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Selectivity of attack on a Si–C(sp^3) sigma bond coordinated to Ni^{II} ☆

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ABSTRACT

(PNP)Ni^+ (as its $(BAr^F{}_4)^-$ salt) adds PhCN to Ni, but HX cleaves the Si–CH_2 bond to form Ni[η^2–(^{t}Bu$_2$PCH$_2$SiMe$_2$)N(H)(SiMe$_2$X)][η^2–CH$_2$^{t}Bu$_2$P]$^+$, for X = OMe, piperidyl, N(H)CH_2Ph, N(H)Ph, morpholinyl. The diprotic reagent H_2O gives (η^2–^{t}Bu$_2$PCH$_2$SiMe$_2$OSiMe$_2$NH$_2$)(η^2–^{t}Bu$_2$CH$_2$P)Ni^+. RCCH (R = Ph, $SiMe_3$, ^{t}Bu) reacts, through three detected intermediates, to form (^{t}Bu$_2$PCH$_2$SiMe$_2$)N(H)(SiMe$_2$CH$_2$^{t}Bu$_2$PCCR)Ni^+, a product where one P has been oxidized and Ni reduced, each by two electrons. This shows the dominant influence on reactivity of Si–C bond activation by its unconventional donation to nickel in the structure of (PNP)Ni^+.

1. Introduction

We have shown that the species (PNP)Ni^+, **1**, where PNP is the anion (^{t}Bu$_2$PCH$_2$SiMe$_2$)$_2$N^{-1}, synthesized by chloride removal from (PNP)NiCl using anhydrous NaB(C$_6$H$_3$(CF$_3$)$_2$)$_4$ (NaBAr$_F{}^4$) in non-coordinating solvent, is not simply a T-shaped three coordinate species [1]. The Lewis acidity of such a structure is apparently very high, since the ground state structure of the species (Scheme 1) has one P located transoid to the amide nitrogen, and the electron density of one Si–C sigma bond donates to nickel, stretching that bond by ~0.2 Å. Studies with nucleophiles as weak as triflate show that its addition product to (PNP)Ni^+ is not that from binding to nickel, but rather cleavage of the Si–C bond, to form a ^{t}Bu$_2$PCH$_2^-$ ligand which binds η^2 to the metal. The LUMO of structure **1** [1] is along the coordinated Si–C bond, indicating that Lewis base attack occurs perpendicular to that bond, not "back side," *anti* to the stretched Si–C bond. When fluoride is the attacking nucleophile, the analogous reaction happens, and it was possible to show that this Si/C cleavage product is more thermodynamically stable than the conventional isomeric (PNP)Ni–nucleophile structure. However, in its reaction with H_2, (PNP)Ni^+ shows addition of nucleophilic H^- to nickel, not to the Si–C bond [2].

Both chloride and carbon monoxide bind at nickel however. In short, the unconventional (PNP)Ni^+ structure makes this cation a multifunctional reagent, electrophilic at both Ni and Si.

We report here a more general exploration of the reactivity of (PNP)Ni^+ with nucleophiles of a variety of types, which reveal that attack selectivity is determined by the arriving nucleophile. Using alcohols, or primary or secondary amines and even unconventional nucleophiles such as RCCH, reveals that (PNP)Ni^+ also shows Bronsted basicity at its amide nitrogen. Efforts to systematically understand the multifunctional reactivity of (PNP)Ni^+ are discussed. In general, this report seeks to understand which of the product structures in Scheme 1 is produced for a variety of reagents in their reactions with (PNP)Ni^+. Will reaction occur *at nickel*, **3**, with displacement of this unique Si–C donation to the metal, or will *the Si–C bond* be directly attacked, **2**?

We will explore here OH nucleophiles and also primary amines.

2. Results

2.1. General

The reaction of (PNP)Ni^+, as its BAr^F salt, is conventional with PhCN: a 1:1 adduct forms completely at nickel, and this adduct is unchanged by vacuum drying at 25 °C. One additional equivalent of PhCN causes no change in the spectra of (PNP)Ni(NCPh)$^+$, indicating that this four coordinate planar (C_{2v}) species is not significantly Lewis acidic, nor is there any attack at the Si–C bond.

There is no reaction between (PNP)Ni^+ and 1 atm of N_2 or N_2O, showing the limits of reactivity of this cation; ethylene, 1 atm, is likewise unreactive, as is styrene, in equimolar amount. There is no reaction (e.g., no proton transfer) between (PNP)Ni^+ and 2,4,6-^{t}Bu$_3$C$_6$H$_2$(OH), nor with CO_2 or ethyl vinyl ether, all carried out in CD_2Cl_2.

2.2. Water

One reaction was discovered, apparently due to adventitious water in the unreactive reagents N_2 and N_2O. This product

☆ In honor of Wolfgang Kaim, who showed us much about spin delocalization.

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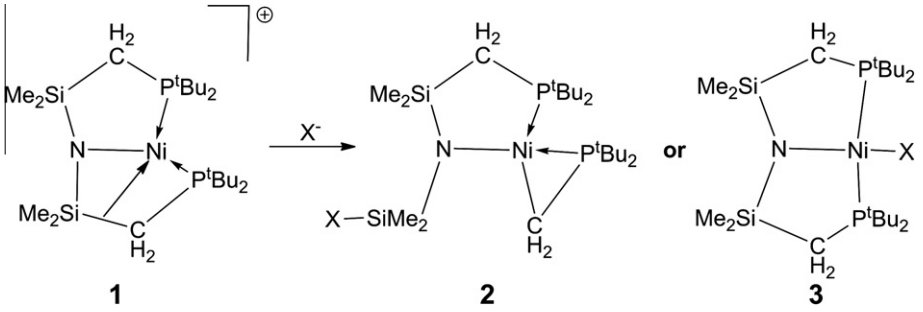
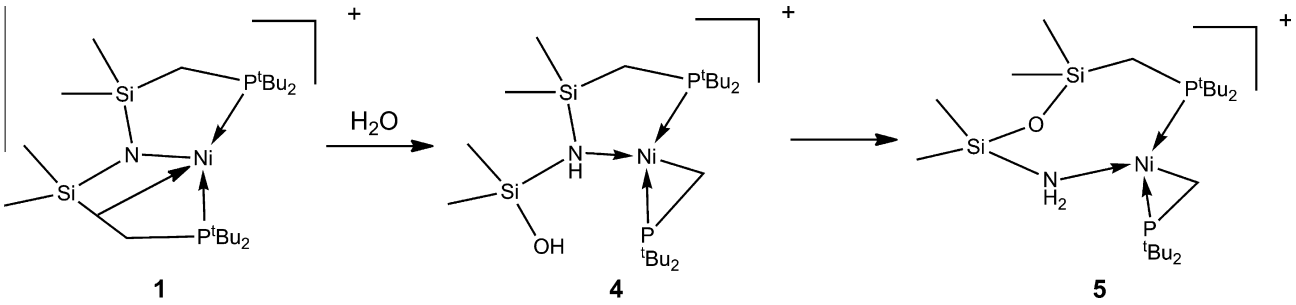


Scheme 1.



Scheme 2.

(Scheme 2) has an AX $^{31}P\{^1H\}$ NMR pattern, and shows only C_s symmetry in its ^1H NMR spectrum. A crystal structure determination of **5** shows this to be the product of nucleophilic attack of water oxygen on one silicon of the PNP ligand. Rearrangement, together with two proton transfer steps, leaves one $^tBu_2PCH_2SiMe_2$–O–$SiMe_2$–NH_2 ligand, together with the $^tBu_2PCH_2$ ligand (Fig. 1). It is thus a cation with atom composition being that of (PNP)Ni^+ plus one H_2O. In the solid state, this exists as an ion pair via hydrogen bonding of one of the NH protons to one F of CF_3 of the BAr^4_F anion. The identity of this product clearly establishes that silicon shows its characteristic reactivity, and the reaction does not stop at the simple adduct, (PNP)Ni$(H_2O)^+$. At shorter reaction times, an intermediate is seen, then disappears; this species has the ^{31}P NMR signature of the single Si/C cleavage product, **4**, with *trans* phosphorus groups, by comparison to other products reported later here.

