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DOI: 10.1039/C8DT03403F

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ARTICLE

Monomeric nickel hydroxide stabilized by a sterically demanding phosphorus-nitrogen PN^{3}P-pincer ligand: synthesis, reactivity and catalysis

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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Terminal nickel hydroxide complex (PN^{3}P)Ni(OH) (**3**) bearing the 2nd generation phosphorus-nitrogen PN^{3}P-pincer ligand has been synthesized and structurally characterized. As a nucleophile, **3** reacts with CO to afford the hydroxycarbonyl complex **4**, (PN^{3}P)Ni(COOH). **3** can also activate CO_2 and CS_2 to produce nickel bicarbonate (PN^{3}P)Ni(OCOOH) (**5**) and bimetallic dithiocarbonate [(PN^{3}P)NiS]$_2$CO (**6**) respectively, as well as to promote aryl isocyanate and isothiocyanate insertion into the Ni-OH bond to give the corresponding (PN^{3}P)NiEC(O)NHAr complexes (E = O, **7**; E= S, **8**). In addition, **3** catalyzes the nitrile hydration to various amides with well-defined intermediates (PN^{3}P)Ni-NHC(O)R (R = Me,**9**, R = Ph, **10**).

Introduction

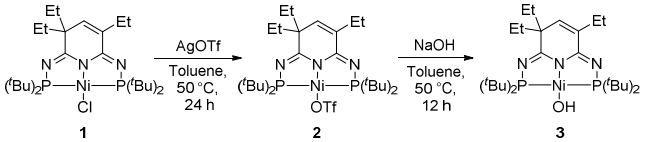
Late transition-metal (LTM) hydroxide complexes are some of the most captivating intermediates involved in biological and catalytic processes,[1-4] such as the Wacker reaction.[5, 6] Different from their group 4–6 inert counterparts, LTM hydroxides are very exiguous and reactive due to the inherent weakness of their M-OH bond.[1, 3, 7-9] Over past decades, LTM hydroxide complexes have emerged as the important synthons for preparing new metal compounds; however, the thermal instability makes their synthesis very challenging.[10-12] Up to now several monomeric palladium and platinum hydroxides have been isolated and structurally characterized,[13-18] however, their nickel analogs have less been explored despite their higher oxophilicity.[19-31] Campora *et al*.[19] and Hazari *et al*.[24] reported the synthesis and reactivity of the terminal (^{iPr}PCP)Ni-OH and (^{tBu}PCP)Ni-OH complexes, respectively; Holm and co-workers synthesized and studied the reactions of an anionic hydroxo nickel complex [Ni(pyN_2^{Me2})(OH)]$^-$.[26] The Piers group reported the selective hydration of nitriles to amides by using (PCP)Ni-OH as the catalyst.[25] Recently, Wendt and co-workers demonstrated the reactivities towards CO/CO_2 of two nickel hydroxides supported by POC$_{sp3}$OP and PCN ligands, respectively.[29, 31]

Over recent years, pincer ligands have been extensively recognized for their strong coordination capacity to stabilize various metals.[32-39] We have been particularly interested in the exploration of the metal–ligand cooperative catalysis utilizing a new class of pyridine-based phosphorus-nitrogen PN^3-pincer complexes through deprotonation and reprotonation of one of the NH arms.[40-42] Very importantly, in contrast to their CH_2 analogs,[43-45] we have demonstarted that the small change of the arm has led to distinct catalytic reactvities[46-53] and different thermodynamic and kinetic properties.[54-56] Furthermore, we have very recently extended these PN^{3}P-pincer systems to prepare a new series of second-generation diimine-amido PN^{3}P pincer complexes using a ligand post-modification strategy.[57-59] Herein, we demonstrated that the exceptional stability shown by these new compounds allowed us to synthesize the corresponding monomeric hydroxo nickel complex for the investigation on its reactivity and catalysis.

Results and discussion

Synthesis and characterization of complex (PN^{3}P)Ni(OH) (3)

Pincer complex (PN^{3}P)NiCl (**1**) was first converted into Ni triflate compound **2** in a high yield of 95% via a metathesis reaction, followed by the reaction with sodium hydroxide to



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†Electronic Supplementary Information (ESI) available: NMR and FTIR spectra. CCDC 1817531, 1817541, 1817542, 1817545, 1817553, 1834798 contain the supplementary crystallographic data for this paper. See DOI: 10.1039/x0xx00000x

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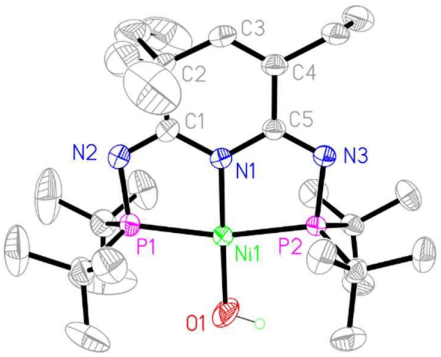


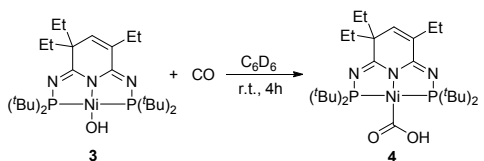
Scheme 1. Synthesis of complex **3** via metathesis reactions.

Fig. 1 Molecular structure of complex **3**. Thermal ellipsoids are displayed at 50 % probability level; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ni(1)-N(1) 1.9056(19), Ni(1)-P(1) 2.1835(9), Ni(1)-P(2) 2.1795(9), Ni(1)-O(1) 1.930(2), O(1)-H(100) 0.860(9); N(1)-Ni(1)-O(1) 177.88(9), P(1)-Ni(1)-P(2) 165.97(3), P(1)-Ni(1)-O(1) 97.66(6), P(2)-Ni(1)-O(1) 96.37(6), Ni(1)-O(1)-H(100) 111.3(14).

quantitatively produce the target nickel hydroxide complex **3** (Scheme 1). After 12 h at 50 °C, it was observed that the phosphorus resonance of **2** (δ 109.43 ppm) completely disappeared with the appearance of a new signal at δ 98.85 ppm, indicative of the formation of a new species. The presence of a Ni-OH fragment was confirmed by its characteristic resonance at δ -3.73 ppm in ^{1}H NMR spectrum, consistent with those of Ni-OH groups previously reported in literature.[26, 29, 31, 60, 61] To unambiguously establish the atom connectivity in **3**, single crystals suitable for X-ray diffraction analysis were grown from a concentrated pentane solution at room temperature. The Ni-O bond length of 1.930(2) Å shows a covalent bond between the nickel and the oxygen atom; the N1–Ni1–O1 angle of 177.88° exhibits that these three atoms are almost in a straight line (Fig. 1).

