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Synthesis and reactivity of a masked PSiP pincer supported nickel hydride

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ABSTRACT

Tridentate PSiP pincer ligands featuring two phosphine donors and an anionic Si donor have attracted considerable attention in recent years. Here, we report the synthesis of the η^3-cyclooctenyl complex, $(^{Ph}PSiP)Ni(\eta^3$-cyclooctenyl) (**1**; $^{Ph}PSiP = Si(Me)(2\text{-}PPh_2\text{–}C_6H_4)_2$) through the reaction of $Ni(COD)_2$ with $^{Ph}PSi^{H}P$ ($^{Ph}PSi^{H}P = HSi(Me)(2\text{-}PPh_2\text{–}C_6H_4)_2$). We propose, that as a result of β-hydride elimination of 1,3-COD, **1** can act as a synthetic equivalent for $(^{Ph}PSiP)NiH$. The reaction of **1** with a variety of different reagents including another equivalent of $^{Ph}PSi^{H}P$ to form $(^{Ph}PSiP)_2Ni$ (**2**), 1,3-COD and H_2, PPh_3 to form the Ni(0) species $(^{Ph}PSi^{H}P)Ni(PPh_3)$ (**3**) and 1,3-COD and 2,6-lutidine·HCl to generate $(^{Ph}PSiP)NiCl$ (**4**), 1,3-COD and H_2 are in agreement with this hypothesis. In addition, in the reaction of **1** with BH_3·THF, $(^{Ph}PSiP)Ni(\kappa^2\text{-}BH_4)$ (**5**) was observed but could not be isolated. This reaction presumably proceeds via $(^{Ph}PSiP)NiH$. This is supported by the observation that the reaction of $(^{Cy}PSiP)NiH$ ($^{Cy}PSiP = Si(Me)(2\text{-}PCy_2\text{-}C_6H_4)_2$) with BH_3·THF formed $(^{Cy}PSiP)Ni(\kappa^2\text{-}BH_4)$ (**6**). Catalytic reactions such as alkene isomerization and CO_2 reduction using **1** as precatalyst are also consistent with a nickel hydride being accessible. Compounds **1**, **2** and **6** were characterized by X-ray crystallography.

1. Introduction

Over the last 20 years pincer ligands have become ubiquitous due to their ability to stabilize reactive transition metal complexes and generate species with high thermal stability [1]. In many cases the syntheses of pincer ligands are modular, which allows for the facile preparation of complexes with tunable steric and electronic properties. As a result complexes supported by pincer ligands have been used in a wide variety of different applications including organic synthesis [2], the activation of small molecules such as N_2 [3] and CO_2 [4], and as catalysts for alkane dehydrogenation and metathesis [5] and olefin polymerization [6]. Lately, pincer ligands which contain two phosphine donors and a central anionic Si donor (PSiP ligands) have attracted particular attention due to the high *trans*-influence of the Si atom [7]. Iwasawa has demonstrated that Pd complexes supported by PSiP ligands can be used as catalysts for the carboxylation of allenes with CO_2 [7d], while our group has demonstrated that CO_2 insertion into Ni and Pd hydrides is more favorable for complexes supported by PSiP ligands compared to those containing other pincer ligands [7q].

Recently, it has been demonstrated that the substituents on the phosphine donors of a PSiP ligand with phenylene backbones can affect the reactivity of Pd and Ni complexes with PSiP ligands. For example, treatment of $(^{Cy}PSiP)MCl$ (M = Ni or Pd; $^{Cy}PSiP = Si(Me)(2\text{-}PCy_2\text{–}C_6H_4)_2$) with $LiEt_3BH$ results in the formation of $(^{Cy}PSiP)MH$ [7q], whereas the reaction of the related species $(^{Ph}PSiP)MCl$ ($^{Ph}PSiP = Si(Me)(2\text{-}PPh_2\text{–}C_6H_4)_2$) with $LiEt_3BH$ generates an unusual dimeric species with five coordinate hypervalent bridging Si atoms, without any evidence for the formation of a well-defined metal hydride [7s]. In fact the preparation of a nickel hydride supported by the $^{Ph}PSiP$ ligand has been elusive, as both the Sun [7r] and Iwasawa [7j] groups have independently demonstrated that the reaction of $Ni(PR_3)_4$ with $^{Ph}PSi^{H}P$ ($^{Ph}PSi^{H}P = HSi(Me)(2\text{-}PPh_2\text{–}C_6H_4)_2$) generates a Ni(0) species with an η^2-Si–H ligand (Eq. (1)). Although these species have been proposed to be in equilibrium with a nickel hydride, there is relatively little evidence for this process and the free phosphine which is present in solution can interfere in further reactions. Here, we describe the preparation of a masked $^{Ph}PSiP$ Ni hydride, along with an unusual example of trigonal bipyramidal Ni complex.

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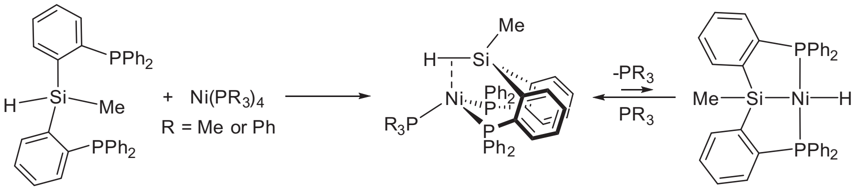


(1)