This prompted us to consider more broadly the question of where various weakly acidic nucleophiles will attack the unusual structure of (PNP)Ni^+, given that the Si–C bond is "activated" by being bound to the metal. We have undertaken this study with progressively more complicated analogs of water, being amines (primary and secondary) and alcohols, to evaluate the effect of different numbers of mobile protons.

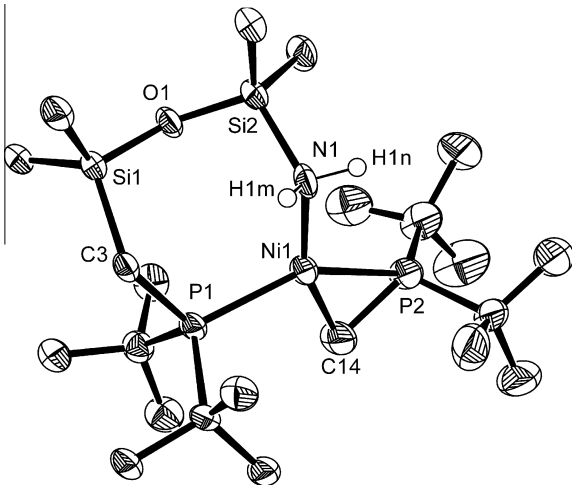


Fig. 1. ORTEP view (50% probabilities) of the non-hydrogen atoms of ($^tBu_2PCH_2SiMe_2OSiMe_2NH_2$)($^tBu_2CH_2P$)$Ni^+$ from its $B(C_6H_3(CF_3)_2)_4$ salt, showing selected atom labeling. Unlabelled atoms are carbons, and the two H on nitrogen are indicated. Selected structural parameters (Å, °): Ni1–C14, 1.961(5); Ni1–N1, 2.001(4); Ni1–P2, 2.1802(13); Ni1–P1, 2.2574(12); Si1–O1, 1.650(3); Si2–O1, 1.625(3); C14–Ni1–N1, 159.00(17); N1–Ni1–P2, 109.61(11); C14–Ni1–P1, 99.61(14); N1–Ni1–P1, 101.08(10); P2–Ni1–P1, 148.82(6); Si2–O1–Si1, 137.42(19); Si2–N1–Ni1, 121.3(2).

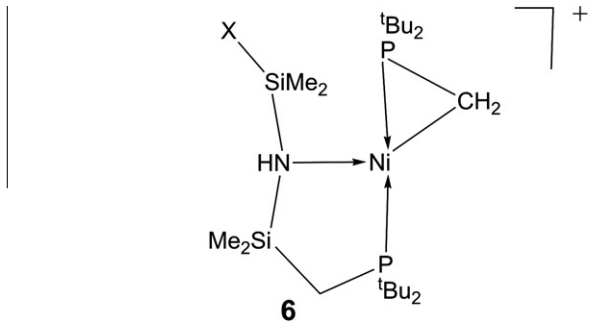
2.3. MeOH [3–5]

Methanol was chosen to prevent formation of two Si/O bonds. (PNP)Ni^+ reacts with equimolar methanol in dichloromethane within time of mixing at −78 °C to give complete conversion to a single product with an AX $^{31}P\{^1H\}$ NMR spectrum whose $J_{PP'}$ value, 182 Hz, indicates the phosphorus atoms to be *trans* in the coordination sphere. Structure **6**, Scheme 3, is consistent with the ^1H NMR spectrum for this species, including an NH proton observed (very broad) at 6.1 ppm. This shows that isomerization of the $^tBu_2PCH_2$ ligand to a location with the two P mutually *trans* has already occurred, but there is no proton migration to this CH_2 on nickel.

2.4. Primary amines

Benzyl amine reveals behavior similar to that of methanol in spite of it being a primary amine, hence having two mobile protons. The reaction of equimolar reagents in dichloromethane gives an AX pattern ($J_{PP'}$ = 178 Hz); all of these chemical shifts and J values are very similar to those observed with methanol, consistent with the ring-opened product.

Reaction of (PNP)Ni^+ with $^tBuNH_2$ (chosen to simplify the ^1H NMR spectrum of the amine substituent) in CD_2Cl_2 proceeds to a



X = MeO, HO, piperidyl, NH(CH_2Ph), NH(^{t}Bu), morpholinyl

Scheme 3.

steady state in less than 10 min to produce one major product, having an AX $^{31}P\{^1H\}$ NMR pattern. The *J* value in the AX pattern, 182 Hz, shows that these two phosphorus are mutually trans. The AX product is unchanged in solution over a period of 5 days.

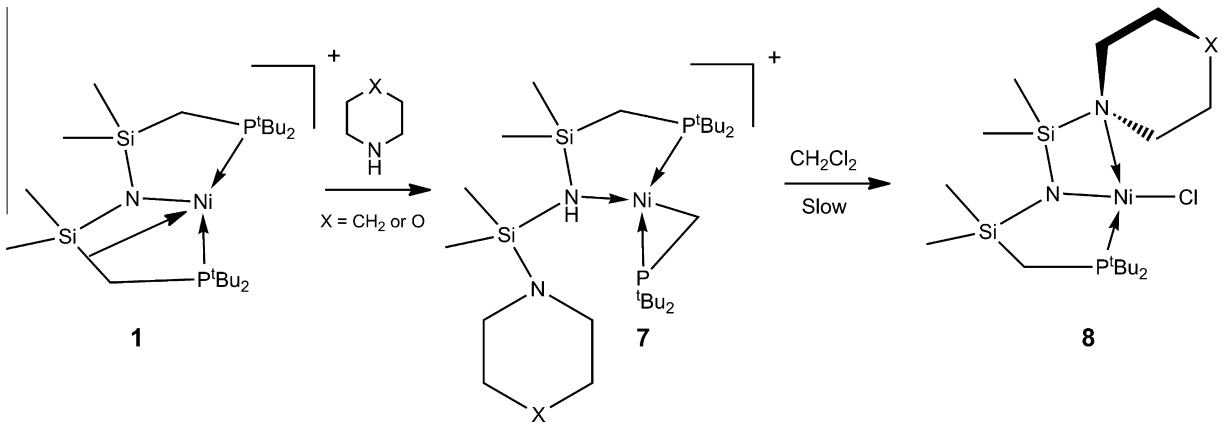
Even a less nucleophilic primary amine also attacks away from the metal, to cleave the Si–C bond. Reaction with aniline is complete in less than 5 min to form a product with spectra somewhat analogous to the others reported above. The proton NMR shows a molecule with no symmetry, and ^{t}Bu doublets indicate no strong coupling between phosphorus nuclei (hence phosphorus are not *trans*). The absence of any symmetry indicates that the PNP nitrogen has been protonated (i.e., chiral N), as well as its backbone ruptured. The curious feature of the room temperature $^{31}P\{^1H\}$ NMR spectrum is the fact that one of the peaks (~9 ppm) is very broad, and the other peak, while sharper, is broad enough to not resolve any PP′ coupling of less than 200 Hz. Variable temperature ^{31}P NMR spectra show reversible sharpening of this 9 ppm feature, but never sharpening to the point where $J_{PP'}$ is resolved, even at −60 °C. Thus, the product detected has inequivalent phosphorus nuclei, consistent with the other nucleophile reactions. The dynamic effects on phosphorus NMR are suggested to originate in alternate conformations of the phenyl substituent, or also perhaps hydrogen bonding involving either of the two NH protons.