Reaction of 3 with CO

LTM hydroxide complexes are known to serve as precursors for preparing various metal compounds.[24, 26, 62-64] With complex **3** in hand, we set out to explore its reactivity in relation to its nucleophilic character. Treatment of the degassed C_6D_6 solution of **3** with CO under the atmospheric pressure and room temperature resulted in a color change from red to colorless and formation of a hydroxycarbonyl complex **4,** proved by NMR spectroscopy and element analysis (Scheme 2). Different from the recent report of Wendt's group[29], the acidic proton at 10.23 ppm in ^{1}H NMR and an apparent triplet peak at 209.02 ppm in ^{13}C NMR corresponding to the –COOH group were both found

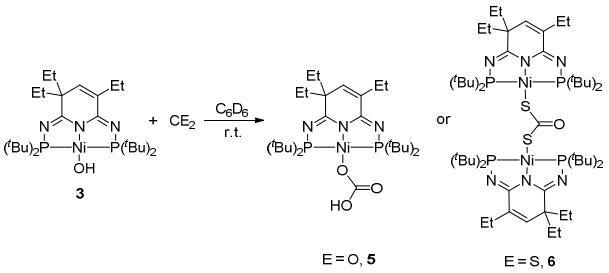


Scheme 2. Reaction of complex **3** with CO.

respectively. The degassed C_6D_6 solution of **4** was further exposed to the argon atmosphere for one week, no change was detected in the NMR spectroscopy. This is different from the reports by the groups of Cámpora[19] and Wendt[29], where the bridged dimeric μ-CO_2-κ^2C,O species was formed via decarbonylation of two hydroxycarbonyl complexes or decomposition to multiple products, respectively, suggesting that the ligand plays a significant role in determining the stability and reactivity.

Activation of CO_2 and CS_2

At room temperature, complex **3** underwent a fast insertion of CO_2 to afford the bicarbonate complex (PN^3P)NiOCOOH (**5**), as corroborated by NMR signals of the bicarbonate proton and carbon at 12.70 and 161.46 ppm respectively, as well as the IR absorption bands at 1618 and 1345 cm^{-1}.[29, 65] An attempt to isolate this bicarbonate complex by removing the volatiles under reduced pressure led to a complete deinsertion of CO_2[66] to regenerate hydroxide **3**. Again in contrast to the complexes



Scheme 3. Activation of CO_2 and CS_2 using complex **3.**

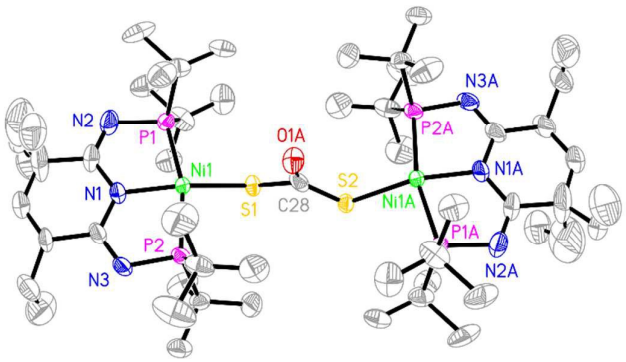


Fig. 2 Molecular structure of complex **6**. Thermal ellipsoids are displayed at 50% probability level; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]:Ni(1)-N(1) 1.912(2), Ni(1)-P(1) 2.2026(9), Ni(1)-P(2) 2.2201(10), Ni(1)-S(1) 2.2180(13), S(1)-C(28) 1.7330(12), C(28)-O(1A) 1.399(3), C(28)-S(2) 1.6059(12), S(2)-Ni(1A) 2.2727(13); P(1)-Ni(1)-P(2) 165.21(3), P(1)-Ni(1)-S(1) 94.76(5), P(1)-Ni(1)-S(2A) 94.23(4), P(2)-Ni(1)-S(1) 98.25(4), P(2)-Ni(1)-S(2A) 99.97(4), N(1)-Ni(1)-S(1) 159.72(8), O(1A)-C(28)-S(1) 117.18(15), S(1)-C(28)-S(2) 118.80(6).

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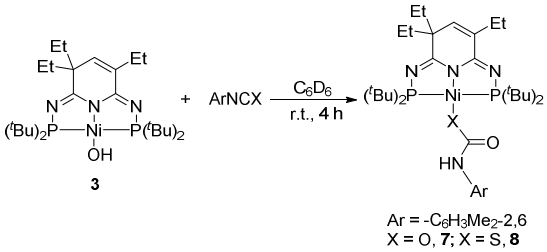
(^{iPr}PCP)NiOCOOH and (POC$_{sp3}$OP)NiOCOOH obtained by Cámpora[65] and Wendt[29], our bicarbonate complex cannot be further converted into a binuclear carbonate compound, in accordance with Holm's reversible process.[23, 67]

This reversible insertion process intrigued us to explore the reactivity of **3** and CS_2, a surrogate for CO_2. Upon addition of excess CS_2 to the C_6D_6 solution of **3** and keeping the resultant solution at room temperature for 2 h, the monitored ^{31}P NMR spectrum showed a new signal at 104.36 ppm, and no O*H* resonance was detected in ^{1}H NMR spectrum, indicating a new species formed. Interestingly, a new carbon signal with an apparent quintet peak (*J* = 4.1 Hz) was observed at 194.89 ppm in ^{13}C NMR spectrum, consistent with the CS_2 insertion into the Ni-OH bond to produce a C=O moiety located in a specific position with respect to four phosphorus atoms. The presence of C=O vibration at 1670 cm^{-1} in the FTIR spectrum and the HRMS result of $[M+1]^+$ (1169.54) strongly support that the identity of complex **6** is a bimetallic complex with the formula $C_{55}H_{104}N_6Ni_2OP_4S_2$ of [(PN^{3}P)NiS]$_2$CO, consistent with the elemental analysis (see SI). The molecular structure of **6** was unambiguously confirmed by the X-ray diffraction analysis: two Ni fragments ([(PN^{3}P)Ni]) are connected by the -SC(O)S- bridge (Fig. 2), a unique core structure unknown in the literature.[68-70] Several reactions of metal hydroxides with CS_2 have been reported to exclusively give the hydrosulfido complexes products or intermediates.[71-73] In those systems, CS_2 initially inserts into the M-OH bond to form the –SC(S)OH moiety followed by extrusion of COS to yield hydrosulfido complexes in part driven by the favorable formation of the M–S bond. However, in our case, no Ni-SH formation was detected by NMR. Our observations suggest that once CS_2 inserts into the Ni-OH bond, the proton of -SC(S)OH intermediate can be rapidly deprotonated by another **3** to afford the bimetallic complex **6** with water as the by-product, presumably due to the strong basicity of **3**.

Reactions of 3 with isocyanate/isothiocyanate

The nucleophilic property of **3** was further examined with isocyanate and isothiocyanate as electrophiles. Hydroxide **3** reacts readily with 2,6-dimethylphenyl isocyanate via formal addition of the O-H bond to the C=N double bond at room temperature to generate (PN^{3}P)NiOC(O)NHAr species **7**, with a -CON*H*- group confirmed by ^{1}H and ^{13}C NMR.[24, 74, 75] Identification of species **7** as a carbamate is also supported by X-ray diffraction (Fig. 3): the carbamato moiety coordinates to Ni as a monodentate ligand, presumably due to the presence



Scheme 4. Reactions of **3** and isocyanate/isothiocyanate.