2. Results and discussion

To prevent formation of Ni–PR_3 species, we investigated the reaction of ^{Ph}PSi^{H}P with a phosphine-free metal starting material. Both Ozerov et al. [8] and Liang et al. [9] have reported the synthesis of (^{R}PNP)NiH (^{R}PNP = N(2-PR_2-4-MeC_6H_3)$_2$; R = alkyl or aryl) complexes through the oxidative addition of ^{R}PN^{H}P (^{R}PN^{H}P = HN(2-PR_2-4-MeC_6H_3)$_2$; R = alkyl or aryl) with Ni(COD)$_2$ (COD = cyclooctadiene, unless otherwise stated 1,5-cyclooctadiene). The reaction of ^{Ph}PSi^{H}P with Ni(COD)$_2$ did not lead to the desired (^{Ph}PSiP)NiH product, instead (^{Ph}PSiP)Ni(η^3-C_8H_{13}) (**1**) was isolated in 78% yield (Scheme 1). Interestingly, Liang and co-workers had reported that although the desired (^{R}PNP)NiH was generated for most substituents on the phosphine through the reaction of ^{R}PN^{H}P ligand with Ni(COD)$_2$, an analogous product to **1** was observed in case of ^{Ph}PN^{H}P (^{Ph}PN^{H}P = HN(2-PPh_2-4-MeC_6H_3)$_2$). This suggests that formation of a stable hydride may be particularly difficult for pincer systems with phenyl substituents on the phosphines, regardless of the identity of the central donor. The ^{31}P{^{1}H} NMR spectrum of **1** contained two doublets at 52.1 and 36.9 ppm with a $^2J_{PP}$ coupling constant of 117 Hz, which is similar to that reported by Turculet and co-workers for the related complex (^{Cy}PSiP)Ni(η^3-C_3H_5).[7h] In the ^{29}Si{^{1}H} spectrum of **1** a doublet of doublets (due to coupling to two inequivalent phosphorus atoms) was observed at 52.9 ppm, which is consistent with the shift for other complexes in which the pincer ligand is bound in a standard tridentate fashion. At this stage we believe that **1** is most likely formed via initial oxidative addition of the Si–H bond of the ^{Ph}PSi^{H}P ligand to Ni(COD)$_2$ to generate (^{Ph}PSiP)NiH, with concomitant release of two equivalents of COD. Subsequently, one equivalent of the free COD can insert into the Ni–H bond of (^{Ph}PSiP)NiH to generate **1**. Interestingly, only 1,3-COD was observed in the ^{1}H NMR spectrum as a by-product of the reaction. This suggests that the insertion of COD into the Ni–H is reversible and that the difference in energies of the proposed Ni–H species and **1** is small. Therefore it is plausible that **1** could act as a masked Ni–H.

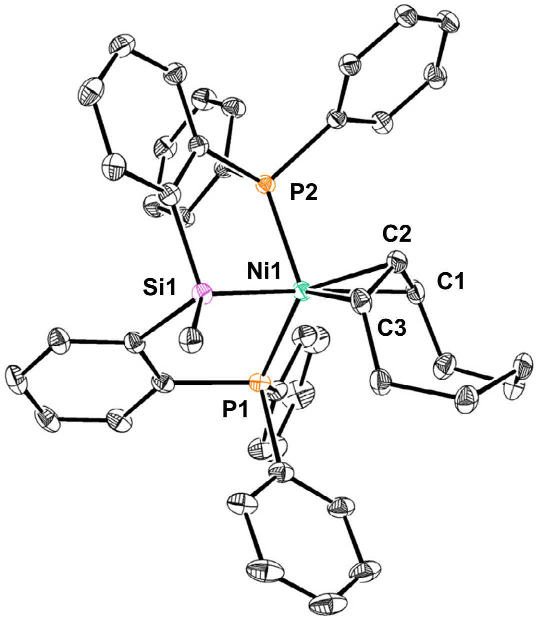
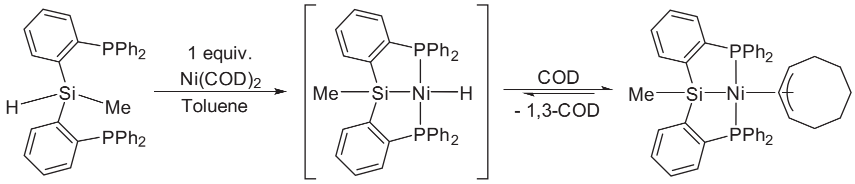


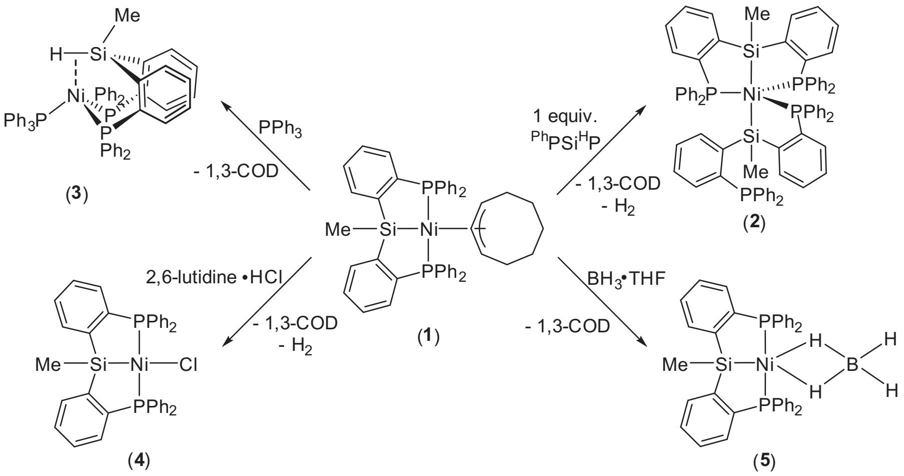
Fig. 1. ORTEP of (^{Ph}PSiP)Ni(η^3-C_8H_{13}) (**1**). Ellipsoids shown at the 30% probability level. There is disorder in the cyclooctenyl ligand and only the major component is shown. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ni(1)–P(1) 2.1778(7), Ni(1)–P(2) 2.2218(7), Ni(1)–Si(1) 2.2271(7), Ni(1)–C(1) 2.163(3), Ni(1)–C(2) 1.987(3), Ni(1)–C(3) 2.117(3), C(1)–C(2) 1.393(4), C(2)–C(3) 1.420(4); P(2)–Ni(1)–Si(1) 86.58(3), P(1)–Ni(1)–Si(1) 87.42(3), P(2)–Ni(1)–P(1) 117.88(3), Si(1)–Ni(1)–C(1) 155.10(8), Si(1)–Ni(1)–C(2) 117.88(3), Si(1)–Ni(1)–C(3) 84.18(8), C(1)–C(2)–C(3) 124.0(3).

