

Oxidative Addition of Ammonium and Iminium Tetrphenylborates to Low-Valent Metal Complexes. Evidence of Selective N–C and N–H Activation. A New, Easy Route to Cationic Allyl- and Hydridonickel Complexes

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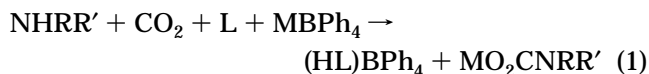
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The reaction of ammonium and iminium tetrphenylborate salts ((CH₂=CHCH₂NH₃)BPh₄, [(CH₂=CHCH₂)HN=CMe₂]BPh₄, and [(PhCH₂)HN=CMe₂]BPh₄) with transition-metal systems in a low oxidation state has been investigated. We report the oxidative addition to (Cy₃P)₂Ni(η²-CO₂) or (Cy₃P)₂NiN≡NNi(PCy₃)₂ under mild conditions (253–293 K) and describe a very selective N–C or N–H bond activation. (CH₂=CHCH₂NH₃)BPh₄ or [(CH₂=CHCH₂)HN=CMe₂]BPh₄ react with (Cy₃P)₂Ni(η²-CO₂) and (Cy₃P)₂NiN≡NNi(PCy₃)₂ to afford the cationic π-allyl–Ni complexes [(η³-C₃H₅)Ni(PCy₃)(NH₃)]BPh₄ (**1**) and [(η³-C₃H₅)Ni(PCy₃)(η¹(N)-HN=CMe₂)]BPh₄ (**2**), respectively. The reaction of [(PhCH₂)HN=CMe₂]BPh₄ with (Cy₃P)₂NiN≡NNi(PCy₃)₂ leads to the hydrido–imino complex [*trans*-(H)Ni(PCy₃)₂(η¹(N)-PhCH₂N=CMe₂)]BPh₄ (**3**) through N–H bond activation. Complexes **1–3** have been fully characterized in solution by NMR (¹H, ¹³C, ³¹P) spectroscopy. The hydrido–imino complex **3**, characterized in the solid state by a X-ray diffraction study, shows a distorted-square-planar coordination around the nickel atom with a very narrow P–Ni–P angle, 148.6(2)°, involving the two P atoms from the *trans* PCy₃ ligands.

Introduction

We have recently described, as a part of our studies on the chemical utilization of carbon dioxide^{1a,b} and coordination chemistry of tetrphenylborates,^{1c,d} a new method of synthesis of alkylammonium tetrphenylborates (HL)BPh₄ (L = primary, secondary, or tertiary aliphatic amine) based on the fixation of carbon dioxide by amines in the presence of an alkali-metal BPh₄[−] salt (eq 1).²



R' = H, alkyl, L = NHRR'; R = aryl, R' = H,
L = NR''₃ (R'' = alkyl); M = Li, Na, K

Reaction **1** was revealed to be a new, versatile route for both the preparation of alkylammonium BPh₄[−] salts under strictly anhydrous conditions and the synthesis

of aliphatic and aromatic alkali-metal carbamates under mild conditions.³

Alkylammonium tetrphenylborates (HL)BPh₄ are currently used as proton transfer agents and act as cocatalysts in some polymerization processes.⁴ The traditional way of synthesis is based on the reaction of NaBPh₄ and an alkylammonium halide in aqueous medium (eq 2),^{5a} affording hydrated (HL)BPh₄ salts,



although some substituted borates, *i.e.* B(C₆F₅)₄ derivatives,^{5b,c} can be prepared by reaction of LiB(C₆F₅)₄ with tertiary amine hydrochlorides ((PhNMe₂H)Cl, for example) in CH₂Cl₂. As the anhydrous form is usually required in most applications, further workup is needed in the cases of hydrated salts and drying *in vacuo* for

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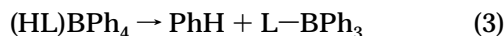
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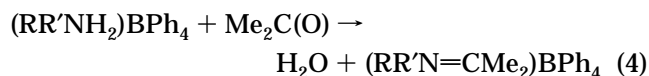
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several days is applied under strictly controlled conditions in order to avoid decomposition. The synthetic methodology we have developed is of general application and has quite improved the availability of the anhydrous salts.

We have now investigated the reactivity of anhydrous alkylammonium tetraphenylborates and found that, in solution, according to the nature of the solvent, they can either undergo an *intramolecular* proton transfer (eq 3)



or *intermolecularly* transfer one proton to the solvent. If acetone is used, iminium BPh_4^- salts are isolated as stable products (eq 4).



Interestingly, in the case of monoalkylammonium salts (L = primary amine), both the *intra*- and *inter*-molecular proton transfer can be totally inhibited if a suitable complexing agent (18-crown-6, for example), able to coordinate the cation, is used.²

The reaction of alkylammonium tetraphenylborates with alkyl or aryl transition-metal complexes, R_nML_m , has been investigated over the last few years, as the former salts promote the protolytic cleavage of several M–C bonds.⁴ In this way, a wide number of cationic or zwitterionic ($\eta^n\text{-Ph}$) BPh_3 metal complexes have been synthesized, a few of which are active as catalysts for alkene polymerization or olefin amination.

Iminium salts themselves occupy a key position in many organic reactions, as they undergo rapid attack by a wide number of nucleophiles.^{6a} As for their reactivity toward transition-metal complexes, iminium ions represent very interesting molecular systems, since they are both isoelectronic and isostructural with olefins. It is known that *N,N*-dialkyl-substituted iminium cations can coordinate to low-valent metal centers through either the C–N double bond ($\eta^2(\text{C},\text{N})$)^{6b,c,d,g} or the electrophilic iminium carbon atom ($\eta^1(\text{C})$).^{6c,g} Low-valent transition-metal complexes can also promote the transformation of iminium moieties into carbenes^{6c} or promote oxidative^{6f} or reductive coupling reactions.^{6g} It is also worth noting that η^2 -coordinated iminium ions are supposed to be intermediates in a few metal-promoted transformations of tertiary amines.^{6h}

In this paper we report a study on the reactivity of alkylammonium and -iminium BPh_4^- salts toward complexes of Ni(0). $(\text{CH}_2=\text{CHCH}_2\text{NH}_3)\text{BPh}_4$, $[(\text{CH}_2=\text{CHCH}_2)\text{HN}=\text{CMe}_2]\text{BPh}_4$, and $[(\text{PhCH}_2)\text{HN}=\text{CMe}_2]\text{BPh}_4$ add oxidatively to Ni(0)–phosphine complexes, under mild conditions, *via* a selective activation of the N–C or N–H bond. The N–C cleavage in ammonium or iminium salts, an uncommon reaction, represents a new, easy way to the direct synthesis of cationic allyl–nickel

systems. The X-ray structure of $[\textit{trans}\text{-}(\text{H})\text{Ni}(\text{PCy}_3)_2(\eta^1(\text{N})\text{-PhCH}_2\text{N}=\text{CMe}_2)]\text{BPh}_4$ shows a distorted-square-planar coordination around the nickel atom with a very narrow P–Ni–P angle, 148.6(2)°, involving the two *trans* P atoms from the PCy_3 groups.