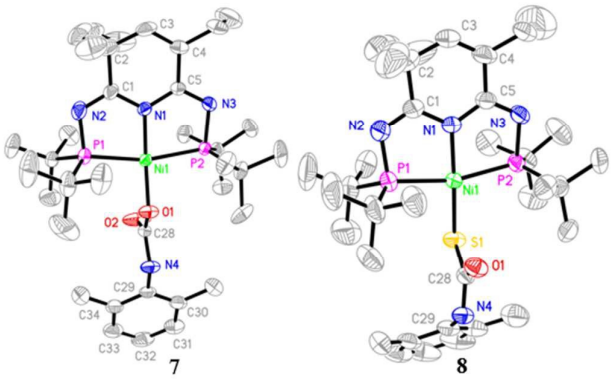
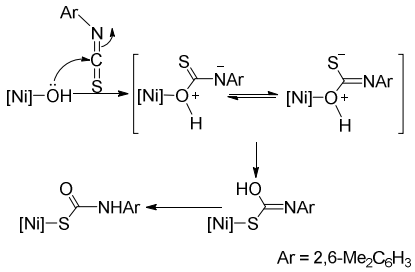


Fig. 3 Molecular structures of complexes **7** and **8**. Thermal ellipsoids are displayed at 50% probability level; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: For complex **7**: Ni(1)-N(1) 1.8951(19), Ni(1)-P(1) 2.2143(9), Ni(1)-P(2) 2.2080(8), Ni(1)-O(1) 1.861(2), O(1)-C(28) 1.280(3), O(2)- C(28) 1.211(3), C(28)-N(4) 1.388(3); N(1)-Ni(1)-O(1) 169.39(9), P(1)-Ni(1)-P(2) 165.47(3), P(1)-Ni(1)-O(1) 97.20(8), P(2)-Ni(1)-O(1) 97.22(8), Ni(1)-O(1)-C(28) 127.51(17). For complex **8**: Ni(1)-N(1) 1.907(3), Ni(1)-P(1) 2.2206(13), Ni(1)-P(2) 2.2035(11), Ni(1)-S(1) 2.2168(12), S(1)-C(28) 1.745(3), O(1)-C(28) 1.241(4), C(28)-N(4) 1.349(4); N(1)-Ni(1)-S(1) 171.23(10), P(1)-Ni(1)-P(2) 164.71(4), P(1)-Ni(1)-S(1) 97.92(5), P(2)-Ni(1)-S(1) 97.32(5), Ni(1)-S(1)-C(28) 105.71(12).

of the bulky substituents. This kind of coordination manner is comparable to Pérez's rhenium complex[76] but in contrast to Esteruelas's osmium compound[77] which features a bidentate carbamato ligand. Three well-defined carbamato nickel compounds have been reported in the literature, however, all of them are generated from the reaction of CO_2 insertion into the Ni-NHR bond.[24, 74, 75] Compared to these square planar nickel carbamates ([(POC$_{sp3}$OP)NiOC(O)NHAr] (1.910 Å), [(PCP)Ni{OC(O)NH$_2$}] (1.925 Å) and (MeSiP^{iPr2})Ni(OC(O)NHAr) (1.948 Å)), complex **7** holds the shortest Ni-O bond distance (1.861 Å). When 2,6-dimethylphenyl isothiocyanate as used, an analogous product (PN^{3}P)NiSC(O)NHAr (**8**) was also obtained, presumably because sulfur's soft property is beneficial to a stronger Ni-S bond, in good agreement with the report of the Pérez group (Scheme 5).[76]



Scheme 5. Proposed mechanism for the formation of **8** from **3**.

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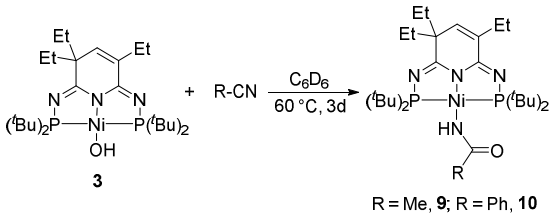
Nitriles hydration to amides catalyzed by 3

The formation of amides by hydration of nitriles using LTM hydroxides as catalysts has been reported in literature.[25, 78-81] However, to the best of our knowledge, only Piers' investigation refers to the isolable intermediate with the role of the hydroxo compound (PCP)Ni-OH unconfirmed.[25] This prompted us to investigate the reaction of **3** and nitriles (Scheme 6). After heating the C_6D_6 solution of **3** and excess acetonitrile at 60 °C for 72 h in the absence of water, the activation of acetonitrile was successfully achieved to form (PN^3P)NiNHC(O)Me (**9**), a bound acetamide nickel complex, in sharp contrast to Piers' work where no reaction occurred between benzonitrile and the hydroxo nickel complex without



Scheme 6. Reactions of **3** and nitriles.

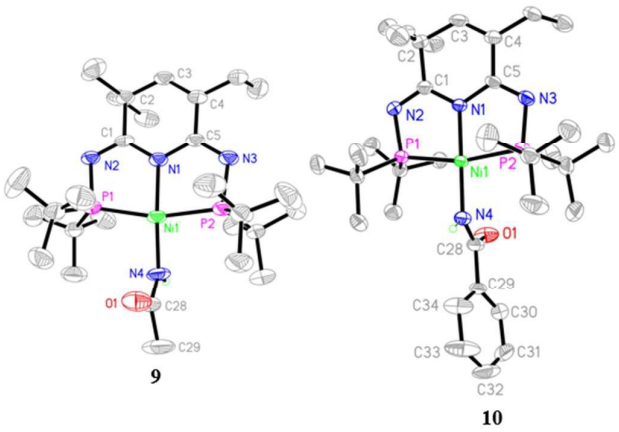
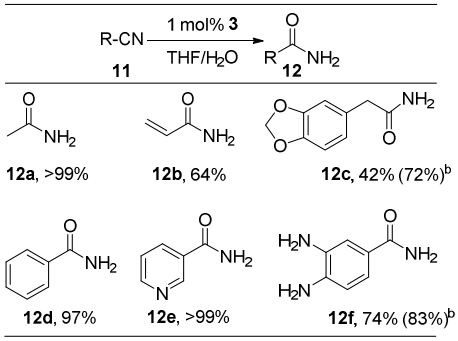


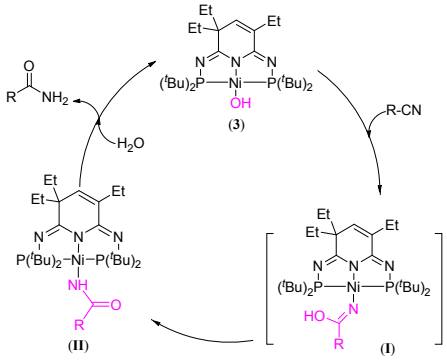
Fig. 4 Molecular structures of complexes **9** and **10**. Thermal ellipsoids are displayed at 50% probability level; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: For complex **9**: Ni(1)-N(1) 1.905(4), Ni(1)-P(1) 2.2186(12), Ni(1)-P(2) 2.1970(12), Ni(1)-N(4) 1.876(4), N(4)-C(28) 1.318(6), C(28)-O(1) 1.242(7); N(1)-Ni(1)-N(4) 176.50(18), P(1)-Ni(1)-P(2) 165.04(5), P(1)-Ni(1)-N(4) 99.07(12), P(2)-Ni(1)-N(4) 95.86(12), Ni(1)-N(4)-C(28) 128.3(4), N(4)-C(28)-O(1) 123.4(5), N(4)-C(28)-C(29) 117.8(5), O(1)-C(28)-C(29) 118.7(5). For complex **10**: Ni(1)-N(1) 1.903(2), Ni(1)-P(1) 2.2113(10), Ni(1)-P(2) 2.2029(10), Ni(1)-N(4) 11.888(2), N(4)-C(28) 1.309(4), C(28)-O(1) 1.241(4); N(1)-Ni(1)-N(4) 176.04(10), P(1)-Ni(1)-P(2) 165.62(3), P(1)-Ni(1)-N(4) 98.55(7), P(2)-Ni(1)-N(4) 95.77(8), Ni(1)-N(4)-C(28) 127.6(2), N(4)-C(28)-O(1) 123.7(3), N(4)-C(28)-C(29) 118.2(3), O(1)-C(28)-C(29) 118.1(3).