Orange crystals of **1** suitable for X-ray crystallography were obtained from a concentrated THF solution layered with pentane at room temperature. The solid state structure (Fig. 1) clearly shows that the cyclooctenyl ligand is bound in an η^3-fashion and confirms that the Ni center is five coordinate. The terminal Ni–C bond distances are almost identical (Ni(1)–C(1) is 2.163(3) Å and Ni(1)–C(3) is 2.117(3) Å), while the central Ni–C bond is considerably shorter (Ni(1)–C(2) is 1.987(3) Å). The C–C bond distances in the cyclooctenyl ring are also in agreement with η^3-binding, as the C(1)–C(2) and C(2)–C(3) (approximately 1.40 Å) bond distances are significantly shorter than the other C–C bond distances (approximately 1.50 Å). The geometry around Ni is in between square pyramidal and trigonal pyramidal. The degree of distortion from square pyramidal to trigonal bipyramidal was quantified by calculating the value τ [10]. On the scale of 0 to 1, where 0 denotes idealized square pyramidal character, τ is 0.56 for 1. Interestingly, the solid state structure shows a P(1)–Ni(1)–P(2) angle of 117.88(3)° for the pincer ligand. This is consistent with facial binding [7g,7h,7j] of the ^{Ph}PSiP ligand rather than the more common



(**1**)

Scheme 1. Reaction of ^{Ph}PSi^{H}P ligand with Ni(COD)$_2$ to generate (^{Ph}PSiP)Ni(η^3-C_8H_{13}) (**1**).



Scheme 2. Stoichiometric reactivity of (^{Ph}PSiP)Ni(η^3-C$_8$H$_{13}$) (**1**).

meridional binding [7q] and demonstrates the flexibility of the ^{Ph}PSiP ligand despite the phenylene linkers. The Ni(1)–Si(1) bond distance of 2.2271(7) Å and the Ni–P bond lengths (Ni(1)–P(1) is 2.1778(7) Å and Ni(1)–P(2) is 2.2218(7) Å) are consistent with those observed in other PSiP supported complexes.[7h,7j,7q] Overall, the structure of **1** closely resembles that of (^{Ph}PSiP)Ni(η^3-C$_3$H$_5$) [7h]. Previously, similarities between η^3-allyl and η^3-cyclooctenyl complexes have also been observed in L$_3$(CO)$_2$Co(η^3-cyclooctenyl) complexes [11].

The stoichiometric reactivity of **1** was probed to determine if it was a true synthetic equivalent of a Ni hydride. The reaction of **1** with an additional equivalent of the ^{Ph}PSi^{H}P ligand produced the new homoleptic Ni(II) complex, (^{Ph}PSiP)$_2$Ni (**2**) (Scheme 2). The by-products observed in this reaction were one equivalent of 1,3-COD and H$_2$. This suggests that the reaction may proceed via β-hydride elimination of 1,3-COD from the η^3-cyclooctenyl complex **1** to generate (^{Ph}PSiP)NiH, followed by protonation of the Ni–H by the free ligand to generate H$_2$ and **2**. Alternatively, after β-hydride elimination of 1,3-COD, the Si–H bond of the second equivalent of free ligand could undergo oxidative addition to (^{Ph}PSiP)NiH, followed by reductive elimination of H$_2$. Recently, Hu and co-workers reported that the pincer supported Ni–H complex, (^{Me}NNN)NiH (^{Me}NNN = N(2-NMe$_2$–C$_6$H$_4$)$_2$), decomposed to a five coordinate homoleptic Ni(II) complex with release of H$_2$, but additional products were also formed in the process [12]. Nevertheless, this reaction is presumably related to what is observed with the ^{Ph}PSiP ligand. The ^{31}P{^{1}H} NMR spectrum of **2** displays four distinct resonances, including a singlet at −7.66 ppm, which is consistent with a phosphine which is not bound to the metal as it is only slightly downfield of the free ligand resonance (−10.9 ppm). The ^{29}Si{^{1}H} spectrum contains two resonances at 58.4 and 44.1 ppm, consistent with two different ^{Ph}PSiP ligands being present. Compound **2** could also be synthesized through the direct reaction of Ni(COD)$_2$ with two equivalents of ^{Ph}PSi^{H}P without the isolation of **1**.

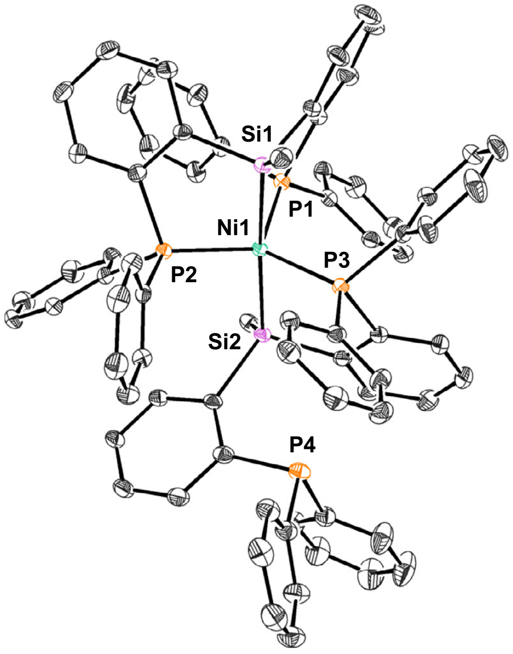
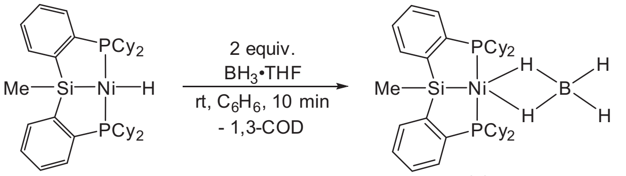