Results and Discussion

Synthesis and Characterization of Alkylammonium and -iminium BPh_4 Salts. $(\text{CH}_2=\text{CHCH}_2\text{NH}_3)\text{BPh}_4$ and $(\text{PhCH}_2\text{NH}_3)\text{BPh}_4$ were obtained by reacting NaBPh_4 or LiBPh_4 with the amine (allylamine and benzylamine, respectively) in the presence of carbon dioxide ($P_{\text{CO}_2} = 0.1$ MPa) (eq 1). $[(\text{CH}_2=\text{CHCH}_2)\text{HN}=\text{CMe}_2]\text{BPh}_4$ and $[(\text{PhCH}_2)\text{HN}=\text{CMe}_2]\text{BPh}_4$ have been synthesized by reaction of $(\text{CH}_2=\text{CHCH}_2\text{NH}_3)\text{BPh}_4$ and $(\text{PhCH}_2\text{NH}_3)\text{BPh}_4$, respectively, with acetone in the presence of 4 Å molecular sieves as dehydrating agent, at room temperature (293 K), according to eq 4 ($\text{R}' = \text{H}$; $\text{R} =$ allyl, benzyl).

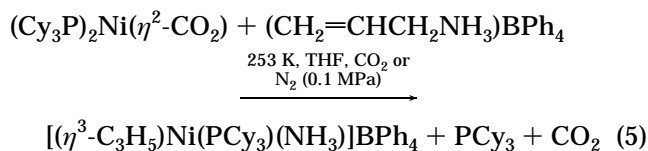
All the salts have been characterized by elemental analysis and spectroscopic techniques (IR, ^1H and ^{13}C NMR). The IR and ^1H NMR spectra of $(\text{CH}_2=\text{CHCH}_2\text{NH}_3)\text{BPh}_4$ and $(\text{PhCH}_2\text{NH}_3)\text{BPh}_4$ have been reported in a previous paper.²

The IR spectra of the iminium salts show a characteristic medium-strong absorption around 1675 cm^{-1} assigned to the stretching of the iminium C=N bond. The double bond hinders the CMe_2 group rotation, making the methyl groups nonequivalent. Such rigidity is demonstrated by the existence of two distinct resonances in the ^1H and ^{13}C NMR spectra of $[(\text{CH}_2=\text{CHCH}_2)\text{HN}=\text{CMe}_2]\text{BPh}_4$ and $[(\text{PhCH}_2)\text{HN}=\text{CMe}_2]\text{BPh}_4$.

The resonance of the iminium carbon atom is observed near 192.5 ppm for both the salts, showing a considerable downfield shift with respect to the parent imine, $\text{Me}_2\text{C}=\text{NH}$, which resonates at 163.4 ppm.⁷

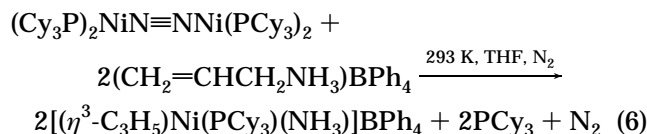
Reactivity of $(\text{CH}_2=\text{CHCH}_2\text{NH}_3)\text{BPh}_4$ toward Ni(0)–Tertiary Phosphine Complexes: N–C Bond Activation. In previous papers,^{8,9} we have reported that $(\text{Cy}_3\text{P})_2\text{Ni}(\eta^2\text{-CO}_2)$ can react with Brønsted acids HX ($\text{X} = \text{HS}$, PhS , Cl , Br , I) by two different reaction pathways, depending on (i) the temperature and (ii) the nature of the acid. Below 250 K, using H_2S and PhSH , which can act as ($1e^- + 1\text{H}^+$) transfer agents (HCl is much less active) protonation of the bound CO_2 with subsequent reduction to bound CO is observed. At room temperature, the oxidative addition of HX (Cl , Br , I) to Ni is the preferential process (with formation of $(\text{Cy}_3\text{P})_2\text{Ni}(\text{H})\text{X}$ and CO_2 elimination).

We have now investigated the reactivity of $(\text{CH}_2=\text{CHCH}_2\text{NH}_3)\text{BPh}_4$ toward $(\text{Cy}_3\text{P})_2\text{Ni}(\eta^2\text{-CO}_2)$. Not surprisingly, in THF at 253 K, $[(\eta^3\text{-C}_3\text{H}_5)\text{Ni}(\text{PCy}_3)(\text{NH}_3)]\text{BPh}_4$ (**1**) is formed as the only product according to eq 5.

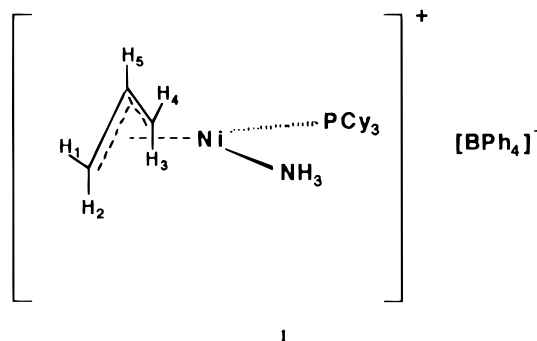


Similarly, $(\text{CH}_2=\text{CHCH}_2\text{NH}_3)\text{BPh}_4$ reacts with $(\text{Cy}_3\text{P})_2\text{NiN}\equiv\text{NNi}(\text{PCy}_3)_2$ according to eq 6.

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Complex **1** has been characterized by IR spectroscopy and NMR techniques (^1H , ^{13}C , ^{31}P). The IR spectrum of



1 shows, in addition to the typical absorptions of the uncoordinated BPh_4^- anion (1578, 1477, 1426, 745, 735, 705, 612 cm^{-1}),² characteristic bands in the range 3350–3100 cm^{-1} (ν_{NH}) and at 1605 (δ_{NH}) and 513 cm^{-1} . The last absorption strongly supports the presence of an allyl group π -coordinated to Ni.¹⁰ The presence of such a group has been definitively confirmed by NMR spectroscopy.

The ^1H NMR spectrum (CD_2Cl_2 , 500 MHz, 293 K) of **1** shows four signals (2.60 and 2.57 (broad partially overlapped singlets, 2 H, H2 and H4), 3.54 (broad singlet, 1 H, H1), 5.19 (m, 1 H, H5, $J \cong 7$ Hz)) that can be assigned to π -allyl protons.¹¹ The resonance due to H3 cannot be located, as it is obscured by the signals of the PCy_3 protons.¹²

In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (CD_2Cl_2 , 125.76 MHz, 293 K) of **1** the three allyl carbon atoms resonate at 45.06 (s, broad, allylic C_{cis}), 73.89 (d, allylic C_{trans} , $^2J_{\text{C-P}} = 14$ Hz), and 113.83 ppm (s, allylic C_{meso}), respectively, in good agreement with the results obtained by other authors for structurally relevant systems.¹³ The presence of two signals for the end carbon atoms of the allyl group clearly demonstrates that these nuclei are not equivalent. This feature allows us to rule out a tetrahedral coordination to the nickel atom, being strongly indicative of a square-planar ligand arrangement around the metal center.