2.5. Secondary amines

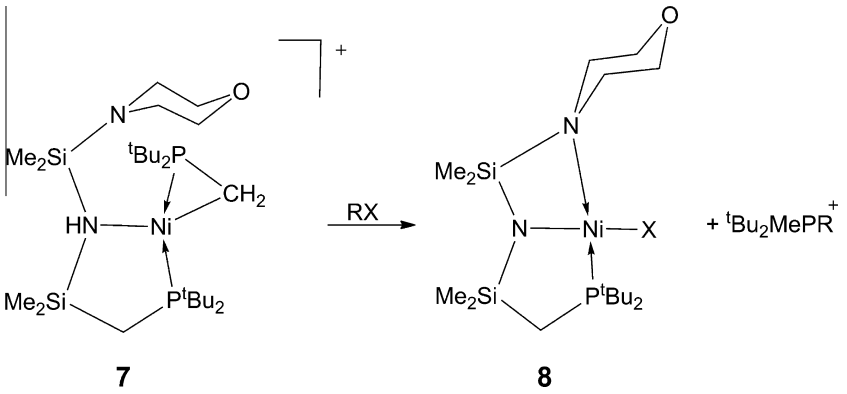
The secondary amine piperidine was added to (PNP)Ni^+ in dichloromethane at 25 °C. An evident color change and ^{31}P NMR were used to establish complete conversion (**7**, Scheme 4) of **1** to an AX spectrum ($J_{PP'}$ = 183 Hz), together with lesser amounts of three other singlet signals. This AX NMR pattern immediately confirms attack on the Si–C bond, to cleave the ligand backbone. If the reaction is carried out at −78 °C, only the AX species is produced; this solution converts to one of the three singlet species slowly (2 days) at 25 °C, indicating the reaction path to involve an AX intermediate which transforms to a species **8** with one phosphorus NMR signal.

In the proton chemical shift region near 3 ppm of this final product we observe a non-first order NMR pattern due to two non-equivalent protons on the CH_2 group adjacent to piperidine N; these are well separated in chemical shift from the other $CH_2CH_2CH_2$ protons. This non-equivalence alone indicates that the nitrogen is four coordinate (no rapid inversion at N), hence bound to nickel. These signals undergo no change under conditions of phosphorus decoupling, so any $^4J_{PH}$ is unresolved. Extraction into pentane shows NMR spectra indicative of C_s symmetry: one ^{t}Bu chemical shift (a doublet), 2 $SiMe_2$ chemical shifts, one CH_2 chemical shift and no signals for BAr^4_F. The ESI-mass spectrum showed the presence in **8** of one (solvent-derived) chloride, and only one phosphorus in this compound, which is thus not a salt, but a neutral molecule.

In order to simplify the ^1H NMR spectral interpretation for the amine ring hydrogens, the reaction of (PNP)Ni^+ with morpholine was studied, since then only CH_2CH_2 groups are involved. Reaction (1:1, at 25 °C) in CD_2Cl_2 shows primarily production of an AX $^{31}P\{^1H\}$ NMR pattern. The $J_{PP'}$ value in the AX pattern, 180 Hz, indicates the two phosphorus nuclei to be mutually trans. After 5 days in CD_2Cl_2, extraction of the dried residue into pentane shows this fraction to have a phosphorus NMR singlet; the proton NMR spectrum of this pentane soluble fraction, recorded in benzene, shows four chemical shifts in the 2.8–3.8 ppm region for the morpholine hydrogens, thus indicating that this ring is not rapidly inverting, consistent with the morpholine nitrogen being coordinated to Ni. Two of these protons show geminal coupling, while the other two show one additional coupling which we attribute to one resolved mutual vicinal coupling; this is characteristic of the dihedral angle dependence of these hydrogens (Karplus relationship). The proton NMR integrations are consistent with the presence of two (non-equivalent) $SiMe_2$ groups, but only one $^tBu_2P$ group (doublet) in this species, consistent with structure **8**, Scheme 5. The formula, and the presence of chloride, was established by ESI-MS of the pentane soluble product; chloride was suggested to originate from CH_2Cl_2. The pentane soluble fraction showed no BAr^4_F ^1H NMR signals, consistent with this neutral complex identity. If the reaction is repeated in fluorobenzene solvent, the product, which now persists at 25 °C, has an AX $^{31}P\{^1H\}$ NMR spectrum with the large (180 Hz) coupling constant characteristic of structure **7**.



Scheme 4.



Scheme 5.

The recurrent abstraction of chloride from solvent represented an undesirable feature, but is evidence of the intrinsic electrophilicity of the primary product **7**, Scheme 5 and the need for product stabilization if the amine proton is to migrate to the $NiCH_2P^tBu_2$ carbon, forming PMe^tBu_2. With this in mind, we attempted to quench this product by adding MeI or benzyl bromide after the morpholine attack at silicon was completed. Benzyl bromide (equimolar) was the more effective of these two, and led to formation of neutral **8** and $[^tBu_2PMe(CH_2Ph)][BAr^4_F]$, Scheme 5, which were separated by their distinct solubilities in pentane; the phosphonium salt was identified by comparison to an independently synthesized sample (from PMe^tBu_2 and $PhCH_2Br$ in benzene). We interpret these results as indicating that the ammonium center is acidic enough to protonate the Ni/C bond if there is a nucleophile (better than BAr^4_F) to coordinate to nickel.

The silyl morpholine complex was identified by its distinctive ^1H and ^{31}P NMR spectra and (for the bromide) by ESI-MS. We prefer coordination of nickel to the morpholine N based on the better ring size involving nickel than by morpholine oxygen.

There is no reaction between $(PNP)Ni^+$ and equimolar NEt_3.

2.6. Terminal alkynes

Terminal acetylenes, HC≡CR might be expected to protonate the amide nitrogen of $(PNP)Ni^+$, to form a terminal acetylide complex of the neutral ligand PN(H)P; RCCH are not nucleophiles capable of attack at silicon. In fact, in time of mixing, $(PNP)Ni^+$ reacts with RCCH where R = $SiMe_3$, Me_3C and phenyl. In each case the product has C_s symmetry, but inequivalent phosphorus nuclei. The coupling constant between the two phosphorus is small (10 Hz) indicating a structure without two *trans* phosphorus. A single crystal structure determination of the Me_3C analog (Fig. 2 and **9**) shows that there has been P/C bond formation to the terminal acetylide carbon,[6] and the alkyne is η^2 bonded to the nickel. The presence of the former acetylene proton on N of the pincer ligand is established by the fact that this nitrogen is now pyramidal with two Si and one Ni substituents, as well as by the longer Ni/N distance than it is in related amide PNP/Ni complexes. The product is thus a phosphonium species, so this is the site of the positive charge in this monocation, and thus nickel has been reduced to oxidation state zero in this reaction. The product contains three-coordinate planar Ni(0). The source of the two reduction equivalents is identified as the phosphorus, which is now pentavalent. The best way to understand the formation of this P/C bond is to consider that an intermediate nickel acetylide is electrophilic at C_α, especially as P migrates to this carbon, and two electrons can "flow" to nickel. Given the similar spectroscopic properties, the same