Fig. 2. ORTEP of (^{Ph}PSiP)$_2$Ni (**2**). Ellipsoids shown at the 30% probability level. Hydrogen atoms and solvent of crystallization are omitted for clarity. Selected bond lengths (Å) and angles (°): Ni(1)–Si(1) 2.3197(9), Ni(1)–Si(2) 2.3710(9), Ni(1)–P(1) 2.2870(7), Ni(1)–P(2) 2.2144(7), Ni(1)–P(3) 2.1868(7), Si(1)–Ni(1)–Si(2) 175.21(3), P(1)–Ni(1)–P(2) 114.53(3), P(2)–Ni(1)–P(3) 131.00(3), P(3)–Ni(1)–P(1) 112.93(3), Si(1)–Ni(1)–P(1) 82.96(3), Si(1)–Ni(1)–P(2) 83.15(3), Si(1)–Ni(1)–P(3) 91.19(3), Si(2)–Ni(1)–P(1) 99.60(3), Si(2)–Ni(1)–P(2) 99.34(3), Si(2)–Ni(1)–P(3) 84.09(3).

Single crystals of **2** were grown at room temperature from a concentrated solution of toluene layered with pentane. The solid state structure (Fig. 2) indicates that one of the pincer ligands binds in a facial manner (the P(1)–Ni(1)–P(2) angle is 114.53(3)°), whereas the other binds as a bidentate ligand with a dangling phosphine arm. The Si–Ni–P bond angles are similar in the bidentate ligand, but slightly larger for the tridentate ligand presumably due to steric factors (Si(1)–Ni(1)–P(1) is 82.96(3)°, Si(1)–Ni(1)–P(2) is 83.15(3)° and Si(2)–Ni(1)–P93) is 84.09(3). The five-coordinate Ni center has a distorted trigonal bipyramidal geometry with a τ value of 0.74. There are a number of other examples of trigonal bipyramidal Ni complexes with pincer ligands [13], although to the best of our knowledge there are only two other homoleptic five coordinate Ni complexes with pincer ligands [12,14]. Interestingly, the two strong *trans* influence Si atoms are located *trans* to each other (the Si(1)–Ni(1)–Si(2) angle is 175.21(3)°) and as a result the Ni–Si bond lengths are elongated (Ni(1)–Si(1) is 2.3197(9) Å and Ni(1)–Si(2) is 2.3710(9) Å). The Ni–P bond lengths are similar to those observed in **1**. To the best of our knowledge **2** is the first example of a compound that contains the ^{Ph}PSiP ligand bound in a bidentate fashion, and demonstrates the versatility of these ligands.

The addition of one equivalent of PPh$_3$ to **1** resulted in complete conversion to the Ni(0) species (^{Ph}PSi^{H}P)Ni(PPh$_3$) (**3**) (Scheme 2), a product which features an η^2-silane and has previously been reported by the Iwasawa group [9]. The formation of **3** was confirmed by ^{1}H NMR spectroscopy, where a characteristic η^2-Si–H resonance was observed at −2.9 ppm. The only byproduct of this reaction is 1,3-COD, and we suggest a pathway which involves β-hydride elimination of 1,3-COD followed by reductive formation of a Si–H bond from the postulated (^{Ph}PSiP)NiH intermediate and coordination of PPh_3 to generate **3**. Similarly, it is proposed that initial β-hydride elimination of 1,3-COD to generate (^{Ph}PSiP)NiH occurs in the reaction between **1** and 2,6-lutidine·HCl. In this case the final metal product is (^{Ph}PSiP)NiCl (**4**),[7q] which is most likely formed via a protonation of (^{Ph}PSiP)NiH to generate H_2, along with coordination of Cl^-.

Recently, Guan and co-workers demonstrated that POCOP supported Ni hydrides of the type {2,6-$(R_2PO)_2C_6H_3$}NiH (R = ^{t}Bu, ^{i}Pr or ^{c}Pe) react with BH_3·THF to produce borohydride complexes with κ^2-BH_4 ligands.[15] The reaction of **1** with BH_3·THF resulted in the loss of 1,3-COD and the formation of (^{Ph}PSiP)Ni(κ^2-BH_4) (**5**). In the ^{1}H NMR spectrum a broad resonance in the baseline was observed between 1 and 2 ppm at room temperature, consistent with a fluxional κ^2-BH_4 ligand at room temperature [15]. The ^{31}P{^{1}H} NMR spectrum was consistent with a C_s symmetric product. However, compound **5** was relatively insoluble in most common organic solvents which precluded ^{1}H NMR studies at low temperature and also prevented us from isolating this species in a pure form. Previously, we have demonstrated that ^{Cy}PSiP ligand normally generates complexes with greater solubility than the ^{Ph}PSiP ligand [7q]. In order to confirm our assignment of **5**, two equivalents of BH_3·THF were added to a solution of (^{Cy}PSiP)NiH in benzene (Eq. (2)). The κ^2-BH_4 complex (^{Cy}PSiP)Ni(κ^2-BH_4) (**6**) was isolated from the reaction mixture in 57% yield, again providing support that **1** can access (^{Ph}PSiP)NiH. Unfortunately the BH_4 resonance could not be clearly observed in the ^{1}H NMR spectrum of **6** as it was overlapping with the cyclohexyl signals of the ligand. However, the ^{31}P{^{1}H} and ^{29}Si{^{1}H} spectra were both consistent with a product in which the ^{Cy}PSiP ligand was bound in a standard tridentate fashion.