Table 1. Catalytic hydration of nitriles by using complex **3**.[a]



[a]Conditions (isolated yields): Complex **3** (20 μmol, 11.1 mg), nitrile (2 mmol), distilled water (0.1 mL), THF (1 mL), temperature (100 °C), Time (24 h). [b]Time (72h).

water. The structure of **9** was again confirmed by X-ray diffraction analysis (Fig. 4). The deprotonated acetamide coordinates to the Ni center *trans* to the central N of the pincer ligand. When the reaction of **3** with PhCN was carried out, the bound benzamide compound (PN^3P)NiNHC(O)Ph (**10**) was obtained. The molecular structure of **10** was also identified crystallographically (Fig. 4). The reaction of **9** with H_2O in THF at 100 °C regenerates **3** and affords the corresponding amide compounds, suggesting that it is the intermediate for hydration of acetonitrile and hydroxide **3** can play a role of catalyst. Our results serve as a clear evidence to support that the catalytic cycle is completed by regeneration of the hydroxo complex **3**. The catalytic activity of **3** for the nitrile hydration was thus further examined with a range of nitriles including alkyl/aryl nitriles, unsaturated nitriles, heteroatom-containing nitriles, *etc*. (Table 1). All the target amides were successfully obtained in moderate to high yields. As monitored by NMR, acrylonitrile was completely consumed, but only 64% acrylamide was obtained, probably involving the subsequent addition reaction of the resultant C=C double bond with water at the high temperature.[25] The low yields of **12c**



and **12f** were presumably attributed to the competitive coordination of the oxygen atoms

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Scheme 7. A proposed catalytic mechanism for nitrile hydration by complex **3**.

and amino groups with the nitrile nitrogen to the central nickel. Nevertheless, the yields could be improved with a longer reaction time. Compared to Piers' system, nickel hydroxide (**3**) displays a lower catalytic activity for nitrile hydration at 100 °C, probably due to the enhanced stability of the bound amide intermediate, which was not observed in Piers' study.[25]

Based on the synthetic cycle and hydration results, the plausible catalytic mechanism was proposed (Scheme 7). The hydroxide ligand undergoes the nucleophilic attack on the (presumably coordinated) nitrile substrate to form intermediate **I**, which then isomerizes to afford the bound amide intermediate **II**. Finally, regeneration of nickel hydroxide complex **3** proceeds with the reaction of **II** and H_2O and generates the amide product.

Conclusions

In summary, we have synthesized a new monomeric Ni-OH complex (**3**) via a metathesis reaction of its triflate precursor with NaOH, and demonstrated its diverse reactivity in respect of its nucleophilic character. **3** can react with CO at 1 atm to give a hydroxycarbonyl complex **4**. It is able to activate reversibly CO_2 to form a nickel bicarbonate compound **5**, and activate CS_2 to generate the unprecedented binuclear dithiocarbonate complex $[(PN^3P)NiS]_2CO$ (**6**). Moreover, aryl isocyanate and isothiocyanate undergo the insertion into the Ni-OH bond to afford corresponding (PN^3P)Ni-EC(O)NHAr (E = O, S) compounds. **3** also serves as a catalyst for the hydration of nitriles to amides with the well-defined (PN^3P)Ni-NHC(O)R intermediates.

Experimental section

General procedures

All experiments (if not mentioned otherwise) with metal complexes were carried out under an atmosphere of dry argon in a glovebox or using standard Schlenk techniques. All glassware was rigorously dried. All solvents were distilled from sodium benzophenone ketyl prior to use. All other chemicals were commercially available and used as received. Complex **1** was prepared according to the literature procedure[57]. NMR spectra were recorded at 400 MHz (^{1}H), 101 MHz (^{13}C), and 162 MHz (^{31}P) using a Bruker Avance-400 NMR spectrometer, 500 MHz (^{1}H), 126 MHz (^{13}C), and 202 MHz (^{31}P) using a Bruker Avance-500 NMR spectrometer, and 600 MHz (^{1}H), 152 MHz (^{13}C), and 243 MHz (^{31}P) using a Bruker Avance-600 NMR spectrometer. All spectra were recorded at 25 °C. ^{1}H NMR chemical shifts were referenced to the residual hydrogen signals of the deuterated solvents (7.16 ppm, C_6D_6), and the ^{13}C NMR chemical shifts were referenced to the ^{13}C signals of the deuterated solvents (128.06 ppm, C_6D_6). Elemental analyses were carried out on a Flash 2000 elemental analyzer. HRMS data were recorded on a Finnigan MAT 95 system. The X-ray diffraction data were collected using Bruker-AXS KAPPA-APEXII CCD diffractometer.

Synthesis of complex 2, (PN^3P)Ni(OTf)

AgOTf (308 mg, 1.2 mmol) was added to the toluene solution of (PN^3P)NiCl (**1**) (10 mL, 575 mg, 1.0 mmol). The resulting suspension was stirred 24 h at 50 °C, filtered and all the volatiles were removed *in vacuo* to yield a red solid (654 mg, 95.0 %). The elemental analysis sample was crystallized from pentane. ^{1}H NMR (500 MHz, C_6D_6) δ = 5.25 (t, *J* = 3.4 Hz, 1H, -C(Et)=C*H*-), 2.38 (q, *J* = 7.4 Hz, 2H, -CH_2CH$_3$), 1.91 (dq, *J* = 14.7 Hz, 7.4 Hz, 2H, -CH_2CH$_3$), 1.52 (dt, *J* = 18.3 Hz, 7.1 Hz, 36H, -PC(CH_3)$_3$), 1.17 (dq, *J* = 14.8 Hz, 7.4 Hz, 2H, -CH_2CH$_3$), 1.03 (t, *J* = 7.4 Hz, 3H, -CH$_2$CH_3), 0.59 (t, *J* = 7.4 Hz, 6H, -CH$_2$CH_3); ^{31}P{^{1}H} NMR (202 MHz, C_6D_6): δ 109.43 (s); ^{13}C NMR (126 MHz, C_6D_6) δ = 182.32 (t, *J* = 4.9 Hz, -N=*C*-), 170.41 (t, *J* = 5.5 Hz, -N=*C*-), 139.31 (s, -C(Et)=C*H*-), 135.37 (t, *J* = 8.5 Hz, -*C*(Et)=CH-), 118.83 (q, *J* = 318.9 Hz, -*C*F$_3$), 50.80 (t, *J* = 7.3 Hz, -*C*(Et)$_2$), 38.48 (t, *J* = 9.9 Hz, -P*C*(CH$_3$)$_3$), 36.34 (s, -C(*C*H$_2$CH$_3$)$_2$), 28.40 (d, *J* = 2.9 Hz, -PC(*C*H$_3$)$_3$), 28.18 (d, *J* = 2.7 Hz, -PC(*C*H$_3$)$_3$), 27.19 (s, -C(*C*H$_2$CH$_3$)=CH-), 14.46 (s, -C(CH$_2$*C*H$_3$)=CH-), 9.79 (s, -C(CH$_2$*C*H$_3$)$_2$). Elemental analysis (%) for $C_{28}H_{52}F_3N_3NiO_3P_2S$: Calc. C, 48.85; H, 7.61; N, 6.10. Found: C, 48.72; H, 7.80; N, 5.93.