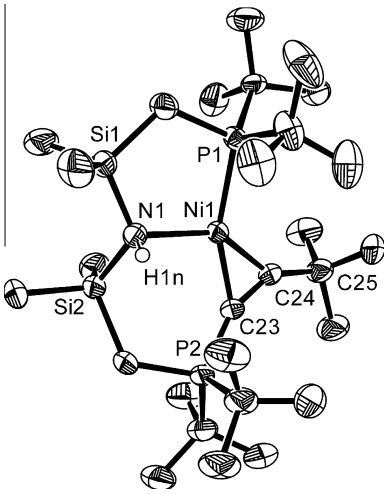
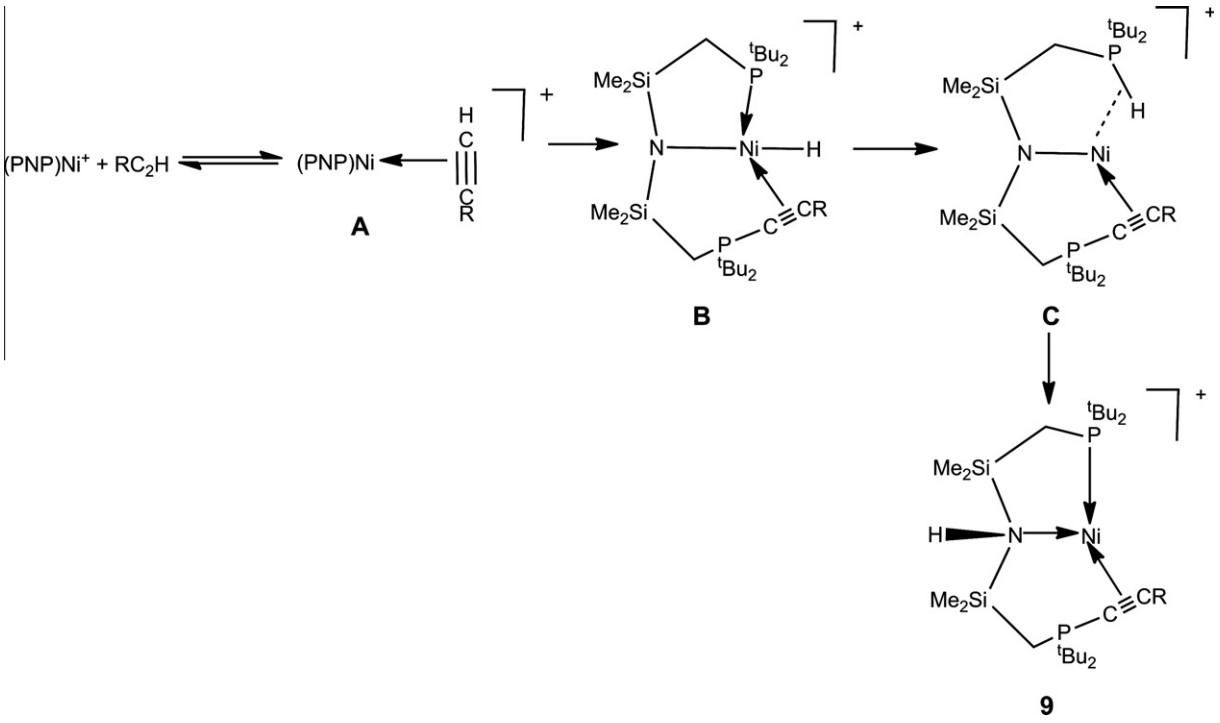


Fig. 2. ORTEP view (50% probabilities) of the non-hydrogen atoms of $(^tBu_2PCH_2SiMe_2)N(H)(SiMe_2CH_2{}^tBu_2PC{}^tBu)Ni^+$ from its $B(C_6H_3(CF_3)_2)_4$ salt, showing selected atom labeling. Unlabelled atoms are carbons, and one H on nitrogen is shown. Selected structural parameters(Å, °): Ni1–C24, 1.887(4); Ni1–C23, 1.896(4); Ni1–N1, 2.087(3); Ni1–P1, 2.2225(10); C23–C24, 1.295(5); P2–C23, 1.729(3);C24–Ni1–N1, 144.36(14); C23–Ni1–N1, 104.89(14); C24–Ni1–P1, 121.36(11); C23–Ni1–P1, 159.34(11); N1–Ni1–P1, 94.28(9); P2–C23–C24, 157.73(3).

functionality is formed in the product with the other two acetylenes. It is of interest that the cations with R = ^{t}Bu and $SiMe_3$ both show (by ^1H NMR) mirror symmetry in the molecular plane: geminal ^{t}Bu are pairwise equivalent as are geminal silyl methyls; in contrast, for R = Ph, there are four ^{t}Bu chemical shifts and four SiMe chemical shifts. We attribute this to inversion of the amine proton being rapid for the former two cases and slower for R = Ph, perhaps enhanced by the ring current effect of phenyl increasing chemical shift differences of geminal groups.

Since the observed terminal acetylene products involve multiple bond making and breaking, can an intermediate (Scheme 6) be detected? In fact, the slower case, where R = ^{t}Bu, shows, at 25 °C at intermediate reaction times, two species with singlet $^{31}P\{^1H\}$ NMR signatures, but these are converted to the AX pattern species after heating; they are thus candidate intermediates. If equimolar $(PNP)Ni^+$ and ^{t}BuCCH are combined at −80 °C in CD_2Cl_2 and monitored by ^1H and ^{31}P NMR with 10° increments of temperature, one observes, from −40 to −20°, one broad ^{31}P NMR peak whose chemical shift is temperature dependent, indicating a rapid equilibrium showing only one population-weighted average chemical shift. We suggest that this is an η^2-adduct of the intact alkyne



Scheme 6.

on (PNP)Ni$^+$, where the adduct may have either one or both phosphorus donors coordinated, **A**. The proton NMR spectrum shows two ^{t}BuP and one ^{t}BuCCH chemical shifts and three SiMe chemical shifts. Beginning at −10 °C, the above species declines in population smoothly with formation of a new species **B** with an AX $^{31}P\{^1H\}$ NMR pattern with a small $J_{PP'}$ (5 Hz), suggesting a structure similar to the final product (hence the P/C bond has formed). The fate of the acetylenyl hydrogen is established, in **B**, as being a hydride on Ni, which couples differently to the two inequivalent P (28 and 4 Hz). Already at 0 °C, this species begins to transform into the final product: hydrogen migration thus is somewhat slow from Ni to amide N. At −20 °C, a second ^1H NMR peak seen at −2.2 ppm is a doublet (140 Hz) of doublets (15 Hz), and this we attribute (**C**) to the acetylenic proton already on P (the larger J value indicates[7] direct P–H bonding), which is then hydrogen bonded to the metal, to give a second resolved J_{PH} value. This is now zerovalent nickel in **C**, so it is a good candidate for hydrogen bonding. A proton on phosphorus is an attractive mechanism for transport of this H from nickel to N, and indeed this species (as well as **B**) decreases in intensity as the temperature rises further, with growth of the crystallographic product. Note that in species **B** the redox change at Ni has not yet occurred, and that the redox change involves phosphorus reducing nickel by 2 e as H migrates to P, forming the pentavalent phosphorus of the phosphonium functionality.

3. Results and discussion

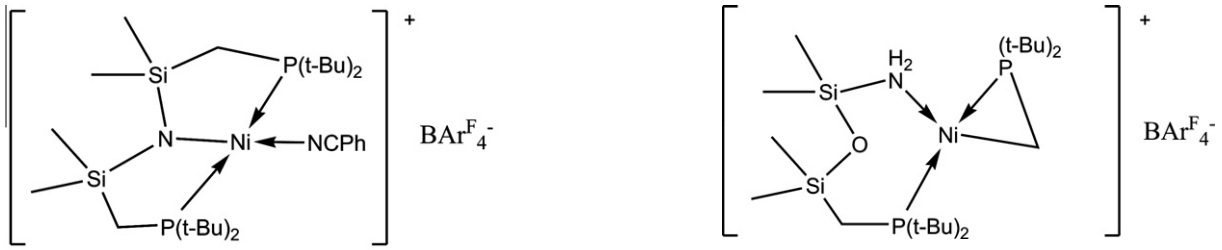
This and earlier work confirms (Scheme 7) some of the reactivity expected from a Si–heteroatom bond, but in a different version. In our earlier observations of this reaction, fluoride or even triflate nucleophiles gave neutral products with an ^{t}Bu$_2$PCH$_2$ ligand η^2-coordinated to Ni. In the present cases, an active proton leads to protonation of the amide nitrogen. The case of terminal alkynes represent different behavior since the acetylide ligand on nickel is apparently sufficiently electrophilic that it succumbs to attack by phosphorus.