(**6**)

(2)

Slow evaporation of a concentrated solution of **6** in pentane at room temperature gave red crystalline solids suitable for X-ray crystallography. The high quality solid state structure of **6** (Fig. 3) allowed for the location and refinement of the B–H hydrogen atoms and unambiguously confirms the proposed κ^2-binding mode of the borohydride ligand, analogous to the POCOP supported Ni borohydride complexes observed by Guan and co-workers.[15] The Ni–H bond lengths show significant elongation (1.70(5) and 1.62(5) Å) compared to terminal Ni–H bond distances and are similar to those in (^{R}POCOP)Ni(κ^2-BH_4) (R = ^{t}Bu, ^{i}Pr or ^{c}Pe), in which the Ni–H distance varies from 1.60(3) to 1.88(4) Å. These distances are also comparable to those observed in five coordinate Ni borohydride complexes with other ligands [16]. The Ni(1)···B(1) distance (2.170(6) Å) is the shortest of the previously known Ni κ^2-borohydride complexes (2.180(3)–2.240(7) Å) [15,16], but considerably longer than that of a κ^3-borohydride (2.048(5) Å) [17]. The geometry at boron is approximately tetrahedral. In contrast the exact geometry at the Ni center is ambiguous, but the P(1)–Ni(1)–P(2) angle of 145.70(5)° suggests a distortion from a purely meridionally bound pincer ligand. There is no significant difference in the Ni–Si bond length (2.234(1) Å) and Ni–P bond distances (Ni(1)–P(1) is 2.182(1) and Ni(1)–P(2) is 2.189(1) Å) compared to other PSiP supported systems [7h,7q].

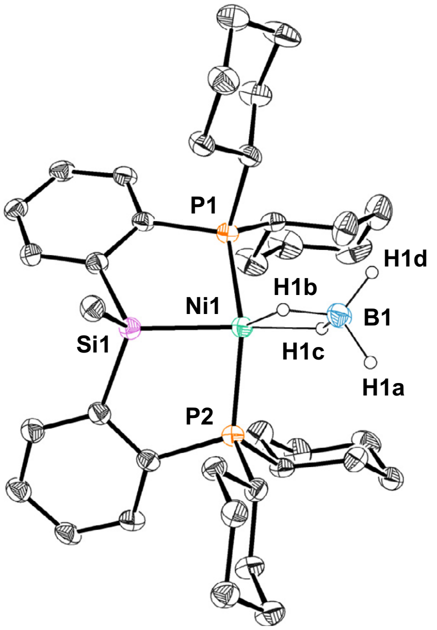
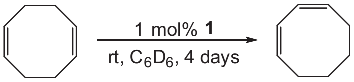


Fig. 3. ORTEP of (^{Cy}PSiP)Ni(κ^2-BH_4) (**6**). Thermal ellipsoids shown at 30% probability. Selected hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ni(1)–P(1) 2.182(1), Ni(1)–P(2) 2.189(1), Ni(1)–Si(1) 2.234(1), Ni(1)–H(1b) 1.70(5), Ni(1)–H(1c) 1.62(5), B(1)–H(1b) 1.18(4), B(1)–H(1c) 1.34(5), B(1)–H(1a) 1.14(5), B(1)–H(1d) 1.05(5), Ni(1)···B(1) 2.170(6), P(1)–Ni(1)–Si(1) 85.26(4), P(2)–Ni(1)–Si(1) 84.86(4), P(1)–Ni(1)–P(2) 145.70(5), Si(1)–Ni(1)···B(1) 145.7(2), H(1b)–Ni(1)–H(1c) 71(2), H(1b)–B(1)–H(1c) 99(3), H(1a)–B(1)–H(1d) 107(4), Si(1)–Ni(1)–H(1b) 176(2), Si(1)–Ni(1)–H(1c) 113(2).

Metal hydrides are often active catalysts for the isomerization of alkenes [18]. Given that our stoichiometric reactions suggest that **1** can readily β-hydride eliminate 1,3-COD to generate (^{Ph}PSiP)NiH, **1** was tested as catalyst for alkene isomerization. The addition of 100 equivalents of 1,5-COD to a solution of **1** in C_6D_6 resulted in complete isomerization to 1,3-COD over 4 days at room temperature (Eq. (3)). Similarly, **1** is an active catalyst for the isomerization of 1-hexene, initially to *cis*- and *trans*-2-hexene and eventually to a thermodynamic mixture of hexene isomers, including *cis*- and *trans*-3-hexene (Eq. (4)).



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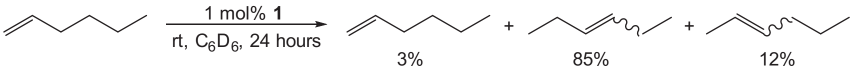

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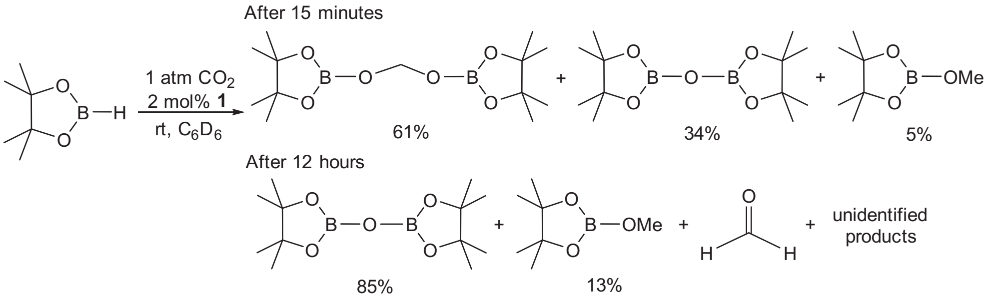

(5)