Synthesis of complex 3, (PN^3P)Ni(OH)

NaOH (48 mg, 1.2 mmol) was added to the toluene solution of (PN^3P)NiOTf (**2**) (10 mL, 688 mg, 1.0 mmol). The resulting suspension was stirred 12 h at 50 °C, filtered and all the volatiles were removed *in vacuo* to yield a red solid (550 mg, 99.0 %). The sample suitable for X-ray diffraction analysis was crystallized from concentrated pentane. ^{1}H NMR (500 MHz, C_6D_6) δ = 5.39 (t, *J* = 3.3 Hz, 1H, -C(Et)=C*H*-), 2.55 (q, *J* = 7.4 Hz, 2H, -CH_2CH$_3$), 2.11 (dq, *J* = 14.7 Hz, 7.4 Hz, 2H, -CH_2CH$_3$), 1.54 (ddd, *J* = 11.1 Hz, 9.1 Hz, 2.4 Hz, 36H, -PC(CH_3)$_3$), 1.29 (dq, *J* = 14.9 Hz, 7.5 Hz, 2H, -CH_2CH$_3$), 1.16 (t, *J* = 7.4 Hz, 3H, -CH$_2$CH_3), 0.71 (t, *J* = 7.4 Hz, 6H, -CH$_2$CH_3), -3.73 (t, *J* = 6.2 Hz, 1H, -O*H*); ^{31}P{^{1}H}NMR (202 MHz, C_6D_6): δ 98.85 (d, *J* = 301.2 Hz), 98.35 (d, *J* = 301.2 Hz); ^{13}C NMR (126 MHz, C_6D_6) δ = 181.84 (dd, *J* = 9.3 Hz, 4.2 Hz, -N=*C*-), 170.29 (dd, *J* = 9.2 Hz, 5.0 Hz, -N=*C*-), 138.89 (s, -C(Et)=C*H*-), 135.85 (dd, *J* = 9.2 Hz, 5.0 Hz, -*C*(Et)=CH-), 49.91 (dd, *J* = 12.0 Hz, 2.6 Hz, -*C*(Et)$_2$), 36.80 (td, *J* = 14.7 Hz, 14.3 Hz, 6.4 Hz, -P*C*(CH$_3$)$_3$), 36.22 (s, -C(*C*H$_2$CH$_3$)$_2$), 28.21 (dd, *J* = 29.2 Hz, 4.3 Hz, -PC(*C*H$_3$)$_3$), 27.13 (s, -C(*C*H$_2$CH$_3$)=CH-), 14.81 (s, -C(CH$_2$*C*H$_3$)=CH-), 9.89 (s, -C(CH$_2$*C*H$_3$)$_2$). Elemental analysis (%) for $C_{27}H_{53}N_3P_2ONi$: Calc. C, 58.29; H, 9.60; N, 7.55. Found: C, 58.46; H, 9.68; N, 7.62.

Synthesis of complex 4, (PN^3P)Ni(COOH)

A solution of complex **3** (11.1 mg, 20.0 μmol in C_6D_6) was put in a *J-Young* NMR tube. The tube was connected to Schlenk line and then degassed and saturated with CO three times. The color of the solution changed to colorless and completion of the reaction after 4 hours. The resultant C_6D_6 solution was directly used for analysis in NMR experiments. ^{1}H NMR (500 MHz, C_6D_6) δ = 10.23 (br, 1H, -COO*H*), 5.50 (t, *J* = 3.1 Hz, 1H, -C(Et)=C*H*-), 2.61 (q, *J* = 7.4 Hz, 2H, -CH_2CH$_3$), 2.16 (dq, *J* = 12.7 Hz, 7.4 Hz, 2H, -CH_2CH$_3$), 1.56–1.43 (m, 36H, -PC(CH_3)$_3$), 1.36 (dq, *J* = 12.8 Hz, 7.4 Hz, 2H, -CH_2CH$_3$), 1.20 (t, *J* = 7.4 Hz, 3H, -CH$_2$CH_3), 0.74 (t, *J* = 7.4 Hz, 6H, -CH$_2$CH_3); ^{31}P{^{1}H} (202 MHz, C_6D_6) δ = 114.63 (d, *J* = 194.2 Hz), 112.92 (d, *J* = 194.2 Hz); ^{13}C

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DOI: 10.1039/C8DT03403F

NMR (126 MHz, , C_6D_6) δ = 209.93–208.34 (m, -*C*OOH), 184.48 (s, excess *C*O), 180.10 (d, *J* = 9.2 Hz, -N=*C*-), 168.71 (d, *J* = 9.7 Hz, -N=*C*-), 139.35 (s, -C(Et)=C*H*-), 136.07 (d, *J* = 16.3 Hz, -*C*(Et)=CH-), 49.87 (d, *J* = 13.8 Hz, -*C*(Et)$_2$), 37.88 (ddd, *J* = 19.6 Hz, 11.7 Hz, 4.4 Hz, -P*C*(CH$_3$)$_3$), 36.22 (s, -C(*C*H$_2$CH$_3$)$_2$), 28.35 (dd, *J* = 24.1 Hz, 4.2 Hz, -PC(*C*H$_3$)$_3$), 27.02 (s, -C(*C*H$_2$CH$_3$)=CH-), 14.80 (s, -C(CH$_2$*C*H$_3$)=CH-), 9.94 (s, -C(CH$_2$*C*H$_3$)$_2$). The sample suitable for elemental analysis was crystallized from concentrated pentane. Elemental analysis (%) for $C_{28}H_{53}N_3P_2O_2Ni$: Calc. C, 57.55; H, 9.14; N, 7.19. Found: C, 57.74; H, 9.23; N, 7.08.