A recent report [8] describes reactions of the phenylene-backbone-ligated (pincer)Pd(OTf), where triflate leaving group should provide a synthon for (pincer)Pd$^+$, with various weak acids HX (X = OR, PR$_2$, CCR, SR...). That work, where the absence of silicon eliminates any pincer backbone cleavage reactivity, shows either addition of the H–X bond across the N/Pd bond, or simply coordination of the lone pair of X in HX to form (pincer)Pd(XH)$^+$. The outcome is thermodynamically controlled.

4. Experimental

4.1. General considerations

All manipulations were performed using standard Schlenk techniques or in an argon-filled glovebox unless otherwise noted. Pentane and THF were purified using an Innovative Technologies solvent purification system Pure Solv 400-6-MD. Ethyl vinyl ether (CH_2=CH–OC_2H_5) was dried under molecular sieves, benzene D-6 was dried under Ph_2CO/Na, PhCN was dried under CaH_2 and each chemical was vacuum transferred and stored in the glovebox under argon. H_2O was degassed by freeze–pump–thaw technique before use. Carbon dioxide, nitrogen, N_2O and ethylene were purchased through commercial vendors and used without further purification. All reactions with gases were accomplished with a gas line equipped with manometer (0–760 Torr) for accurate dosage. {[(^{t}Bu$_2$PCH$_2$SiMe$_2$)$_2$N]Ni}B(C$_6$H$_3$(CF$_3$)$_2$)$_4$ was prepared following the published synthesis [1]. NMR chemical shifts are reported in ppm relative to protio impurities in the deutero solvents. Coupling constants are given in Hz. ^{31}P NMR spectra are referenced to external standards of H_3PO_4. NMR spectra were recorded with a Varian Unity INOVA instrument (400 MHz ^1H; 162 MHz ^{31}P). Infrared spectra were recorded on a Nicolet 510P FT-IR spectrometer. Mass spectra were acquired on a MAT-95-XP spectrometer (Thermo Electron Corp., Bremen, Germany). "PNP" is N(SiMe$_2$CH$_2$PBu$_2^t$)$_2$. Ar^F is 3,5-bis-trifluoromethylphenyl.

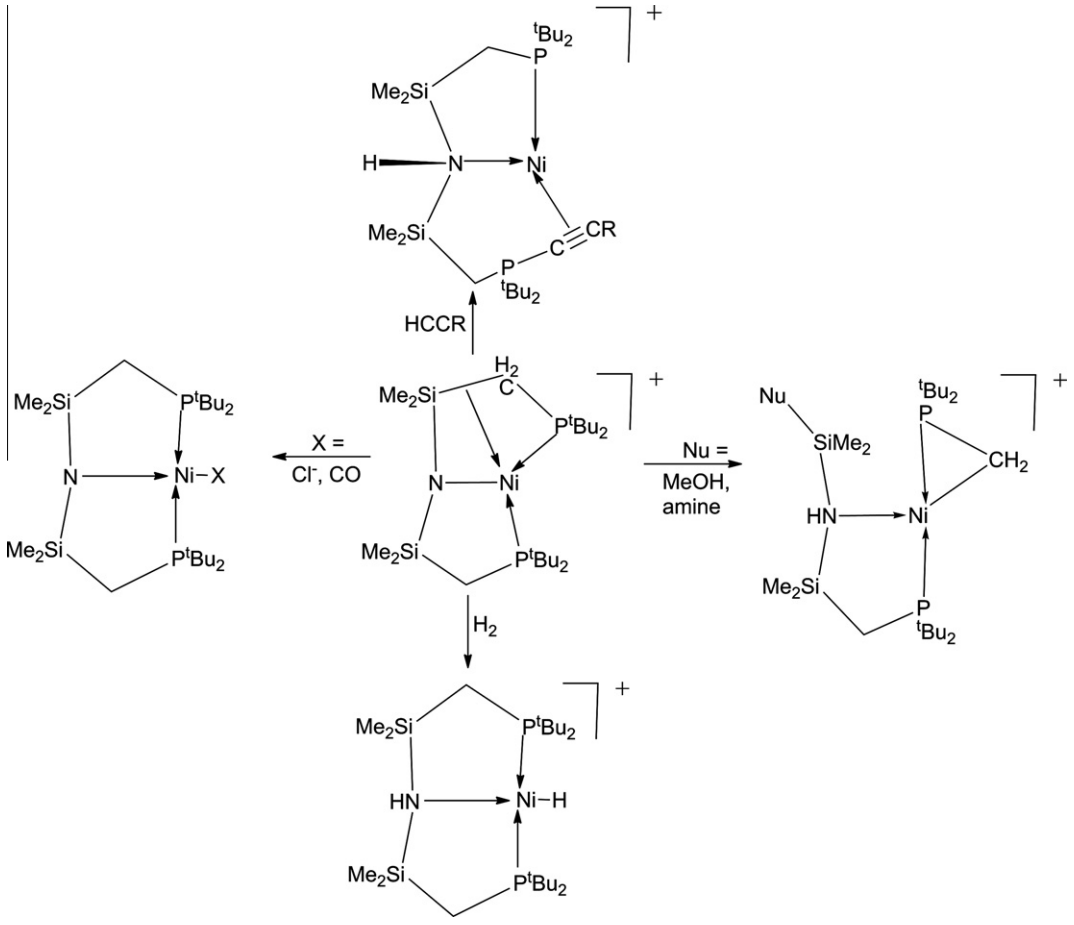


4.1.1. Synthesis of [(PNP)Ni(PhCN)](BAr^4_F)

30.0 mg (0.022 mmol) of [(PNP)Ni](BAr^4_F) was dissolved in 0.5 mL of CD_2Cl_2 in a J-Young NMR tube yielding a dark reddish brown solution. To this solution, 0.0022 mL of benzonitrile (2.3 mg, 0.022 mmol) was added at 25 °C via syringe. In time of mixing, the solution became brown in color. Full conversion of the starting material to the single product, [(PNP)Ni(PhCN)](BAr^{4-}_F) was observed. ^{1}H NMR (25 °C, CD_2Cl_2): 0.23 (s, SiMe, 12H), 0.84 (t, J = 5.8, 4H, CH_2), 1.45 (t, J = 6.3, 36H, ^{t}Bu), 7.50–7.90 (m, 17H, Ar). ^{31}P{^{1}H} NMR (25 °C, CD_2Cl_2): 58.8 (s). This solution was concentrated in vacuum and pumped for 30 min at 25 °C to give 28.4 mg (88%) of the product. The residue was dissolved in CD_2Cl_2 and NMR spectra did not show any changes. One more equivalent of benzonitrile (0.0022 mL) was added and no changes were seen in the ^{1}H and ^{31}P NMR.