It has been demonstrated that a number of pincer supported Ni hydrides can catalyze the selective reduction of CO_2 in the presence of boranes [4c,19], while previously we have demonstrated that (^{Cy}PSiP)PdH can catalyze the conversion of CO_2 and pinacolborane, HB(pin), to HC(O)OB(pin) [20]. The reaction of CO_2 and HB(pin) in the presence of 2 mol% **1**, led to the formation of a number of different CO_2 reduction products (Eq. (5)). After 15 min (pin)BOB(pin), (pin)BOMe and (pin)$BOCH_2OB$(pin) were all present in 61:34:5 ratio. After 12 h, all the HB(pin) had been consumed and integration of the products showed that 13% (pin)BOMe and 85% (pin)BOB(pin) were present, along with several other products that could not be identified. Noticeably, a peak at 8.72 ppm, which corresponds to formaldehyde was also observed, while only a trace amount of (pin)$BOCH_2OB$(pin) remained. Recently, Bontemps and Sabo-Etienne observed similar products from the reaction of CO_2 and HB(pin) with a Ru catalyst [21]. This reaction indicates that small changes to both the metal and ligand greatly affect the products that are generated, as a similar reaction using (^{Cy}PSiP)PdH as the catalyst was selective. Further tuning of the catalyst may result in different selectivity.

3. Conclusions

In conclusion, we describe the synthesis of an unusual η^3-cyclooctenyl complex, (^{Ph}PSiP)Ni(η^3-cyclooctenyl) (**1**). Using a combination of stoichiometric and catalytic reactions we provide strong evidence that **1** can act as a synthetic equivalent of (^{Ph}PSiP)NiH through β-hydride elimination of 1,3-COD. For example the reactions of **1** with both BH_3·THF and PPh_3 result in the elimination of 1,3-COD and the formation of complexes which contain either a Ni–H bond or an Si–H bond, which likely forms via the rearrangement of an intermediate with a Ni–H bond. In contrast, the reaction of **1** with 2,6-lutidine·HCl or ^{Ph}PSi^{H}P, results in the release of H_2, presumably through protonation of (^{Ph}PSiP)NiH. Compound **1** not only undergoes stoichiometric reactivity which is consistent with the formation of (^{Ph}PSiP)NiH but can also catalyze reactions that are typically believed to involve metal hydrides. In future work, we intend to fully explore the activity of **1** for a range of reactions normally catalyzed by Ni hydrides.

4. Experimental

4.1. General

All experiments were carried out under a dinitrogen atmosphere using standard Schlenk techniques or in an MBraun glovebox (under standard glovebox conditions purging was not performed between uses of pentane, diethyl ether, benzene, toluene and THF; thus when any of these solvents were used, traces of all these solvents were in the atmosphere and could be found intermixed in the solvent bottles). Solvents for air- and moisture-sensitive reactions were deoxygenated and dried by sparging with dinitrogen followed by passage through a column of activated alumina from Innovative Technology Inc. All commercial chemicals were used as received unless noted otherwise. 1.0 M BH_3·THF solution and 1-hexene were acquired from Alfa Aesar. $LiEt_3BH$ (1 M in THF) and pinacolborane were purchased from Acros Organics. 1,5-cyclooctadiene were obtained from Strem Chemicals, Inc. Anhydrous carbon dioxide was obtained from Airgas, Inc. C_6D_6 was purchased from Cambridge Isotopes Laboratories, Inc., dried over sodium/benzophenone ketyl and vacuum transferred prior to use. NMR spectra were recorded on Bruker AMX-400 and -500 spectrometers or Agilent DD2-500, -600 spectrometers at ambient probe temperatures. Chemical shifts are reported with respect to residual internal protio solvent for ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra, or to an external standard for $^{31}P\{^{1}H\}$ (85% H_3PO_4 in D_2O at δ 0.0 ppm) and $^{29}Si\{^{1}H\}$ spectra ($SiMe_4$ in C_6D_6 at δ 0.0 ppm). Elemental analyses were performed by Robertson Microlit Laboratories, Inc. under inert atmosphere. ^{Ph}PSi^{H}P,[7a] Ni(COD)$_2$,[22] 2,6-lutidine ·HCl[23] and (^{Cy}PSiP)-NiH[7q] were synthesized following literature procedures.

4.2. X-ray crystallography

Low temperature diffraction data was collected on either a Rigaku R-AXIS RAPID diffractometer coupled to a R-AXIS RAPID imaging plate detector with Mo Kα radiation (λ = 0.71073 Å), a Rigaku SCXMini diffractometer with a Rigaku CCD detector using filtered MoKα radiation (λ = 0.71073 Å) or a Rigaku MicroMax-007HF diffractometer coupled to a Saturn994+ CCD detector with Cu Kα radiation (λ = 1.54178 Å). The crystals were mounted on MiTeGen polyimide loops with immersion oil. The data frames were processed using Rigaku CrystalClear and corrected for Lorentz and polarization effects. Using OLEX2 [24] the structure was solved with the XS [25] structure solution program by direct methods and refined with the XL [25] refinement package using least-squares minimization. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. Details of the crystal structure and refinement data for **1**, **2** and **6** are given in the Supporting information.

4.3. Synthesis and characterization of compounds

4.3.1. (^{Ph}PSiP)Ni(η^3-C_8H_{13}) (1)

A solution of ^{Ph}PSi^{H}P (103.0 mg, 0.182 mmol) in 5 mL of toluene was added to a suspension of Ni(COD)$_2$ (50 mg, 0.182 mmol) in 4 mL toluene. The resulting mixture was sonicated for 15 min. The volatiles were removed and the resulting oil was triturated with pentane to give **1** in 78% yield (104.5 mg, 0.142 mmol). The resulting solid was recrystallized at room temperature from THF–pentane to give orange crystals suitable for X-ray crystallography.