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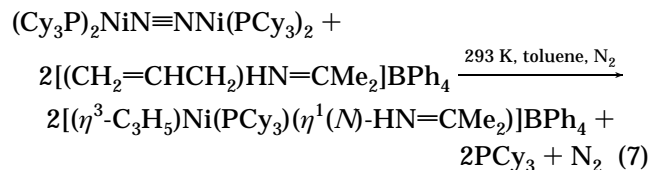
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(12) The reported assignment for the allyl protons H1–H4 is based on decoupling experiments and the following considerations: (a) the *anti* protons are, usually, more shielded than the corresponding *syn* protons ($\delta_{\text{H1}} > \delta_{\text{H2}}$; $\delta_{\text{H4}} > \delta_{\text{H3}}$);¹⁰ (b) in related systems of formula $(\pi\text{-allyl})\text{Ni}(\text{P})(\text{X})$ (P = phosphine ligand; X = halide, alkyl, aryl)¹¹ the resonance of the H1 proton is observed in the range 3–4.5 ppm, at lower fields than the signals due to the H3–H4 protons.

(13) The assignment of the allyl carbon atoms is based on the values of the chemical shift (see, for example, ref 11 and: Jolly, P. W.; Stobbe, S.; Wilke, G.; Goddard, R.; Kruger, C.; Sekutowski, J. C.; Tsay, Y.-H. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 124) and the fact that the allyl carbon *trans* to a P-ligand is more strongly coupled to P than the *cis* carbon atom.¹¹

The line broadening of both the ^{13}C resonances of the end allyl carbon atoms and ^1H signals assigned to the H1, H2, and H4 protons of **1** suggests that the allyl group in this complex is not rigidly bound to the metal but is involved in a slow (with respect to the NMR time scale) fluxional process.^{14,15} The slow fluxionality of the system is also further supported by decoupling experiments (Figure 1) in $\text{THF-}d_6$, at 500 MHz and 293 K (the uncoupled ^1H spectrum under these conditions is reported in the Experimental Section). Upon irradiation of the signal at 3.73 ppm (H1), the multiplet at 5.38 ppm (H5) converts into a triplet ($J \cong 13.5$ Hz), revealing that under these conditions H5 can couple only to the *anti* protons (H2 and H3)¹¹ and no longer to H4 because of saturation transfer¹⁶ from H1 to H4 through an exchange process. Accordingly, when the signal at 2.80 ppm (due to accidentally isochronous H2 and H4) is saturated, the signal at 3.73 ppm (H1) practically disappears and the multiplet at 5.38 ppm (H5) collapses into a broad singlet as a result of saturation transfer from H4 and H2 to H1 and H3, respectively.¹⁷ The above experiments allow us also to establish the nature of the fluxional process that involves left-to-right exchange of *syn* and *anti* protons (Scheme 1). In principle, such a process could take place through free rotation of the allyl group or the dissociation of the NH_3 or PCy_3 ligand. The first mechanism seems to be favored, at least under the working conditions (293 K). In fact, the ^{13}C spectrum of **1** (at 293 K) shows C–P coupling between the phosphorus atom of the ligand and one of the end allyl carbon atoms, thus excluding the possibility of a dissociative mechanism involving the P-ligand. Furthermore, NH_3 dissociation also appears to be quite unlikely, as no spectroscopic evidence was found for the formation of carbamic acid derivatives¹⁸ when reaction 5 was carried out under a carbon dioxide atmosphere.

Reactivity of $[(\text{CH}_2=\text{CHCH}_2)\text{HN}=\text{CMe}_2]\text{BPh}_4$ toward $(\text{C}_3\text{P})_2\text{NiN}\equiv\text{NNi}(\text{PCy}_3)_2$: N–C Bond Activation. The transfer of the allyl group from nitrogen to nickel has been the only observed process also when Ni(0) systems have been reacted with $[(\text{CH}_2=\text{CHCH}_2)\text{HN}=\text{CMe}_2]\text{BPh}_4$. In fact, the reaction of the iminium tetraphenylborate salt with $(\text{C}_3\text{P})_2\text{NiN}\equiv\text{NNi}(\text{PCy}_3)_2$ affords selectively $[(\eta^3\text{-C}_3\text{H}_5)\text{Ni}(\text{PCy}_3)(\eta^1\text{-N})\text{HN}=\text{CMe}_2]\text{BPh}_4$ (**2**) in almost quantitative yield (eq 7).



Imine coordination to nickel is strongly inferred by the presence of both a sharp band at 3251 cm^{-1} (ν_{NH}) and a medium-weak absorption at 1656 cm^{-1} ($\nu_{\text{C=N}}$)¹⁹ in the IR spectrum of **2**. Coordination of imines to metal

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(17) The signal due to H3 cannot be observed in the spectrum, as it is masked by the phosphine protons.

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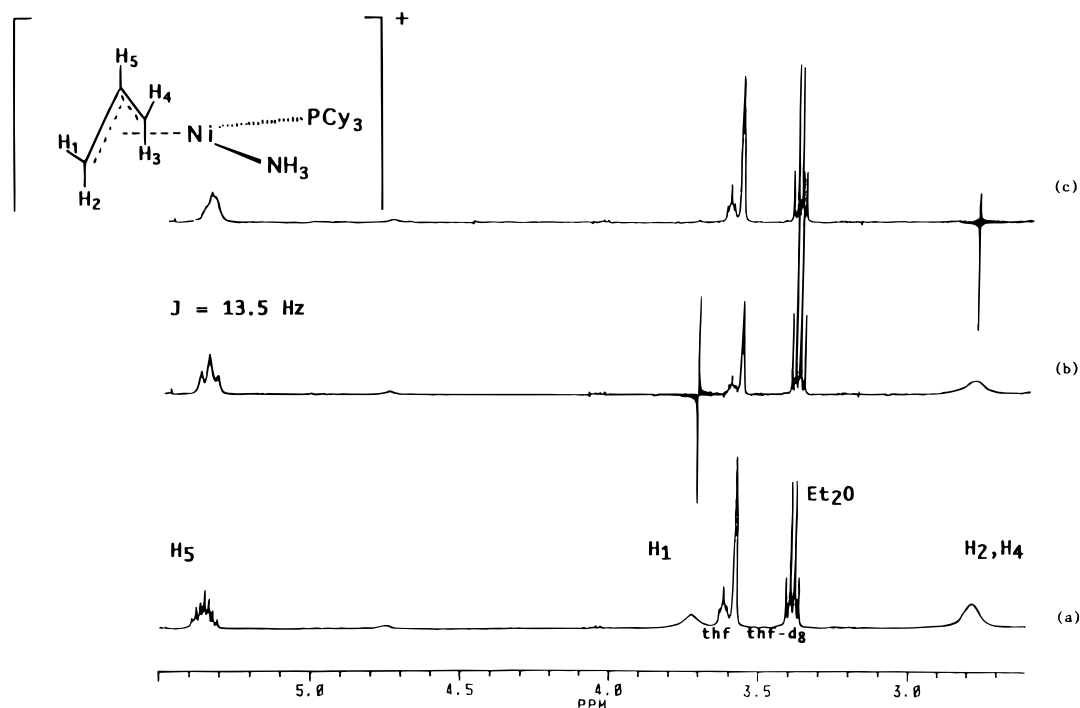
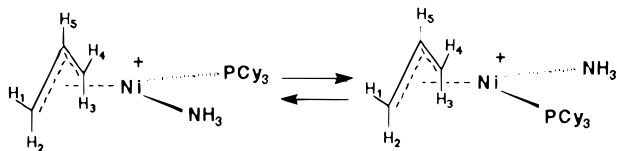
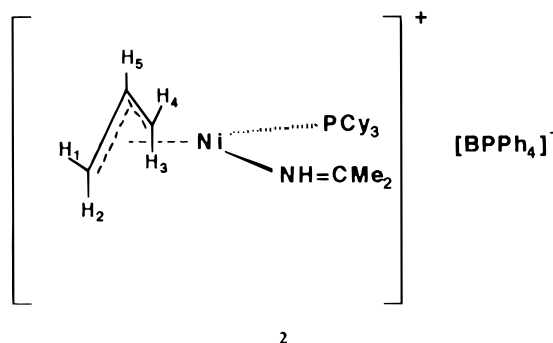