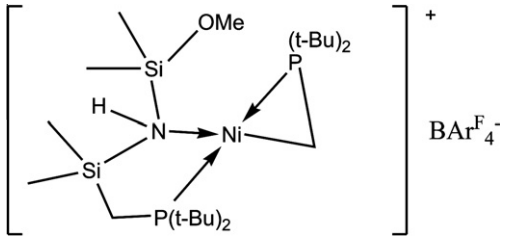
4.1.2. Reaction of (PNP)Ni$^+$ (BAr^{4-}_F) with H_2O

30.0 mg (0.022 mmol) of [(PNP)Ni](BAr^4_F) was dissolved in 0.5 mL of CD_2Cl_2 in a J-Young NMR tube yielding a dark reddish brown solution. To this solution, 0.0004 mL of H_2O (0.4 mg, 0.022 mmol) was added at 25 °C via syringe. In time of mixing, the solution became orange in color. Full conversion of the starting material to the mixture of two products was observed. One could see complete conversion of one of these two into another in 16 h in CD_2Cl_2. *Trans* (thermodynamic) isomer: ^{1}H NMR (25 °C, CD_2Cl_2): 1.29 and 1.40 (both d, 18H each, ^{t}Bu, J = 13.6 and 15.2), 7.56 and 7.71 (both s, Ar, 4 and 8H), other signals (SiMe and CH_2 protons and NH_2) were not identified due to the broad nature of these peaks. ^{31}P{^{1}H} NMR (25 °C, CD_2Cl_2): 2.0 and 38.6 (both d, J = 164). The intermediate, containing only one Si–O bond, was identified by ^{31}P{^{1}H} NMR (25 °C, CD_2Cl_2): −14.9 and 51.2 (both



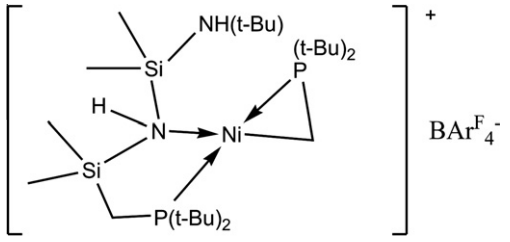
Scheme 7.

d, J = 174) as a structure similar to the "MeOH product" (see below). Crystals suitable for X-ray diffraction analysis were grown in 2 days at 25 °C after a solution of the final product in CD_2Cl_2 was layered with pentane.



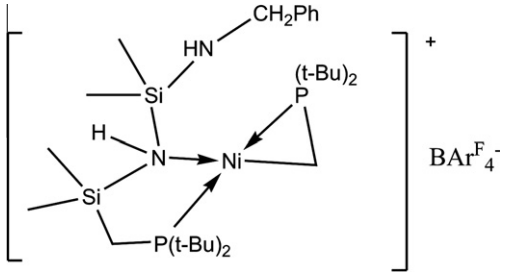
4.1.3. Reaction of (PNP)Ni$^+$ (BAr^{4-}_F) with MeOH

30.0 mg (0.022 mmol) of [(PNP)Ni](BAr^4_F) was dissolved in 0.5 mL of CD_2Cl_2 in a J-Young NMR tube yielding a dark reddish brown solution. This solution was frozen with liquid nitrogen and 0.0009 mL of methanol (0.7 mg, 0.022 mmol) was vacuum transferred. The solution was allowed to warm and the tube was shaken and one could see a color change to orange. Full conversion of the starting material to one product was observed. ^{1}H NMR (25 °C, CD_2Cl_2): 1.34 and 1.40 (both d, J = 13.7 and 15.5, 18H, ^{t}Bu), 3.43 (s, 3H, OCH_3), 6.3 (br. s, 1H, N–H), 7.58 and 7.75 (both s, 4 and 8H, Ar^F); CH_2 and SiMe signals were not assigned with certainty due to strong interfering signals. ^{31}P{^{1}H} NMR (25 °C, CD_2Cl_2): −26.5 and 49.8 (both d, J = 182).



4.1.4. Reaction of (PNP)Ni$^+$ (BAr^{4-}_F) with ^{t}BuNH$_2$

30.0 mg (0.022 mmol) of [(PNP)Ni](BAr^4_F) was dissolved in 0.5 mL of CD_2Cl_2 in a J-Young NMR tube yielding a dark reddish brown solution. To this solution, 0.0023 mL of t-butylamine (1.6 mg, 0.022 mmol) was vacuum transferred. After the solution was allowed to warm to room temperature and shaken, the color became orange. Full conversion of the starting material to one product was observed. ^{1}H NMR (25 °C, CD_2Cl_2): 1.18 (s, 9H, ^{t}Bu), 1.36 and 1.43 (both d, 18H each, ^{t}Bu, J = 15.0 and 15.4), 7.58 and 7.75 (both s, Ar, 4 and 8H). ^{31}P{^{1}H} NMR (25 °C, CD_2Cl_2): −31.4 and 46.2 (both d, J = 182).



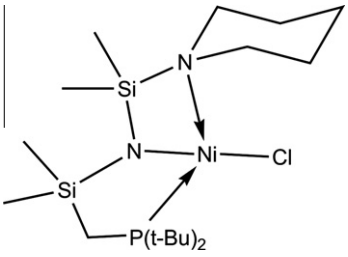
4.1.5. Reaction of (PNP)Ni$^+$ (BAr^{4-}_F) with $PhCH_2NH_2$

30.0 mg (0.022 mmol) of [(PNP)Ni](BAr^4_F) was dissolved in 0.5 mL of CD_2Cl_2 in a J-Young NMR tube yielding a dark reddish brown solution. To this solution, 0.0024 mL of benzylamine (2.35 mg, 0.022 mmol) was added at 25 °C via syringe. Full conversion of the starting material to the mixture of products was observed. ^{31}P{^{1}H} NMR (25 °C, CD_2Cl_2): −32.4 and 47.0 (both d, J = 178). Other products are seen as singlets at 11.4, 58.9 and 64.5 ppm in ^{31}P NMR. Ratio (AX):singlets = 2:1. There is no change in population of these products after 12 h at 25 °C.

4.1.6. Reaction of (PNP)Ni$^+$ (BAr^{4-}_F) with $PhNH_2$

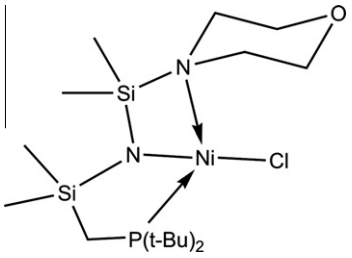
15.5 mg (0.0113 mmol) of [(PNP)Ni](BAr^4_F) was dissolved in 0.5 mL of CD_2Cl_2 at room temperature in a J-Young NMR tube, yielding a dark reddish brown solution. To this solution, 1.01 μL of aniline (1.03 mg, 0.0113 mmol) was added at 25 °C via syringe. Five minutes after mixing, a reddish-purple product was observed, with compete consumption of starting material, with the following spectroscopic features.

^{1}H NMR (25 °C, CD_2Cl_2): 0.05 (s, 3H, SiMe), 0.16 (s, 6H, $SiMe_2$), 0.33 (s, 3H, SiMe), 0.78 (d, 2H, CH_2), 1.43 and 1.36 (both d, J = 16.0 for each, 18H, ^{t}Bu), 1.48 and 1.56 (both d, J = 12.0 for each, 18H, ^{t}Bu), 3.23 (d, J = 12.0, 1H, PhN**H**), 7.36 (m, ∼4H, Ph), 7.58 and 7.71 (both s, 4 and 8H, Ar^F). The other CH_2 signal was not identified due to masking by stronger signals. ^{31}P{^{1}H} NMR (25 °C, CD_2Cl_2): 90% of the signals are those at 12.36 (s, vb), and 69.68 (s). ^{31}P{^{1}H} NMR (−60 °C, CD_2Cl_2): 69.5 (s) and 9.52 (s, br). HRMS (ESI^+, CH_2Cl_2): Observed at 599.3041 ($C_{28}H_{59}N_2Si_2P_2Ni$, $[M]^+$), calc. 599.3046.