^{1}H NMR (C$_6$D$_6$, 500 MHz): δ 8.31(2H, ddd, Ar*H*, J = 9.6, 7.4, 2.0 Hz), 8.08 (1H, d, Ar*H*, J = 7.3 Hz), 7.77 (1H, d, Ar*H*, J = 7.1 Hz), 7.66 (1H, app t, Ar*H*, J = 6.5 Hz), 7.37 (2H, t, Ar*H*, J = 7.3 Hz), 7.26 (2H, m, Ar*H*), 7.15–6.86 (16H, Ar*H*), 6.64 (1H, t, Ar*H*, J = 7.3 Hz), 6.53 (2H, td, Ar*H*, J = 7.4, 1.4 Hz), 3.96 (2H, br p, C$_8H_{13}$, J = 7.2 Hz), 3.72 (1H, dt, C$_8H_{13}$, J = 15.3, 7.8 Hz), 2.09 (1H, m, C$_8H_{13}$), 1.92 (2H, m, C$_8H_{13}$), 1.84 (1H, m, C$_8H_{13}$), 1.36 (3H, s, Si*Me*), 1.35–1.17 (3H, C$_8H_{13}$), 1.09–0.97 (3H, C$_8H_{13}$). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 126 MHz): δ 160.0 (d, J = 56.6 Hz), 157.6 (dd, J = 68.1, 5.2 Hz), 148.0 (d, J = 45.7 Hz), 146.5 (dd, J = 41.0, 3.0 Hz), 139.1 (m), 138.5 (d, J = 18.8 Hz), 136.9 (d, J = 16.1 Hz), 136.5 (dd, J = 21.5, 6.7 Hz), 135.2 (d, J = 23.9 Hz), 133.1, 132.7 (d, J = 21.2 Hz), 132.5 (d, J = 12.9 Hz), 132.2 (d, J = 10.4 Hz), 132.0, 131.9 (d, J = 9.4 Hz), 130.1 (dd, J = 51.3, 1.7 Hz), 129.1 (d, J = 49.6 Hz), 128.8 (d, J = 4.2 Hz), 128.4, 99.3, 66.9, 65.8 (dd, J = 15.5, 4.3 Hz), 32.6 (d, J = 10.1 Hz), 31.7 (d, J = 5.0 Hz), 30.7 (d, J = 5.7 Hz), 29.5 (d, J = 8.1 Hz), 24.1, 3.65 (d, J = 5.8 Hz). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 202.0 MHz): δ 52.1 (d, J_{PP} = 117.0 Hz), 36.9 (d, J_{PP} = 116.9 Hz). ^{29}Si{^{1}H} NMR (99 MHz, C$_6$D$_6$) δ 52.9 (dd, J_{SiP} = 21.5, 15.5 Hz). *Anal.* Calc. for C$_{45}$H$_{44}$NiP$_2$Si: C, 73.68; H, 6.05. Found: C, 73.43; H, 5.93%.

*4.3.2. (^{Ph}PSiP)$_2$Ni (**2**)*

A solution of ^{Ph}PSi^{H}P (123.6 mg, 0.218 mmol) in 5 mL of toluene at room temperature was added to a solution of Ni(COD)$_2$ (30.0 mg, 0.109 mmol) in 5 mL toluene under an N$_2$ atmosphere. The reaction mixture was allowed to stir at room temperature for twelve hours. The volatiles were removed under reduced pressure, and the remaining solids were washed with pentane (4 × 3 mL) to give **2** as a yellow powder in 53% yield (68.3 mg, 0.057 mmol). The resulting solid was recrystallized at room temperature from toluene–pentane to give yellow crystals suitable for X-ray crystallography.

^{1}H NMR (C$_6$D$_6$, 400 MHz): δ 7.58 (1H, d, Ar*H*, J = 7.4 Hz), 7.53 (2H, t, Ar*H*, J = 8.5 Hz), 7.45 (3H, t, Ar*H*, J = 7.4 Hz), 7.34 (1H, d, Ar*H*, J = 7.2 Hz), 7.26 (1H, t, Ar*H*, J = 6.6 Hz), 7.2–6.68 (42H, Ar*H*), 6.62 (2H, t, Ar*H*, J = 6.5 Hz), 6.43 (2H, t, Ar*H*, J = 7.7 Hz), 6.32 (1H, t, Ar*H*, J = 6.2 Hz), 6.25 (1H, t, Ar*H*, J = 6.0 Hz), 1.33 (3H, s, Si*Me*), 0.93 (3H, s, Si*Me*). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 126 MHz): δ 161.0 (d, J = 61.4 Hz), 156.6 (d, J = 42.7 Hz), 155.6 (dd, J = 79.7, 57.1 Hz), 150.7 (t, J = 47.3 Hz), 146.8 (d, J = 36.7 Hz), 141.8 (apparent t, J = 16.8 Hz), 140.6 (d, J = 11.1 Hz), 140.4 (d, J = 16.9 Hz), 139.9 (dd, J = 33.7, 17.2 Hz), 139.8 (dd, J = 22.5, 9.8 Hz), 138.9–138.3 (overlapping resonances), 138.0 (dd, J = 32.6, 5.4 Hz), 136.5 (d, J = 13.3 Hz), 135.7 (d, J = 12.3 Hz), 135.3, 134.8 (d, J = 12.0 Hz), 134.3 (dd, J = 49.1, 18.8 Hz), 133.4 (d, J = 9.7 Hz), 133.0 (d, J = 9.9 Hz), 132.3 (d, J = 22.8 Hz), 132.1, 132.1, 131.2 (d, J = 21.5 Hz), 131.1, 130.7, 130.6, 129.8, 129.2, 128.8, 127.6, 127.4, 127.2, 127.2, 126.7, 126.6, 11.0 (dd, J = 14.5, 10.4 Hz), 3.54 (t, J = 6.4 Hz). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 202 MHz): δ 58.3 (dd, J = 143.2, 91.0 Hz), 51.9 (dd, J = 143.8, 89.6 Hz), 38.7 (t, J = 90.7 Hz), −7.66. ^{29}Si{^{1}H} NMR (C$_6$D$_6$, 99 MHz): δ 58.4, 44.1. *Anal.* Calc. for C$_{74}$H$_{62}$NiP$_4$Si$_2$: C, 74.69; H, 5.25. Found: C, 74.60; H, 5.52%.