Figure 1. ^1H NMR (THF- d_8 , 500 MHz, 293 K) of $[(\eta^3\text{-C}_3\text{H}_5)\text{Ni}(\text{PCy}_3)(\text{NH}_3)]\text{BPh}_4$ in the 5.5–2.6 ppm region: (a) undecoupled spectrum; (b) irradiation at 3.75 ppm; (c) irradiation at 2.78 ppm.

Scheme 1. Fluxional Behavior of the $[(\eta^3\text{-C}_3\text{H}_5)\text{Ni}(\text{PCy}_3)(\text{NH}_3)]^+$ Cation



centers is well-documented in the literature and may involve the nitrogen atom ($\eta^1(\text{N})$)¹⁹ or both the N and C atoms ($\eta^2(\text{C},\text{N})$).²⁰ The ^{13}C NMR spectrum of **2** allows us to establish unambiguously that the imine ligand mode of bonding is $\eta^1(\text{N})$ in complex **2**. In fact, $\eta^2(\text{C},\text{N})$



imine coordination to a metal center causes a significant high-field shift of the iminium carbon resonance,²⁰ as is the case in other π -systems (olefins, arenes, etc.). However, in complex **2** the iminium carbon resonance is shifted downfield (188.38 ppm) with respect to the free imine $\text{Me}_2\text{C}=\text{NH}$ (163.4 ppm), indicating that the N atom is implied in a σ -interaction with the metal center.

π -Coordination of the allyl group to nickel in complex **2** can be easily confirmed by its IR spectrum (showing

a medium absorption at 510 cm^{-1}) and by means of NMR (^1H , ^{13}C) spectroscopy. As is the case for complex **1**, only the signals due to the allyl protons H5 (5.39 ppm, septet, $J \approx 7\text{ Hz}$), H1 (3.95 ppm, broad doublet, $J \approx 7.3\text{ Hz}$), and H2 and H4 (2.98 ppm, two slightly broad and partially overlapping multiplets) can be observed in the ^1H spectrum (CD_2Cl_2 , 200 MHz, 293 K).²¹ The ^{13}C spectrum (CD_2Cl_2 , 125.76 MHz, 293 K) shows the π -allyl resonances in the usual range (48.65 d, allylic C_{cis} , $^2J_{\text{CP}} = 6.06\text{ Hz}$), 73.65 (d, allylic C_{trans} , $^2J_{\text{CP}} = 14.83\text{ Hz}$), 114.09 (s, allylic C_{meso}).^{11,13} Interestingly, both end allyl carbon atoms show coupling to phosphorus, and the signals of protons H1, H2, and H4 exhibit a fine structure. These spectroscopic features suggest that the allyl group in complex **2** is more rigidly bound to nickel than in **1**. Varying the temperature within the range 188–308 K (at 200 MHz) produces some modifications in the region of cyclohexyl protons but leaves practically unchanged the chemical shifts of the allyl protons. However, at 188 K the fine structure of the signals due to the allyl protons is practically lost, probably because of diminished resolution. Decoupling experiments (CD_2Cl_2 as solvent) carried out at 308 K and 200 MHz support the existence of a quite rigid allyl system. In fact, when proton H1 is decoupled, the septet at 5.40 ppm converts into a triplet of doublets, whereas the structure of the multiplets at about 3 ppm is only poorly affected. Moreover, H5 decoupling converts the signal at 3.96 ppm (H1) into a 1:2:2:1 quartet ($J = 2.4\text{ Hz}$), while the overlapping multiplets around 3 ppm (H2 and H4) collapse into a poorly resolved broad signal.

Synthetic Implication of C–N Bond Activation. Reactions 5–7 thus allow the direct synthesis of cationic (π -allyl)nickel complexes **1** and **2**. Ionic π -allyl–Ni complexes are of interest, as they are catalysts or precursors of catalysts for reactions involving either

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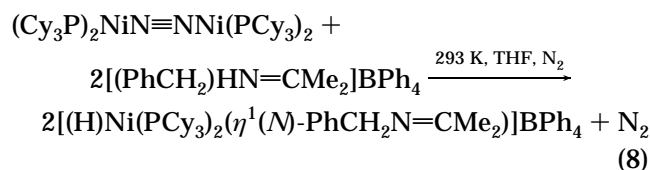
(21) As for the case of **1**, the resonance of H3 is masked by the signals of phosphine protons.

olefins or dienes²² and are generally prepared in two steps via halide abstraction from neutral π -allyl systems.^{22,23} Neibecker and Castro reported the synthesis of a few cationic π -allyl nickel systems from Ni(CO)₄ and allyl derivatives, such as the poorly stable (allyloxy)-tris(dimethylamino)phosphonium salts²⁴ or less reactive *S*-allyltetramethylthiuronium salts.²⁵ These methods involve allyl group transfer from an oxygen or a sulfur atom to nickel and afford symmetric π -allyl complexes of formula $[(\eta^3\text{-allyl})\text{Ni}(\text{L})_2]\text{X}$ (L = MeCN, PPh₃, tetramethylthiourea). The reactions we have reported represent an easy way to obtain ionic π -allyl–Ni complexes using stable, readily available, and very reactive allyl-ammonium or -iminium salts. Interestingly, this way allows the synthesis of unprecedented asymmetric cationic π -allyl complexes bearing both P- and N-ligands in the coordination sphere of nickel.

To the best of our knowledge, the activation of a C–N bond by Ni systems has been reported only once in the literature: the cleavage of one of the C–N bonds of a N,N'-bridged porphyrin by nickel tetracarbonyl under more severe conditions.²⁶ Pt and Ru compounds have been reported²⁷ to promote the cleavage of the allyl–N bond of allylamines with subsequent transfer of the allyl group to the metal center. The formation of nitrido complexes by metathesis of W–W triple bonds with nitriles,²⁸ the four-electron oxidative addition of isocyanates, carbodiimides, and imine C=N double bonds to Mo(II) or W(II) phosphine complexes to give Mo(VI)– or W(VI)–imido compounds,²⁹ and the nucleophile-induced cleavage of a C–N bond of a $\eta^2(\text{C},\text{N})$ -coordinated pyridine ring³⁰ are other examples of multiple C–N bond activation.