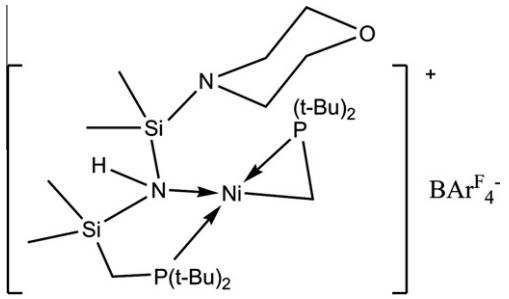
4.1.7. Reaction of (PNP)Ni$^+$ (BAr^{4-}_F) with piperidine in CD_2Cl_2

4.1.7.1. Synthesis of NiCl($CH_2P^tBu_2$)(N($SiMe_2CH_2{}^tBu_2$)($SiMe_2$-N(CH_2)$_5$)]. 30.0 mg (0.022 mmol) of [(PNP)Ni](BAr^4_F) was dissolved in 0.5 mL of CD_2Cl_2 in a J-Young NMR tube forming a dark reddish brown solution. To this solution, one equivalent of piperidine (0.0021 mL) was added at 25 °C via syringe. Initial ^{31}P{^{1}H} NMR spectra showed an AX pattern with J_{PP} = 180, as well as three other singlets. ^{1}H NMR after only 20 min showed complete conversion of (PNP)Ni$^+$. After 30 min the CD_2Cl_2 was stripped off and replaced with pentane and filtered. The pentane-soluble portion was subjected to further characterization and a four coordinate, chloride-containing product with only one phosphorus atom was deduced, by ^{1}H NMR integrations and especially by mass spectrometry. ^{1}H NMR (25 °C, C_6D_6): 0.13, 0.17 (both s, 6H each, SiMe), 1.47 (d, J = 13.8, 18H, ^{t}Bu), 3.26 (d, J = 13.3, 2H, two C–H of two N–CH_2), 3.40 (t, J = 13.3, 2H, two C–H of two N–CH_2); other CH_2 protons on ligand and piperidine are obscured by stronger ligand resonances. ^{31}P{^{1}H} NMR (25 °C, C_6D_6): 59.8. MS (CI, from pentane): Observed at 466.1650 ($C_{18}H_{42}N_2Cl_1Ni_1P_1Si_2$, $[M]^+$), calc. 466.1666; obs. 431.1963 ($C_{18}H_{42}N_2Ni_1P_1Si_2$, $[M-Cl]^+$), calc. 431.1978; obs. 383.0919 ($C_{13}H_{32}N_1Cl_1Ni_1P_1Si_2$, $[M-C_5H_{10}N+H]^+$), calc. 383.0931.



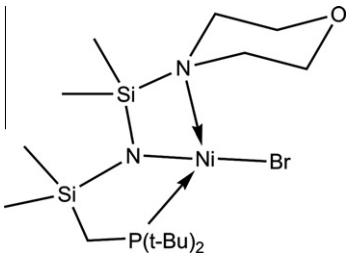
4.1.8. Reaction of (PNP)Ni$^+$ (BAr^{4-}_F) with morpholine in CD_2Cl_2

4.1.8.1. Synthesis of [NiCl(N(SiMe$_2$CH$_2$^{t}Bu$_2$)(SiMe$_2$N(CH$_2$CH$_2$)$_2$-O))]. Reaction was carried out as with piperidine, above, but substituting morpholine. ^{1}H NMR (25 °C, C_6D_6): 0.05, 0.09 (both s, 6H each, SiMe), 1.44 (d, J = 13.8, 18H, ^{t}Bu), 2.89 (d, J = 13.7, 2H, two CH in two equivalent CH_2), 3.04 (t, J = 11.3, 2H, two CH in two equivalent CH_2), 3.34 (d, J = 11.1, 2H, two CH in two equivalent CH_2), 3.64 (t, J = 13.0, 2H, two CH in two equivalent CH_2); CH_2 protons on PNP ligand are obscured by stronger resonances. $^{31}P\{^1H\}$ NMR (25 °C, C_6D_6): 60.4.



4.1.9. Reaction of (PNP)Ni$^+$ (BAr^{4-}_F) with morpholine in PhF

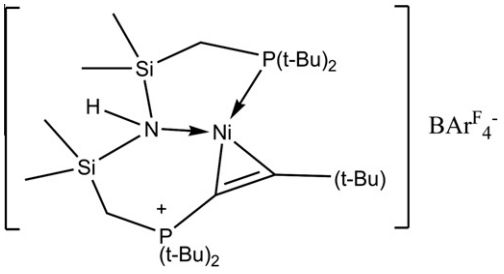
4.1.9.1. Synthesis of [Ni(CH$_2$P^{t}Bu$_2$)(NH(SiMe$_2$CH$_2$ ^{t}Bu$_2$)(SiMe$_2$N(CH$_2$-CH$_2$)$_2$O))]$^+$[BAr^4_F]$^-$. [(PNP)Ni][BAr^4_F] (120 mg, 0.088 mmol) was partially dissolved in dry fluorobenzene (2 mL). The suspension was placed in a freezer and cooled to −40 °C. To the suspension, morpholine (7.6 mg, 0.088 mmol) was slowly added via a pipette. The suspension was left in the freezer for another half an hour to achieve completion: all solids dissolved to produce a dark red solution. $^{31}P\{^1H\}$ NMR (PhF, 25 °C): 47.8 (d, J = 180), −34.3 (d, J = 180).



4.1.10. Reaction of (PNP)Ni$^+$ (BAr^{4-}_F) with morpholine in PhF followed by addition of electrophile

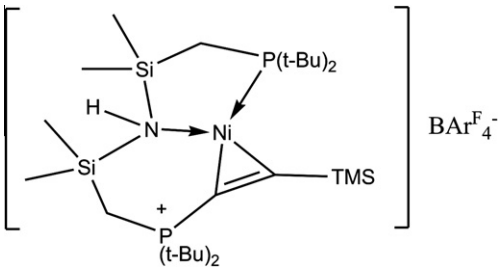
4.1.10.1. Synthesis of [NiBr(N(SiMe$_2$CH$_2$ ^{t}Bu$_2$)(SiMe$_2$N(CH$_2$CH$_2$)$_2$O))]. Pentane soluble fraction. [(PNP)Ni][BAr^4_F] (120 mg, 0.088 mmol) was partially dissolved in dry fluorobenzene (2 mL). The suspension was placed in a freezer and cooled to −40 °C. To the suspension, morpholine (7.6 mg, 0.088 mmol) was slowly added via a pipette. The suspension was left in the freezer for half an hour to produce a dark red solution. Benzyl bromide (15 mg, 0.088 mmol) was then added to the solution, and the solution was kept in freezer for another half hour. The solution was then stripped to dryness. Pentane (5 mL) was added to extract the non-polar fraction which was then filtered to yield a purple solution. The volatiles were removed in vacuo to yield a purple solid for NMR analysis. For the pentane soluble fraction: ^{1}H NMR (C_6D_6, 25 °C): 3.75 (t, two CH in two equivalent CH_2, J = 11.6, 2H), 3.33 (d, two CH in two equivalent CH_2, J = 12.0, 2H), 3.05 (t, two CH in two equivalent CH_2, J = 11.6, 2H), 2.85 (d, two CH in two equivalent CH_2, J = 13.6, 2H), 1.45 (d, 18H, ^{t}Bu, J = 13.8), 0.11 (s, 6H, $SiMe_2$), 0.06 (s, 6H, $SiMe_2$). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): 63.9 (s). Pentane insoluble fraction: [Me($C_6H_5CH_2$)P^{t}Bu$_2$][BAr^4_F]: the pentane insoluble residue above was redissolved in CD_2Cl_2 for NMR study. ^{1}H NMR (CD_2Cl_2, 25 °C): 7.76 (d, J = 7.9, Ar, 2H), 7.56 (d, J = 6.0, Ar, 3H), 4.30 (d, 2H, J_{PH} = 13.8, CH_2), 2.18 (d, 3H, J_{PH} = 12.0, CH_3), 1.61 (d, 18H, two ^{t}Bu, J_{PH} = 15.3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C): 46.6 (s).