*4.3.3. (^{Ph}PSiP)Ni(κ^2-BH$_4$) (**5**)*

A solution of **1** (25.0 mg, 0.0341 mmol) in 2 mL benzene was charged with 3 equivalents of BH$_3$·THF solution (1.0 M in THF, 82 μL, 0.082 mmol) at room temperature. The solution was left to sit for ten minutes. Subsequently, the solution was filtered through Celite and the volatiles were removed. The resulting dark brown oil was washed with cold diethyl ether and dried under vacuum to give **4** as a brown solid in 77% yield (16.7 mg, 0.0261 mmol). The limited solubility of this species in all common organic solvents prevented us from isolating it in a pure form or recording a ^{29}Si{^{1}H} NMR spectrum.

^{1}H NMR (C$_6$D$_6$, 500 MHz): δ 7.98 (2H, q, Ar*H*, J = 5.6 Hz), 7.86 (1H, d, Ar*H*, J = 7.4 Hz), 7.33–7.30 (4H, overlapping resonances), 7.24–6.98 (17H, overlapping resonances under C$_6$D$_6$), 6.92 (2H, t, Ar*H*, J = 7.5 Hz), 6.80 (2H, t, Ar*H*, J = 7.7 Hz), 0.75 (3H, s, Si*Me*). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 151 MHz): δ 153.9 (t, J = 31.1 Hz), 144.9 (t, J = 27.3 Hz), 135.6 (t, J = 20.1 Hz), 133.6 (t, J = 6.6 Hz), 132.7 (t, J = 6.0 Hz), 132.0 (t, J = 12.5 Hz), 131.7, 130.1, 129.8, 129.3 (t, J = 3.1 Hz), 128.9, 128.8, 6.15. ^{31}P{^{1}H} NMR (C$_6$D$_6$, 162 MHz): δ 59.0.

*4.3.4. (^{Cy}PSiP)Ni(κ^2-BH$_4$) (**6**)*

A solution of (^{Cy}PSiP)NiH (30.0 mg, 0.0462 mmol) in 5 mL benzene was charged with 2 equivalents of BH$_3$·THF solution (1.0 M in THF, 92 μL, 0.092 mmol) at room temperature. The solution was left to sit for ten minutes. Subsequently, the solution was filtered through Celite and the volatiles were removed. The resulting orange residue was recrystallized from pentane at −35 °C to yield **6** as bright orange needles in 57% yield (17.4 mg, 0.0262 mmol). Recrystallization of **6** from concentrated pentane solution at room temperature gave red crystals suitable for X-ray crystallography.

^{1}H NMR (C$_6$D$_6$, 400 MHz): δ 7.96 (2H, d, Ar*H*, J = 7.4 Hz), 7.44 (2H, d, Ar*H*, J = 7.8 Hz), 7.29 (2H, t, Ar*H*, J = 7.3 Hz), 7.19 (2H, t, Ar*H*, J = 7.4 Hz), 2.80 (2H, t, Cy*H*, J = 12.6 Hz), 2.63 (2H, d, Cy*H*, J = 12.3 Hz), 2.34 (2H, m, Cy*H*), 2.19 (2H, m, Cy*H*), 2.10–2.07 (2H, Cy*H*, overlapping resonances), 1.98 (2H, d, Cy*H*, J = 12.3 Hz), 1.83 (2H, d, Cy*H*, J = 9.9 Hz), 1.64–1.02 (29H, overlapping resonances, Cy*H* and B*H*$_4$), 0.94–0.72 (5H, overlapping resonances), 0.89 (3H, s, Si*Me*). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 101 MHz): δ 157.6 (t, J = 28.0 Hz), 141.7 (t, J = 22.0 Hz), 132.3 (t, J = 11.2 Hz), 130.4, 130.3, 128.5, 35.0 (t, J = 10.6 Hz), 34.5 (t, J = 10.7 Hz), 30.5, 29.5, 28.4, 27.7 (t, J = 7.1 Hz), 27.7, 27.4 (t, J = 7.2 Hz), 27.4, 27.2 (t, J = 5.6 Hz), 27.0, 26.6, 8.7 (t, J = 1.7 Hz). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 162 MHz): δ 68.5 4. ^{29}Si{^{1}H} NMR (C$_6$D$_6$, 99 MHz): δ 62.09 (t, J = 27.7 Hz).

4.4. Representative procedures for catalysis

4.4.1. Isomerization of alkenes (1-hexene and 1,5-cyclooctadiene)

A solution of **1** (0.3–0.5 mg) in 0.5 mL C$_6$D$_6$ was charged with 100 equivalents of the alkene at room temperature in a screw cap NMR tube. The formation of products over time was monitored by ^{1}H NMR spectroscopy until all starting materials were consumed (1,5-cyclooctadiene), or the relative ratio of the isomers reached equilibrium (1-hexene). See the Supporting information for more details.

4.4.2. Hydroboration of pinacolborane

A solution of 1 mol% **1** (1.0 mg, 0.0014 mmol), HB(pin) (9.9 μL, 0.050 mmol) and 1,3,5-trimethoxybenzene (11.5 mg) in 0.6 mL of C$_6$D$_6$ was added to a J. Young NMR tube. The sample was degassed using three freeze–pump–thaw cycles and 1 atm of CO$_2$ was introduced via a Schlenk line. The formation of products over time was monitored using ^{1}H NMR spectroscopy. See the Supporting information for more details.

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Appendix A. Supplementary data

CCDC 998687–998689 contain the supplementary crystallographic data for **1**, **2** and **6**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Further experimental details about selected stoichiometric and catalytic reactions and X-ray crystallographic information about the structures of **1**, **2** and **6** are available free of charge via the Internet. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2014.05.078.

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