Synthesis of complex 5, (PN^{3}P)Ni(OCOOH)

A solution of complex **3** (11.1 mg, 20.0 μmol in C_6D_6) was put in a *J-Young* NMR tube. The tube was connected to Schlenk line and then degassed and saturated with CO_2 three times. The color of the solution changed to yellow and completion of the reaction immediately. The resultant C_6D_6 solution was directly used for analysis in NMR experiments. ^{1}H NMR (400 MHz, C_6D_6) *δ* = 12.70 (br, 1H, -NiOCOO*H*), 5.35 (t, *J* = 3.3 Hz, 1H, -C(Et)=C*H*-), 2.47 (qd, *J* = 7.3 Hz, 1.0 Hz, 2H, -C*H*$_2$CH$_3$), 2.03 (dq, *J* = 12.8 Hz, 7.4 Hz, 2H, -C*H*$_2$CH$_3$), 1.56 (ddd, *J* = 12.0 Hz, 9.4 Hz, 4.3 Hz, 36H, -PC(C*H*$_3$)$_3$), 1.24 (dq, *J* = 12.8 Hz, 7.4 Hz, 2H, -C*H*$_2$CH$_3$), 1.10 (t, *J* = 7.4 Hz, 3H, -CH$_2$C*H*$_3$), 0.67 (t, *J* = 7.4 Hz, 6H, -CH$_2$C*H*$_3$). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6): *δ* 104.19 (d, *J* = 273.8 Hz), 104.04 (d, *J* = 273.8 Hz); ^{13}C NMR (151 MHz, C_6D_6) *δ* = 182.15 (s, -N=*C*-), 170.48 (t, *J* = 6.4 Hz, -N=*C*-), 161.46 (s, Ni-O*C*OOH), 139.09 (s, -C(Et)=C*H*-), 138.19–133.79 (m, -*C*(Et)=CH-), 124.77 (excess *C*O$_2$), 52.68–45.12 (m, -*C*(Et)$_2$), 37.42 (td, *J* = 11.8 Hz, 6.9 Hz, -P*C*(CH$_3$)$_3$), 36.36 (s, -C(*C*H$_2$CH$_3$)$_2$), 28.05 (dd, *J* = 25.3 Hz, 3.6 Hz, -PC(*C*H$_3$)$_3$), 27.17 (s, -C(*C*H$_2$CH$_3$)=CH-), 14.62 (s, -C(CH$_2$*C*H$_3$)=CH-), 9.81 (s, -C(CH$_2$*C*H$_3$)$_2$).

Synthesis of complex 6, [(PN^{3}P)NiS]CO

A solution of **3** (11.1 mg, 20.0 μmol) and carbon disulfide (7.6 mg, 100.0 μmol) in C_6D_6 (0.6 mL) was put in a *J-Young* NMR tube. The red solution was kept at room temperature for 2 hours, completion of the reaction was confirmed by ^{31}P NMR spectroscopy. Removal of volatiles in *vacuo* resulted in a dark red solid that was used for analysis in NMR experiments (11.2 mg, 95.9 %). Crystals suitable for X-ray diffraction were grown by slow evaporation of a THF solution. ^{1}H NMR (600 MHz, C_6D_6) *δ* = 5.44 (t, *J* = 3.2 Hz, 1H, -C(Et)=C*H*-), 2.58 (qd, *J* = 7.4 Hz, 1.1 Hz, 2H, -C*H*$_2$CH$_3$), 2.13 (dq, *J* = 12.8 Hz, 7.3 Hz, 2H, -C*H*$_2$CH$_3$), 1.63 (ddd, *J* = 20.0 Hz, 9.6 Hz, 4.0 Hz, 36H, -PC(C*H*$_3$)$_3$), 1.33 (dq, *J* = 12.8 Hz, 7.4 Hz, 2H, -C*H*$_2$CH$_3$), 1.17 (t, *J* = 7.4 Hz, 3H, -CH$_2$C*H*$_3$), 0.74 (t, *J* = 7.4 Hz, 6H, -CH$_2$C*H*$_3$); ^{31}P{^{1}H}NMR (243 MHz, C_6D_6): *δ* 104.36 (d, *J* = 281.9 Hz), 104.24 (d, *J* = 281.9 Hz); ^{13}C NMR (126 MHz, C_6D_6) *δ* = 194.89 (q, *J* = 4.1 Hz, -S*C*O-), 180.21 (dd, *J* = 7.3 Hz, 4.1 Hz, -N=*C*-), 169.17–168.92 (m, -N=*C*-), 138.72 (s, -C(Et)=C*H*-), 135.94 (dd, *J* = 11.4 Hz, 5.3 Hz, -*C*(Et)=CH-), 50.24 (dd, *J* = 9.7 Hz, 4.6 Hz, -*C*(Et)$_2$), 38.49 (td, *J* = 11.2 Hz, 7.9 Hz, -P*C*(CH$_3$)$_3$), 36.43 (s, -C(*C*H$_2$CH$_3$)$_2$), 29.06 (d, *J* = 19.9 Hz, -PC(*C*H$_3$)$_3$), 27.29 (s, -C(*C*H$_2$CH$_3$)=CH-), 14.74 (s, -C(CH$_2$*C*H$_3$)=CH-), 9.99 (s, -C(CH$_2$*C*H$_3$)$_2$). Elemental analysis (%) for $C_{55}H_{104}N_6Ni_2OP_4S_2$: Calc. C, 56.42; H, 8.95; N, 7.18. Found: C, 56.65; H, 8.63; N, 7.09. HRMS (APCI) Calcd. for $C_{55}H_{104}N_6Ni_2OP_4S_2$: requires $[M+H]^+$ 1169.5449, Found: 1169.5443.

Synthesis of complex 7, (PN^{3}P)Ni(OCONHC$_6$H$_3$-2,6-Me$_2$)

A solution of **3** (11.1 mg, 20.0 μmol) and 2,6-dimethylphenyl isocyanate (2.9 mg, 20.0 μmol) in C_6D_6 (0.6 mL) was put in a *J-Young* NMR tube. The red solution was stirred for 4 hours at room temperature, completion of the reaction was confirmed by ^{31}P NMR spectroscopy. Removal of volatiles in *vacuo* resulted in a red solid that was used for analysis in NMR experiments (13.6 mg, 97.0 %). Crystals suitable for X-ray diffraction were grown by slow evaporation of a pentane solution. ^{1}H NMR (500 MHz, C_6D_6) *δ* = 7.04 (d, *J* = 7.4 Hz, 2H, Ph-*H*), 6.97 (dd, *J* = 8.3 Hz, 6.5 Hz, 1H, Ph-*H*), 5.45 (s, 1H, -CON*H*-), 5.36 (t, *J* = 3.2 Hz, 1H, -C(Et)=C*H*-), 2.51 (q, *J* = 7.3 Hz, 2H, -C*H*$_2$CH$_3$), 2.33 (s, 6H, -PhC*H*$_3$), 2.07 (dq, *J* = 14.7 Hz, 7.4 Hz, 2H, -C*H*$_2$CH$_3$), 1.58 (ddd, *J* = 17.9 Hz, 9.6 Hz, 4.2 Hz, 36H, -PC(C*H*$_3$)$_3$), 1.26 (dq, *J* = 14.8 Hz, 7.4 Hz, 2H, -C*H*$_2$CH$_3$), 1.13 (t, *J* = 7.4 Hz, 3H, -CH$_2$C*H*$_3$), 0.71 (t, *J*=7.4 Hz, 6H, -CH$_2$C*H*$_3$); ^{31}P{^{1}H}NMR (202 MHz, C_6D_6): *δ* 103.31 (d, *J* = 280.8 Hz), 103.16 (d, *J* = 280.8 Hz); ^{13}C NMR (126 MHz, C_6D_6) *δ* = 181.66 (dd, *J* = 7.8 Hz, 4.2 Hz, -N=*C*-), 170.06 dd, *J* = 7.5 Hz, 5.5 Hz, -N=*C*-), 157.30 (s, -*C*ONH-), 138.65 (s, -C(Et)=C*H*-), 138.04 (s, Ph-*C*), 135.37 (dd, *J* = 12.0 Hz, 4.9 Hz, -*C*(Et)=CH-), 134.31(s, Ph-*C*), 124.74(s, Ph-*C*), 49.85 (dd, *J* = 10.4 Hz, 4.3 Hz, -*C*(Et)$_2$), 37.03 (dt, *J* = 12.3 Hz, 7.9 Hz, -P*C*(CH$_3$)$_3$), 36.01 (s, -C(*C*H$_2$CH$_3$)$_2$), 27.72 (dt, *J* = 20.8 Hz, 2.7 Hz, -PC(*C*H$_3$)$_3$), 26.83 (s, -C(*C*H$_2$CH$_3$)=CH-), 19.22 (s, Ph*C*H$_3$), 14.30 (s, -C(CH$_2$*C*H$_3$)=CH-), 9.52 (s, -C(CH$_2$*C*H$_3$)$_2$). Elemental analysis (%) for $C_{36}H_{62}N_4NiO_2P_2$: Calc. C, 61.46; H, 8.88; N, 7.96. Found: C, 61.38; H, 8.95; N, 8.02. HRMS (ESI) Calcd. for $C_{36}H_{62}N_4NiO_2P_2$: requires $[M+H]^+$ 703.3780, Found: 703.3772.

