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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, $(^{Ph}PSiP)Ni(\eta^3\text{-cyclooctenyl})$ (**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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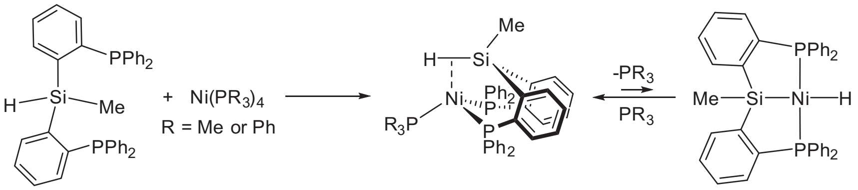


(1)

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$_6$H$_3$)$_2$; R = alkyl or aryl) complexes through the oxidative addition of ^{R}PN^{H}P (^{R}PN^{H}P = HN(2-PR$_2$-4-MeC$_6$H$_3$)$_2$; 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$_8$H$_{13}$) (**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$_6$H$_3$)$_2$). 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 $^{2}J_{PP}$ 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$_3$H$_5$).[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.

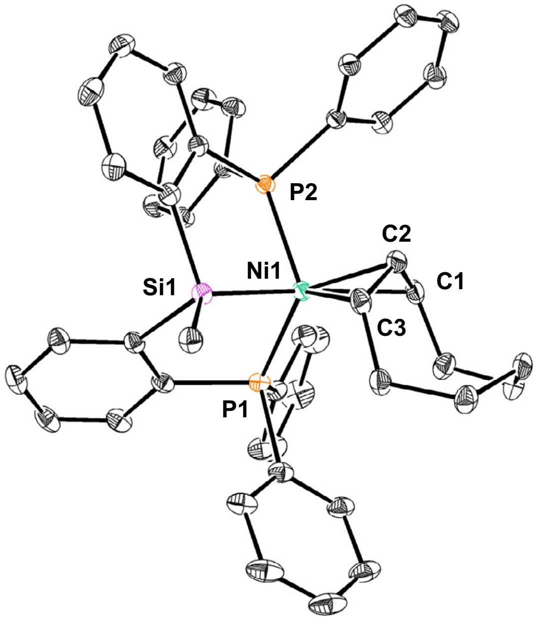
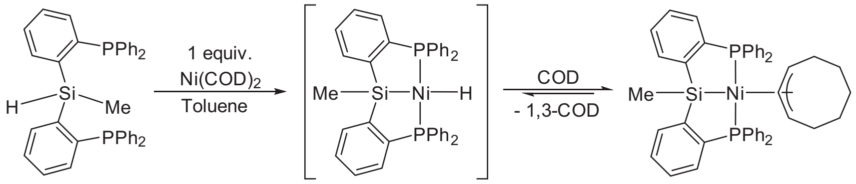


Fig. 1. ORTEP of (^{Ph}PSiP)Ni(η^3-C$_8$H$_{13}$) (**1**). Ellipsoids shown at the 30% probability level. There is disorder in the cyclooctenyl ligand and only the major component is shown. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ni(1)–P(1) 2.1778(7), Ni(1)–P(2) 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$_8$H$_{13}$) (**1**).