Transition-metal-promoted breaking of C–N single bonds³¹ is, probably, a major step in several catalytic processes.³² The present work clearly shows that Ni(0) complexes can promote the activation of a C–N bond under very mild conditions and generate Ni systems with interesting catalytic properties.

Reactivity of [(PhCH₂)HN=CMe₂]BPh₄ toward (Cy₃P)₂NiN≡NNi(PCy₃)₂: N–H Bond Activation. The reactivity of [(PhCH₂)HN=CMe₂]BPh₄ toward (Cy₃P)₂NiN≡NNi(PCy₃)₂ markedly differs from that of [(CH₂=CHCH₂)HN=CMe₂]BPh₄. In fact, the reaction of [(PhCH₂)HN=CMe₂]BPh₄ with (Cy₃P)₂NiN≡NNi(PCy₃)₂, in THF at 293 K, affords the hydrido–imino species [*trans*-(H)Ni(PCy₃)₂($\eta^1(\text{N})$ -PhCH₂N=CMe₂)]BPh₄ (**3**) according to eq 8.



To the best of our knowledge, reaction 8 represents the first example of transition-metal activation of an

iminium N–H bond, other known examples of N–H activation having been reported for ammonia, amines, and amides.³³ Reaction 8 is quite intriguing as, at least from a formal point of view, it is reminiscent of 1-alkene addition.³⁴

Complex **3** has been fully characterized both in solution (¹H, ¹³C, ³¹P NMR) and in the solid state (IR, X-ray). It is stable in the air and does not react with CO₂ (*P*_{CO₂} = 0.1–5 MPa, 293 K) even after long exposure in solution.

The absence of any band above 3100 cm⁻¹ and the medium to weak absorptions observed at 1980 (m-w, $\nu_{\text{N-H}}$)³⁵ and 1638 cm⁻¹ (m, $\nu_{\text{C=N}}$)¹⁹ in the IR spectrum of **3** strongly suggest the presence of both a hydrido and a tertiary imino group in the coordination sphere of nickel. The complete characterization of **3** as a cationic hydrido–imino–Ni complex was firmly established by NMR spectroscopy and X-ray studies.

The ¹³C NMR spectrum (CD₂Cl₂, 125.76 MHz, 293 K) of **3** shows a singlet at 179.42 ppm due to the imine ligand $\eta^1(\text{N})$ -coordinated to the metal (see above). Sound evidence for a hydrido group bound to nickel comes from the appearance in the ¹H NMR spectrum (CD₂Cl₂, 200 MHz, 293 K) of **3** of a triplet at –24.41 ppm (*J*_{HP} = 76.73 Hz). This pattern suggests a hydrido group coupled to two equivalent P nuclei.³⁵ In the ³¹P NMR spectrum (CH₂Cl₂, 81 MHz, 293 K) of **3**, the signal (28.64 ppm) for the phosphorus atom of the phosphine ligands is split into a doublet (*J*_{HP} = 76.73 Hz) because of the coupling to the hydride hydrogen.

These features strongly suggest that, in solution, the [(H)Ni(PCy₃)₂($\eta^1(\text{N})$ -PhCH₂N=CMe₂)]⁺ cation has a square-planar geometry, with the phosphine ligands *trans* to each other.³⁵ Such a coordination geometry around the nickel atom in complex **3** has been confirmed in the solid state by an X-ray diffraction study. It is worth noting that, even though both neutral and ionic hydrido–bis(phosphine)–Ni complexes, (H)Ni(P)₂(L) and [(H)Ni(P)₂(L)]X (P = phosphine; L = ancillary ligand),

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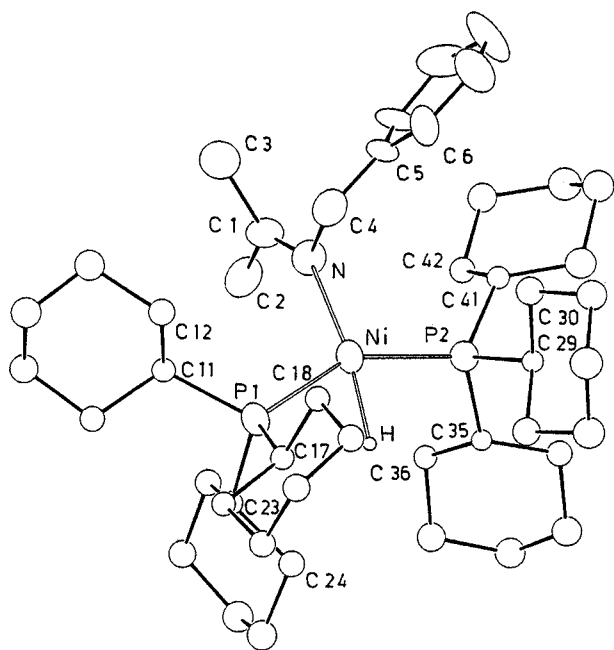


Figure 2. ORTEP view of the structure of the $[trans-(H)Ni(PCy_3)_2(\eta^1(N)-PhCH_2N=CMe_2)]^+$ cation of complex **3** with the atomic numbering scheme. The ellipsoids for the atoms are drawn at the 30% probability level.

Table 1. Selected Bond Distances (Å) and Angles (deg) for $3 \cdot CH_2Cl_2$

Ni–P1	2.220(6)	P2–C35	1.81(2)
Ni–P2	2.223(5)	P2–C41	1.83(2)
Ni–N	1.94(1)	N–Cl	1.25(3)
Ni–H	1.65(9)	N–C4	1.51(3)
P1–C11	1.88(2)	C1–C2	1.48(3)
P1–C17	1.83(2)	C1–C3	1.54(3)
P1–C23	1.87(2)	C4–C5	1.45(3)
P2–C29	1.87(2)		
N–Ni–H	166(3)	Ni–P2–C35	110.0(6)
P2–Ni–H	78(5)	Ni–P2–C29	111.3(6)
P2–Ni–N	110.1(5)	C35–P2–C41	108.2(8)
P1–Ni–H	72(3)	C29–P2–C41	103.1(8)
P1–Ni–N	101.3(5)	C29–P2–C35	103.5(8)
P1–Ni–P2	148.6(2)	Ni–N–C4	115(1)
Ni–P1–C23	112.1(6)	Ni–N–C1	127(1)
Ni–P1–C17	110.1(6)	C1–N–C4	118(2)
Ni–P1–C11	116.8(6)	N–C1–C3	127(2)
C17–P1–C23	103.7(8)	N–C1–C2	121(2)
C11–P1–C23	102.2(8)	C2–C1–C3	112(2)
C11–P1–C17	110.9(8)	N–C4–C5	117(2)
Ni–P2–C41	119.4(6)		

respectively, have been known for a long time,³⁵ their characterization by X-ray diffraction is very incomplete.^{35h,i,36}