4.1.10.2. Independent synthesis of phosphonium salt. One equivalent of benzyl bromide and PMe^{t}Bu$_2$ were mixed in benzene, forming a colorless precipitate. After 12 h at 25 °C all volatiles were removed in vacuum and the residue was dissolved in CD_2Cl_2. ^{1}H and ^{31}P NMR showed spectral data identical to those of the pentane insoluble product (see above).



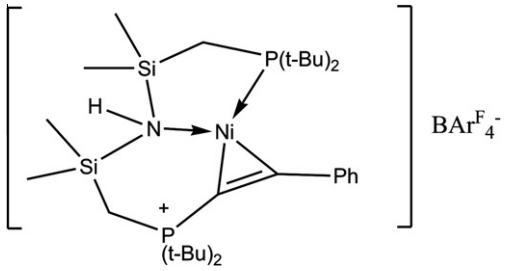
4.1.11. Reaction of (PNP)Ni$^+$ (BAr^{4-}_F) with ^{t}BuC≡CH

30.0 mg (0.022 mmol) of [(PNP)Ni][BAr^4_F] was dissolved in 0.5 mL of THF in a J-Young NMR tube yielding a dark reddish brown solution. To this solution, 0.0027 mL of tert-butyl acetylene (0.022 mmol) was added at 25 °C. The solution became increasingly orange in color, after which it was heated in an oil bath at 60 °C for 2 days. After the heating period, full conversion of the starting material to the single product, [(PNHP$^+$C≡C(t-Bu))Ni] (BAr^{4-}_F) was observed. The solution was dried and dissolved in dichloromethane and layered with pentane, which produced crystals suitable for X-ray diffraction analysis. ^{1}H NMR (25 °C, d_8THF): 0.38 (s, 6H, $SiMe_2$), 0.53 (s.br, 6H, $SiMe_2$), 1.01 (d, J = 9.6, 2H, CH_2), 1.33 (s, 9H, ^{t}Bu), 1.35 (d, J = 12.8, 18H, ^{t}Bu), 1.47 (d, J = 15.4, 18H, ^{t}Bu), 7.57 and 7.78 (both s, 4 and 8H, Ar); N–H proton was not located. $^{31}P\{^1H\}$ NMR (25 °C, d_8THF): 62.2 (d, J = 10), 35.7 (d, J = 10).



4.1.12. Reaction of (PNP)Ni$^+$ (BAr^{4-}_F) with $Me_3SiC{\equiv}CH$

30.0 mg (0.022 mmol) of [(PNP)Ni][BAr^4_F] was dissolved in 0.5 mL of CD_2Cl_2 in a J-Young NMR tube forming a dark reddish brown solution. To this solution, 0.0030 mL of $Me_3SiC{\equiv}CH$ (0.022 mmol) was added at 25 °C. In time of mixing, the solution became orange in color. Full conversion of the starting material to the product, [(PNHP$^+$C≡CTMS)Ni](BAr^4_F) was confirmed by NMR after ten minutes. ^{1}H NMR (25 °C, CD_2Cl_2): 0.24 (s, 9H, TMS), 0.34 (s, 6H, $SiMe_2$), 0.48 (s, 6H, $SiMe_2$), 0.90 (d, J = 9.3, 2H, CH_2), 1.30 (d, J = 13.0, 18H, ^{t}Bu), 1.38 (d, J = 15.5, 18H, ^{t}Bu), 1.53 (d, J = 12.2, 2H, CH_2), 7.57 and 7.74 (both s, 4 and 8H, Ar); N–H proton was not located. ^{31}P{^{1}H} NMR (25 °C, CD_2Cl_2): 64.9 (d, J = 10), 32.8 (d, J = 10).



4.1.13. Reaction of (PNP)Ni$^+$ (BAr^{4-}_F) with PhC≡CH

30.0 mg (0.022 mmol) of [(PNP)Ni][BAr^4_F] was dissolved in 0.5 mL of CD_2Cl_2 in a J-Young NMR tube leaving a dark reddish brown solution. To this solution, 0.0024 mL of phenyl acetylene (0.022 mmol) was added at 25 °C. The solution immediately became orange in color. Full conversion of the starting material to one product, [(PNHP$^+$C≡CPh)Ni] (BAr^4_F) was confirmed by NMR after 10 min. ^{1}H NMR (25 °C, CD_2Cl_2): 0.33, 0.43, 0.44, 0.73 (all s, 3H each, all $SiMe_2$), 0.94 (dd, J = 4.3 and 9.5, 2H, CH_2), 1.10 (d, J = 13.5, 9H, ^{t}Bu), 1.18 (d, J = 13.1, 9H, ^{t}Bu), 1.24 (d, J = 14.8, 9H, ^{t}Bu), 1.39 (d, J = 13.4, 9H, ^{t}Bu), 7.07 and 7.25 (both m, 2 and 3H, Ph), 7.58 and 7.74 (both s, 4 and 8H, B–Ar); N–H proton was not located. ^{31}P{^{1}H} NMR (25 °C, CD_2Cl_2): 65.7 (d, J = 10), 34.4 (d, J = 10).

4.2. Low temperature NMR monitoring of the reaction of (PNP)Ni$^+$ (BAr^{4-}_F) with ^{t}BuC≡CH

30.0 mg (0.022 mmol) of [(PNP)Ni][BAr^4_F] was dissolved in 0.5 mL of CD_2Cl_2 in a J-Young NMR tube equipped with a septum, giving a dark reddish brown solution. The tube was placed into a Dewar containing an acetone/dry ice mixture at −78 °C with special effort to cool the upper glass walls of the tube. To this solution, one equivalent of tert-butyl acetylene (0.0027 mL) was added via syringe. The tube was carefully shaken in order to mix the reagents and NMR spectra were recorded beginning at −60 °C. Species A: ^{31}P{^{1}H} NMR (CD_2Cl_2) 63.5 (br) (−40 °C), 73.4 (br) (−30 °C), 89.0 (br) (−20 °C), 110.0 (br) (−10 °C); ^{1}H NMR: (−20 °C, CD_2Cl_2) 0.04, 0.07, 0.47 (s, $SiMe_2$), 1.02 (s, ^{t}BuC), 1.37–1.45 (m, ^{t}BuP), 7.58, 7.74 (s, Ar). Species B: ^{31}P {^{1}H} NMR (0 °C, CD_2Cl_2) 46.2, 76.3 (both d, J = 5); ^{1}H NMR (0 °C, CD_2Cl_2): −11.21 (dd, J_{HP} = 4.8, 23, Ni–H), 0.09, 0.12 , 0.21, 0.54 (s, $SiMe_2$), 1.27 (s, ^{t}Bu–C), 1.33 (d, ^{t}Bu–P, J = 17), 1.39 (d, ^{t}BuP, J = 16), 1.48 (d, ^{t}BuP, J = 13.6). Species C: ^{1}H NMR (0 °C, CD_2Cl_2): −2.2 (dd, J = 14, 140); ^{31}P {^{1}H} NMR (CD_2Cl_2) 37.1 (d) (−40 °C), 36.6 (d) (−30 °C), 35.6 (d) (−20 °C), 34.1 (d) (−10 °C). The second ^{31}P NMR signal for **C** is considered to be exchange-broadened (H^+ transfer) beyond detection.

Acknowledgments

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Appendix A. Supplementary material

CCDC 789986 and 789987 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2010.12.061.

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