Synthesis of complex 8, (PN^{3}P)Ni(SCONHC$_6$H$_3$-2,6-Me$_2$)

A solution of **3** (11.1 mg, 20.0 μmol) and 2,6-dimethylphenyl isothiocyanate (3.3 mg, 20.0 μmol) in C_6D_6 (0.6 mL) was put in a *J-Young* NMR tube. The red solution was stirred for 4 hours at room temperature, completion of the reaction was confirmed by ^{31}P NMR spectroscopy. Removal of volatiles in *vacuo* resulted in a red solid that was used for analysis in NMR experiments (13.9 mg, 96.5 %). Crystals suitable for X-ray diffraction were grown by slow evaporation of a pentane solution. ^{1}H NMR (500 MHz, C_6D_6) *δ* = 6.97 (m, 3H, Ph-*H*), 6.72 (s, 1H, -CON*H*Ar), 5.43 (t, *J* = 3.3 Hz, 1H, -C(Et)=C*H*-), 2.56 (q, *J* = 7.4 Hz, 2H, -C*H*$_2$CH$_3$), 2.32 (s, 6H, -PhC*H*$_3$), 2.11 (dq, *J* = 12.8 Hz, 7.4 Hz, 2H, -C*H*$_2$CH$_3$), 1.61 (ddd, *J* = 13.6 Hz, 9.3 Hz, 4.2 Hz, 36H, -PC(C*H*$_3$)$_3$), 1.31 (dq, *J* = 12.8 Hz, 7.5 Hz, 2H, -C*H*$_2$CH$_3$), 1.16 (t, *J* = 7.4 Hz, 3H, -CH$_2$C*H*$_3$), 0.73 (t, *J*=7.4 Hz, 6H, -CH$_2$C*H*$_3$); ^{31}P{^{1}H}NMR (202 MHz, C_6D_6): *δ* 103.05 (d, *J* = 290.9 Hz), 102.90 (d, *J* = 290.9 Hz); ^{13}C NMR (126 MHz, C_6D_6) *δ* = 180.89 (dd, *J* = 7.8 Hz, 4.0 Hz, -N=*C*-), 170.35 (s, -*C*ONH-), 169.49 (t, *J* = 6.4 Hz, -N=*C*-), 139.00 (s, -C(Et)=C*H*-), 137.10 (s, Ph-*C*), 135.87 (dd, *J* = 12.0 Hz, 4.8 Hz, -*C*(Et)=CH-), 135.33 (s, Ph-*C*), 126.25 (s, Ph-*C*), 50.32 (dd, *J* = 10.0 Hz, 4.4 Hz, -*C*(Et)$_2$), 38.64 (dt, *J* = 13.1 Hz, 9.6 Hz, -P*C*(CH$_3$)$_3$), 36.47 (s, -C(*C*H$_2$CH$_3$)$_2$), 28.77 (dt, *J* = 21.0 Hz, 2.4 Hz, -PC(*C*H$_3$)$_3$), 27.34 (s, -C(*C*H$_2$CH$_3$)=CH-), 19.03 (s, Ph*C*H$_3$), 14.73 (s, -C(CH$_2$*C*H$_3$)=CH-), 9.96 (s, -C(CH$_2$*C*H$_3$)$_2$). Elemental analysis (%) for $C_{36}H_{62}N_4NiO_2P_2$: Calc. C, 60.09; H, 8.68; N, 7.79. Found: C, 60.06; H, 8.70; N, 7.71. HRMS (ESI) Calcd. for $C_{36}H_{62}N_4NiOP_2S$: requires $[M+H]^+$ 719.3551, Found: 719.3524.

Synthesis of complex 9, (PN^{3}P)Ni(NHCOMe)

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DOI: 10.1039/C8DT03403F

A solution of **3** (11.1 mg, 20.0 μmol) and acetonitrile (4.0 mg, 100.0 μmol) in C_6D_6 (0.6 mL) was put in a *J-Young* NMR tube. The red solution was heated for 72 hours at 60 °C, completion of the reaction was confirmed by ^{31}P NMR spectroscopy. Removal of volatiles in *vacuo* resulted in a red solid that was used for analysis in NMR experiments (11.7 mg, 98.2 %). Crystals suitable for X-ray diffraction were grown by slow evaporation of a pentane solution at room temperature. ^1H NMR (500 MHz, C_6D_6) δ = 5.41 (t, *J* = 3.2 Hz, 1H, -C(Et)=C*H*-), 2.53 (q, *J* = 7.4 Hz, 2H, -CH_2CH$_3$), 2.08 (dq, *J* = 14.6 Hz, 7.4 Hz, 2H, -CH_2CH$_3$), 1.90 (s, 3H, Ni-NHCOCH_3), 1.49 (ddd, *J* = 16.9 Hz, 9.7 Hz, 3.8 Hz, 36H, -PC(CH_3)$_3$), 1.39–1.21 (m, 2H, -CH_2CH$_3$), 1.14 (t, *J* = 7.4 Hz, 3H, -CH$_2$CH_3), 0.94 (s, 1H, Ni-N*H*C(O)CH$_3$), 0.71 (t, *J* = 7.4 Hz, 6H, -CH$_2$CH_3). $^{31}P\{^1H\}$NMR (202 MHz, C_6D_6): δ 103.61 (d, *J* = 292.9 Hz), 103.41 (d, *J* = 292.9 Hz); ^{13}C NMR (101 MHz, C_6D_6) δ = 181.35 (dd, *J* = 7.9 Hz, 4.2 Hz, -N=*C*-), 175.26 (s, -*C*ONH-), 169.93 (dd, *J* = 8.0 Hz, 5.4 Hz, -N=*C*-), 138.99 (s, -C(Et)=C*H*-), 135.85 (dd, *J* = 12.5 Hz, 4.4 Hz, -*C*(Et)=CH-), 50.06 (dd, *J* = 10.8 Hz, 3.9 Hz, -*C*(Et)$_2$), 37.44 (dt, *J* = 12.6 Hz, 8.4 Hz, -P*C*(CH$_3$)$_3$), 36.34 (s, -C(*C*H$_2$CH$_3$)$_2$), 28.29 (dt, *J* = 20.2 Hz, 2.7 Hz, -PC(*C*H$_3$)$_3$), 27.18 (s, -C(*C*H$_2$CH$_3$)=CH-), 26.70 (s, *C*H$_3$C(O)NH-Ni), 14.70 (s, -C(CH$_2$*C*H$_3$)=CH-), 9.89 (s, -C(CH$_2$*C*H$_3$)$_2$). Elemental analysis (%) for $C_{29}H_{56}N_4NiOP_2$: Calc. C, 58.30; H, 9.45; N, 9.38. Found: C, 58.39; H, 9.55; N, 9.38. HRMS (ESI) Calcd. for $C_{29}H_{56}N_4NiOP_2$: requires $[M+H]^+$ 597.3361, Found: 597.3346.