Description of the Crystal Structure of $[trans-(H)Ni(PCy_3)_2(\eta^1(N)-PhCH_2N=CMe_2)]BPh_4 \cdot CH_2Cl_2$ ($3 \cdot CH_2Cl_2$). A single-crystal X-ray study (Table 1) of the dichloromethane solvate of **3** was carried out. In the crystals, cationic moieties $[trans-(H)Ni(PCy_3)_2(\eta^1(N)-PhCH_2N=CMe_2)]^+$, BPh_4^- anions, and molecules of the solvent CH_2Cl_2 are present. The structure of the cationic complex is shown in Figure 2 together with the atom-numbering scheme. Selected bond distances and angles are listed in Table 2. The coordination around the nickel atom is distorted square planar and involves two P atoms from the PCy_3 groups in a *trans* position, a N atom from the imine ligand, and a terminal hydride. The atoms involved in the coordination are practically coplanar, except for the hydride, which is out of the mean plane through the other atoms by 0.3(2) Å. The

Table 2. Experimental Data for the Crystallographic Analysis of $3 \cdot CH_2Cl_2$

formula	$C_{71}H_{102}BCl_2NNiP_2$
mol wt	1171.975
cryst syst	orthorhombic
space group	$P2_12_12_1$
<i>a</i> , Å	14.943(4)
<i>b</i> , Å	32.218(5)
<i>c</i> , Å	13.931(3)
<i>V</i> , Å ³	6707(3)
<i>Z</i>	4
<i>D_c</i> , Mg m ⁻³	1.161
<i>F</i> (000)	2528
temp, K	295
diffractometer	Siemens AED
radiation ($\lambda = 1.541838$ Å)	graphite-monochromated Cu K α
μ , cm ⁻¹	18.89
scan speed, deg min ⁻¹	3–12
scan width, deg	1.20 + 0.142 tan θ
scan mode	$\theta/2\theta$
θ range, deg	3–60
no. of rflns measd	5554
no. of obsd rflns	1819 ($I > 2\sigma(I)$)
$R = \sum \Delta F / \sum F_o $	0.0642
$R_w = [\sum w(\Delta F)^2 / \sum wF_o^2]^{1/2}$	0.0761

Ni–P bonds are equal, 2.220(6) and 2.223(5) Å, and the two *trans* P atoms form with the Ni atom an angle of 148.6(2)°, the strong distortion being due to the presence of three adjacent bulky ligands. The values of the Ni–P bonds are quite normal if compared to the mean value 2.211 Å (from the Cambridge Structural Database) found in four-coordinate nickel(II) complexes with PCy_3 ligands, whereas that of the Ni–N bond, 1.94(1) Å, is slightly longer than the mean value 1.888 Å (from the CSD) found with comparable N-donor ligands. The fragment $(CH_2)_2C=NCH_2$ of the imine ligand (except for the hydrogen atoms) is planar (maximum deviation 0.03(2) Å for N) and is almost perpendicular to the coordination mean plane (dihedral angle 98.1(5)°). Each of the two PCy_3 groups is oriented in such a way that a P–C bond (P1–C11 and P2–C41) eclipses approximately the Ni–N bond, confirming a strong steric hindrance which probably is responsible for the remarkable deviation of the P1–Ni–P2 angle from the theoretical value of 180°. The other two P–C bonds of each PCy_3 group are staggered with respect to the Ni–H bond, and this feature causes the *complete caging* of the hydride, also accentuated by the narrowing of the P1–Ni–P2 angle.

Complex **3** is one of the few structurally characterized nickel(II) complexes with a terminal hydride (Ni–H = 1.65(9) Å). The hydride was not localized in the neutral $(H)Ni(PBz_3)_2(OPh)$ complex,^{35h} in which the values of the Ni–P bonds, 2.163(3) and 2.171(3) Å (tribenzylphosphine ligands), are shorter than those found in **3** and the P–Ni–P angle, 159.0(1)°, is indicative of a strong distortion, as in **3**. In $(H)Ni(PCy_3)[PPh_2CH_2C(CF_3)_2OP, O]^{35i}$ the hydride is localized (Ni–H = 1.37(3) Å), the value of the Ni–P bond (PCy_3 ligand) is 2.181(1) Å, and the P–Ni–P angle is 173.1(1)°, due to a different steric hindrance of the ligands with respect to the other two complexes.

These structural features, as well as the ionic character of the complex and the nature of the ligand *trans* to the hydride (imine vs Ph or Me; see below), can explain the inertness of **3** toward carbon dioxide. The Ni–H bond is quite protected by the P-ligands, which prevents the reaction with CO_2 and makes this complex quite different from $(H)Ni(PCy_3)_2(Me)$ or $(H)Ni(PCy_3)_2-$

(Ph), both of which have been reported to insert CO₂ into the Ni–H bond to give neutral formate Ni complexes.^{35f}

Conclusions

The first examples of oxidative addition of alkylammonium or -iminium cations to a transition-metal center have been described.

The interaction of the allylammonium and -iminium tetraphenylborate salts (CH₂=CHCH₂NH₃)BPh₄ and [(CH₂=CHCH₂)HN=CMe₂]BPh₄ with Ni(0)–phosphine complexes (Cy₃P)₂Ni(η²-CO₂) and (Cy₃P)₂NiN≡NNi(PCy₃)₂ results in the activation, under mild conditions, of the C–N single bond and affords, in one step, unprecedented asymmetric cationic π-allyl–Ni complexes of formula [(η³-C₃H₅)Ni(P)(N)]BPh₄, containing both a P- and N-ligand in the coordination sphere of Ni.

When the allyl group is exchanged for an aliphatic or aromatic group, the reactivity of the BPh₄ salts is strongly influenced and the N–H, rather than the N–C, activation takes place.

In fact, the reaction of [(PhCH₂)HN=CMe₂]BPh₄ with (Cy₃P)₂NiN≡NNi(PCy₃)₂ leads to the hydrido–imino complex [*trans*-(H)Ni(PCy₃)₂(η¹(N)-PhCH₂N=CMe₂)]BPh₄ through N–H bond activation. This reaction represents the first documented example of oxidative addition of an iminium N–H bond to a metal center.

Experimental Section

General Comments. Unless otherwise stated, all reactions and manipulations were conducted under a dinitrogen or carbon dioxide atmosphere (as specified in the text), by using vacuum line techniques. All solvents were dried as described in the literature³⁷ and stored under dinitrogen. Amines (Fluka, Aldrich) were dried³⁷ and distilled before use. NaBPh₄ (Aldrich or Baker) and LiBPh₄·3MeOCH₂CH₂CH₂OMe (Strem or Aldrich) were used as received. (Cy₃P)₂Ni(η²-CO₂) and (Cy₃P)₂NiN≡NNi(PCy₃)₂ have been prepared as previously reported.^{38,39}

IR spectra were obtained with a Perkin-Elmer 883 spectrophotometer. NMR spectra were run on a Varian XL-200 or a Bruker AM 500 instrument. ¹H and ¹³C chemical shifts are in ppm vs TMS and are referenced to the solvent peak. ³¹P resonances are reported in ppm vs H₃PO₄.

