic acid was consumed after a period of 1 day, at which point another portion of formic acid (5.0 µL, 0.13 mmol) was added, and the mixture was heated again at 80 °C. A total of seven aliquots of formic acid were added over a period of 14 days, corresponding to a turnover number of 70. The initial turnover frequency was 1.7 h^{-1} (based on the first two hours), whereas the turnover frequency over the entire experiment was $0.2 h^{-1}$. The formation of H₂ was observed by ¹H NMR spectroscopy, while the formation of CO₂ was confirmed by examining the corresponding reaction of H¹³CO₂H with ¹³C¹H NMR spectroscopy (see below). During the course of the catalysis, Ni(PMe₃)₄ converts to Ni(PMe₃)₃(CO) [¹H NMR (C₆D₆): 1.09 [s]. ${}^{31}P{}^{1}H$ NMR (C_6D_6) : -18.56 [s]],⁴⁷ and a small quantity of methyl formate arising from disproportionation is also observed.

Decarboxylation of H¹³CO₂H catalyzed by Ni(PMe₃)₄

 $\rm H^{13}CO_2H$ (5.0 µL, 0.13 mmol) was added to a yellow solution of Ni(PMe₃)₄ (5.0 mg, 0.014 mmol) in C₆D₆ (*ca.* 0.7 mL). The sample was heated to 80 °C and monitored by ¹H, ³¹P{¹H} and ¹³C{¹H} NMR spectroscopy, which demonstrated the formation of H₂ and ¹³CO₂ over a period of 5 days. A trace quantity of ¹³CH₃OH is also observed.

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- The four-coordinate compounds illustrated in Fig. 1, 28 namely Ni(PMe₃)₂(O₂CH)H and Ni(PMe₃)₂H₂, are represented with a trans-arrangement of PMe₃ ligands. We have also performed calculations on the cis-counterparts, and these are higher in energy (E^{SCF}) by 10.8 and 2.2 kcal mol^{-1} , respectively (cc-pVTZ(-f)++ and LAV3P basis sets). We also note that, in addition to palladium and platinum dihydrides, $M(PR_3)_2H_2$ (M = Pd, Pt), possessing a transarrangement of PR3 ligands (ref. 26), four-coordinate nickel compounds such as Ni(PMe₃)₂Me₂ and Ni(PMe₃)₂(Me)Cl also adopt trans structures (ref. 24). Nevertheless, although the calculated energy of trans-Ni(PMe₃)₂H₂ is lower than that of the cis isomer, the difference is sufficiently small that the latter would be accessible for the step involving reductive elimination of H₂.
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