Synthesis of complex 10, (PN^{3}P)Ni(NHCOPh)

The procedure is similar to that of complex **11** with a yield of 97.7 %. ^1H NMR (500 MHz, C_6D_6) δ = 8.03–7.92 (m, 2H, Ph-*H*), 7.19 (t, *J* = 7.7 Hz, 2H, Ph-*H*), 7.10 (td, *J* = 7.1 Hz, 1.4 Hz, 1H, Ph-*H*), 5.43 (t, *J* = 3.2 Hz, 1H, -C(Et)=C*H*-), 2.55 (q, *J* = 7.4 Hz, 2H, -CH_2CH$_3$), 2.29 (s, 1H, Ni-N*H*C(O)Ph), 2.10 (dq, *J* = 12.8 Hz, 7.4 Hz, 2H, -CH_2CH$_3$), 1.50 (ddd, *J* = 15.9 Hz, 9.7 Hz, 3.8 Hz, 36H, -PC(CH_3)$_3$), 1.31 (dq, *J* = 12.8 Hz, 7.4 Hz, 2H, -CH_2CH$_3$), 1.15 (t, *J* = 7.4 Hz, 3H, -CH$_2$CH_3), 0.74 (t, *J* = 7.4 Hz, 6H, -CH$_2$CH_3). $^{31}P\{^1H\}$NMR (202 MHz, C_6D_6): δ 104.46 (d, *J* = 288.8 Hz), 104.28 (d, *J* = 288.8 Hz); ^{13}C NMR (126 MHz, C_6D_6) δ = 181.48 (dd, *J* = 7.9 Hz, 4.1 Hz, -N=*C*-), 172.39 (s, -*C*ONH-), 170.02 (dd, *J* = 8.1 Hz, 5.3 Hz, -N=*C*-), 140.37 (s, Ph-*C*), 139.04 (s, -C(Et)=C*H*-), 135.88 (dd, *J* = 12.5 Hz, 4.5 Hz, , -*C*(Et)=CH-), 128.84 (s, Ph-*C*), 127.04 (s, Ph-*C*), 50.14 (dd, *J* = 10.7 Hz, 3.9 Hz, -*C*(Et)$_2$), 37.55 (dt, *J* = 12.5 Hz, 8.3 Hz, -P*C*(CH$_3$)$_3$), 36.38 (s, -C(*C*H$_2$CH$_3$)$_2$), 28.35 (dt, *J* = 21.0 Hz, 2.5 Hz,), 27.21 (s, -C(*C*H$_2$CH$_3$)=CH-), 14.71 (s, -C(CH$_2$*C*H$_3$)=CH-), 9.93 (s, -C(CH$_2$*C*H$_3$)$_2$). Elemental analysis (%) for $C_{34}H_{58}N_4NiOP_2$: Calc. C, 61.92; H, 8.86; N, 8.50. Found: C, 62.13; H, 8.92; N, 8.39.

General procedure for the nitrile hydration

In a typical reaction, complex **3** (11.1 mg, 20 μmol, 1 mol %), nitrile (2 mmol), distilled H_2O (0.1 mL) and THF (1.0 mL) were added to a 10 mL Schlenk tube (high vacuum valve). The tube was sealed and heated in the oil bath at 100 °C. After 24 h, the reaction mixture was cooled and then the solvent was evaporated under reduced pressure. Without any workup, the residue were directly purified by flash column chromatography.

Acetamide (isolated yield, > 99%): ^1H NMR (500 MHz, DMSO-d_6) δ = 7.29 (s, 1H), 6.69 (s, 1H), 1.76 (s, 3H); ^{13}C NMR (126 MHz, DMSO-d_6) δ = 171.60, 22.53.

Acrylamide (isolated yield, 64%): ^1H NMR (400 MHz, DMSO-d_6) δ = 7.51 (s, 1H), 7.07 (s, 1H), 6.18 (dd, *J* = 17.2 Hz, 10.0 Hz, 1H), 6.06 (dd, *J* = 17.2 Hz, 2.3 Hz, 1H), 5.59 (dd, *J* = 10.0 Hz, 2.3 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ = 166.35, 132.01, 125.51.

1,3-Benzodioxole-5-acetamide (isolated yield, 42%): ^1H NMR (400 MHz, DMSO-d_6) δ = 7.38 (s, 1H), 6.90–6.77 (m, 3H), 6.70 (dd, *J* = 8.0 Hz, 1.7 Hz, 1H), 5.96 (s, 2H), 3.27 (s, 2H); ^{13}C NMR (101 MHz, DMSO-d_6) δ = 172.37, 147.02, 145.69, 130.15, 122.01, 109.50, 107.94, 100.71, 41.84.

Benzamide (isolated yield, 97%): ^1H NMR (500 MHz, DMSO-d_6) δ = 7.98 (s, 1H), 7.93–7.83 (m, 2H), 7.56–7.49 (m, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.37 (s, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ = 167.93, 134.26, 131.22, 128.21, 127.46.

Nicotinamide (isolated yield, > 99%): ^1H NMR (400 MHz, DMSO-d_6) δ = 9.04 (dd, *J* = 2.3 Hz, 0.9 Hz, 1H), 8.69 (dd, *J* = 4.8 Hz, 1.7, 1H), 8.29–8.11 (m, 2H), 7.62 (s, 1H), 7.48 (ddd, *J* = 7.9 Hz, 4.8 Hz, 0.9 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ = 166.58, 151.94, 148.73, 135.22, 129.72, 123.45.

3,4-Diaminobenzamide (isolated yield, 74%): ^1H NMR (400 MHz, DMSO-d_6) δ = 7.37 (s, 1H), 7.06 (d, *J* = 2.0 Hz, 1H), 6.98 (dd, *J* = 8.0 Hz, 2.0 Hz, 1H), 6.70 (s, 1H), 6.45 (d, *J* = 8.0 Hz, 1H), 4.93 (s, 2H), 4.49 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ = 168.74, 138.49, 133.74, 122.65, 117.72, 114.20, 112.70.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We acknowledge the financial supports from King Abdullah University of Science and Technology (KAUST) and from the Ministry of Science and Technology of Taiwan (MOST 106-2113-M-110-003).

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