Synthesis of (HL)BPh₄ Salts (L = (CH₂=CHCH₂)NH₂, PhCH₂NH₂). The synthesis of (CH₂=CHCH₂NH₃)BPh₄ and (PhCH₂NH₃)BPh₄ from the corresponding amine, NaBPh₄, and CO₂ and their spectroscopic characterization (IR, ¹H NMR) have already been reported elsewhere.² Below we report the synthesis of these salts from LiBPh₄.

(A) (CH₂=CHCH₂NH₃)BPh₄. A THF (35 mL) solution of LiBPh₄·3MeOCH₂CH₂OMe (0.964 g, 1.62 mmol) and CH₂=CHCH₂NH₂ (0.25 mL, 3.32 mmol), prepared under dinitrogen, was saturated with CO₂ at 273 K. The white suspension of LiO₂CNH(CH₂CH=CH₂) was treated with pentane (25 mL), cooled to 253 K, and filtered. After the lithium carbamate was washed on the filter with dichloromethane (2 × 5 mL), the mother liquor and washing solutions were collected and concentrated *in vacuo*. Upon addition of pentane (40 mL) and cooling to 253 K, a white precipitate of (CH₂=CHCH₂NH₃)BPh₄ was obtained and isolated by filtration (0.550 g, 90%). Anal. Calcd for C₂₇H₂₈BN: C, 85.94; H, 7.48; N, 3.71. Found: C, 85.69; H, 7.55; N, 3.61.

(B) (PhCH₂NH₃)BPh₄. A THF (85 mL) solution of LiBPh₄·3MeOCH₂CH₂OMe (2.601 g, 4.36 mmol) and PhCH₂NH₂ (0.95 mL, 8.72 mmol), prepared under dinitrogen, was saturated with CO₂ at 273 K. The white suspension of LiO₂CNH(CH₂Ph) was treated with pentane (20 mL), cooled to 253 K, and filtered. After the lithium carbamate on the filter was washed with THF (3 × 10 mL), the mother liquor and washing solutions were collected and concentrated *in vacuo*. Upon addition of pentane (100 mL) and cooling to 253 K, a white precipitate was obtained, isolated by filtration and identified as (PhCH₂NH₃)BPh₄·0.5THF (1.798 g, 89%). Anal. Calcd for C₃₃H₃₄BNO_{0.5}: C, 85.52; H, 7.39; N, 3.02. Found: C, 85.48; H, 7.26; N, 3.09.

Synthesis of [(CH₂=CHCH₂)HN=CMe₂]BPh₄. The synthesis of [(CH₂=CHCH₂)HN=CMe₂]BPh₄ and its characterization by IR and ¹H NMR have been reported in ref 2. Below we report the ¹³C NMR spectrum. ¹³C{¹H} NMR (THF-*d*₆, 125.76 MHz, 293 K): δ 19.62 (Me), 25.35 (Me), 49.05 (–CH₂CH=CH₂), 119.72 (–CH₂CH=CH₂), 128.16 (CH₂CH=CH₂), 192.86 (Me₂C=NH–), 120.72 (C_{para},BPh₄), 124.60 (q, C_{meta},BPh₄, ³J_{CB} = 2.6 Hz), 135.69 (C_{ortho},BPh₄), 163.72 (q, C_{ipso},BPh₄, ¹J_{CB} = 49.31 Hz). The above assignment is supported by a ¹³C DEPT experiment.

Synthesis of (PhCH₂)HN=CMe₂]BPh₄. To an acetone (10 mL) solution of (PhCH₂NH₃)BPh₄·0.5THF (1.380 g, 2.98 mmol), prepared under dinitrogen, were added 4 Å molecular sieves. The mixture was stirred for 1.5 h at room temperature (293 K) and then filtered. After the residue on the filter was washed with acetone (2 × 5 mL), the mother liquor and washing solutions were collected, treated with diethyl ether (50 mL), and cooled to 253 K. The white solid that precipitated was filtered, washed with diethyl ether (2 × 8 mL), and dried *in vacuo* (0.874 g, 58%). Anal. Calcd for C₃₄H₃₄BN: C, 87.36; H, 7.33; N, 2.99. Found: C, 86.99; H, 7.34; N, 2.78. IR (Nujol, KBr disks, cm⁻¹): 3330 (vw), 3230 (m, broad), 3150 (m), 1673 (m-s, ν_{C=N}), 1580 (m), 1495 (m-w), 1480 (m-s), 1428 (m), 1370 (m-s), 746 (s), 735 (s), 720 (m), 712 (s), 695 (m). ¹H NMR (CD₂Cl₂, 200 MHz, 293 K): δ 1.59 (s, 3 H, Me), 1.80 (s, 3 H, Me), 3.81 (slightly broad, 2 H, PhCH₂), 6.89 (tt, 4 H, H_{para},BPh₄), 7.04 (t, 8 H, H_{meta},BPh₄, ³J = 7.2 Hz), 7.50 (m, 8 H, H_{ortho},BPh₄), 6.82–6.88 and 7.34–7.38 (two multiplets, 5 H, PhCH₂). ¹³C{¹H} NMR (CD₂Cl₂, 125.76 MHz, 293 K): δ 21.04 (Me), 27.30 (Me), 51.52 (–CH₂Ph), 192.44 (Me₂C=NH–), 122.00 (C_{para},BPh₄), 126.03 (q, C_{meta},BPh₄, ³J_{CB} = 2.7 Hz), 135.28 (C_{ortho},BPh₄), 163.84 (q, C_{ipso},BPh₄, ¹J_{CB} = 49.2 Hz), 126.95, 129.00, 130.40, and 133.13 (–CH₂Ph).

Reaction of (CH₂=CHCH₂NH₃)BPh₄ with (Cy₃P)₂Ni(η²-CO₂). Synthesis of [(η³-C₃H₅)Ni(PCy₃)(NH₃)]BPh₄. To a solution of (Cy₃P)₂Ni(η²-CO₂) (0.187 g, 0.282 mmol) in THF (3 mL), prepared under dinitrogen at 253 K, was added 0.110 g of (CH₂=CHCH₂NH₃)BPh₄ (0.292 mmol) dissolved in THF (3 mL) and the resulting mixture was stirred at 253 K. The solution, initially orange, turned to greenish yellow, then to brown and, after a few hours (3–4 h), to yellowish orange. The reaction mixture was filtered and, after addition of pentane (15 mL), cooled to 253 K. The yellow crystals that precipitated were isolated by filtration, washed with pentane (5 mL), and dried *in vacuo* (0.147 g, 74%). Anal. Calcd for C₄₅H₆₁NBPNI: C, 75.43; H, 8.58; N, 1.95; Ni, 8.19; P, 4.32. Found: C, 74.94; H, 8.54; N, 1.92; Ni, 8.11; P, 4.43. IR (Nujol, KBr disks, cm⁻¹):

3337 (m-w), 3310 (m), 3255 (m), 3175 (m-w), 1605 (m-w, broad), 1578 (m), 1477 (m), 1446 (m-s), 1428 (m), 1275 (m), 1265 (m), 1175 (m), 1035 (m), 1005 (m), 935 (m), 845 (m-s), 745 (s), 735 (s), 705 (s), 612 (m-s), 513 (m). ¹H NMR (CD₂Cl₂, 500 MHz, 293 K): δ –0.59 (s, broad, 3 H, NH₃), 1.1–2.0 (34 H, Cy protons and H3), 2.60 and 2.57 (broad partially overlapped singlets, 2 H, H2 and H4), 3.54 (broad singlet, 1 H, H1), 5.19 (septet, 1 H, H5, ³J = 7 Hz), 6.91 (t, 4 H, H_{para},BPh₄, ³J = 6.93 Hz), 7.08 (t, 8 H, H_{meta},BPh₄, ³J = 7.24 Hz), 7.49 (m, 8 H, H_{ortho},BPh₄). The signal at δ –0.59 disappears upon addition of D₂O. ¹H NMR (THF-*d*₆, 500 MHz, 293 K): δ 1.2–2.0 (Cy protons and H3), 2.80 (broad singlet, H2 and H4), 3.73 (broad singlet, H1), 5.38 (septet, H5, ³J = 7 Hz), 6.74 (t, H_{para},BPh₄, ³J =

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7.17 Hz), 6.89 (t, H_{meta,BPh_4} , $J = 7.40$ Hz), 7.32 (m, H_{ortho,BPh_4}). $^{13}C\{^1H\}$ NMR (CD_2Cl_2 , 125.76 MHz, 293 K): δ 25.86 (s, C_{δ,PCy_3}), 27.15 (d, isochronous diastereotopic C_{γ,PCy_3} and C_{γ',PCy_3} , $^3J_{CP} = 10.16$ Hz), 29.67 and 29.76 (singlets, diastereotopic C_{β,PCy_3} and C_{β',PCy_3}), 33.47 (d, C_{α,PCy_3} , $^1J_{CP} = 19.40$ Hz), 45.06 (s, broad, allylic C_{cis}), 73.89 (d, allylic C_{trans} , $^2J_{CP} = 14$ Hz), 113.83 (s, allylic C_{meso}), 121.68 (C_{para,BPh_4}), 125.80 (C_{meta,BPh_4}), 135.38 (C_{ortho,BPh_4}), 163.98 (q, C_{ipso,BPh_4} , $^1J_{CB} = 49.2$ Hz). $^{31}P\{^1H\}$ NMR (CH_2Cl_2 , 202.45 MHz, 293 K): δ 33.46.

Reaction of $[(CH_2=CHCH_2)HN=CMe_2]BPh_4$ with $(Cy_3P)_2NiN\equiv NNi(PCy_3)_2$. Synthesis of $[(\eta^3-C_3H_5)Ni(PCy_3)_2(\eta^1(N)-HN=CMe_2)]BPh_4$. To a solution of $(Cy_3P)_2NiN\equiv NNi(PCy_3)_2$ (0.290 g, 0.229 mmol) in toluene (30 mL) was added 0.199 g (0.477 mmol) of $[(CH_2=CHCH_2)HN=CMe_2]BPh_4$, and the resulting suspension was stirred at room temperature (293 K) under dinitrogen. The purple-red solution fast turned to greenish yellow, then to brown, and, finally, to yellow. The yellow solid that precipitated was filtered, washed with toluene (5 mL) and pentane (5 mL), dried *in vacuo*, and then recrystallized from CH_2Cl_2 /pentane (0.242 g, 70%). Anal. Calcd for $C_{48}H_{65}NBPn$: C, 76.20; H, 8.66; N, 1.85; Ni, 7.76; P, 4.10. Found: C, 76.20; H, 8.58; N, 1.83; Ni, 7.8; P, 4.10. IR (Nujol, KBr disks, cm^{-1}): 3251 (m, sh), 1656 (m-w, br, $\nu_{C=N}$), 1580 (m-w), 1475 (m), 1447 (s), 1425 (m), 1411 (m), 746 (s), 731 (s), 703 (s), 610 (m-s), 510 (m-w). 1H NMR (CD_2Cl_2 , 200 MHz, 293 K): δ 1.1–2.0 (34 H, Cy protons and H3), 2.05 (s, 3 H, Me), 2.25 (s, 3 H, Me), 2.98 (two slightly broad and partially overlapped multiplets, 2 H, H2 and H4), 3.95 (broad doublet, 1 H, H1, $J \approx 7.3$ Hz), 5.39 (septet, 1 H, H5, $J \approx 7$ Hz), 6.88 (t, 4 H, H_{para,BPh_4} , $J = 6.9$ Hz), 7.03 (t, 8 H, H_{meta,BPh_4} , $J = 7.1$ Hz), 7.31 (m, 8 H, H_{ortho,BPh_4}), 7.66 (s, broad, 1 H, NH). $^{13}C\{^1H\}$ NMR (CD_2Cl_2 , 125.76 MHz, 293 K): δ 25.85 (s, C_{δ,PCy_3}), 27.19 (d, diastereotopic C_{γ,PCy_3} , $^3J_{CP} = 10.38$ Hz), 27.23 (d, diastereotopic C_{γ',PCy_3} , $^3J_{CP} = 10.38$ Hz), 28.29 (s, Me), 29.50 (s, Me), 29.74 and 30.01 (singlets, diastereotopic C_{β,PCy_3} and C_{β',PCy_3}), 33.43 (d, C_{α,PCy_3} , $^1J_{CP} = 19.95$ Hz), 48.65 (d, allylic C_{cis} , $^2J_{CP} = 6.06$ Hz), 73.65 (d, allylic C_{trans} , $^2J_{CP} = 14.83$ Hz), 114.09 (s, allylic C_{meso}), 121.39 (C_{para,BPh_4}), 125.29 (C_{meta,BPh_4}), 135.06 (C_{ortho,BPh_4}), 163.7 (q, C_{ipso,BPh_4} , $^1J_{CB} = 49.6$ Hz), 188.38 (s, $Me_2C=N$). The assignment is also supported by the ^{13}C APT NMR (CD_2Cl_2 , 50.3 MHz, 293 K) spectrum. $^{31}P\{^1H\}$ NMR (CH_2Cl_2 , 81 MHz, 293 K): δ 33.60.

Reaction of $[(PhCH_2)HN=CMe_2]BPh_4$ with $(Cy_3P)_2NiN\equiv NNi(PCy_3)_2$. Synthesis of $[(H)Ni(PCy_3)_2(\eta^1(N)PhCH_2N=CMe_2)]BPh_4$. To a solution of $(Cy_3P)_2NiN\equiv NNi(PCy_3)_2$ (0.401 g, 0.317 mmol) in THF (12 mL), prepared under dinitrogen at 293 K, was added 0.309 g of $[(PhCH_2)HN=CMe_2]BPh_4$ (0.660 mmol) dissolved in THF (5 mL). Upon mixing of the reactants, the solution fast turned from purple-red to dark and, then, to yellowish brown. After it was stirred at room temperature for 5 h, the reaction solution was concentrated, added with diethyl ether, and cooled to 253 K.

The separated solid was filtered, washed with diethyl ether (2×10 mL), dried *in vacuo*, and then recrystallized from CH_2Cl_2 (8 mL)/diethyl ether (40 mL) at 253 K. The crystals that precipitated were isolated by filtration, washed with diethyl ether, dried *in vacuo*, and characterized as $[(H)Ni(PCy_3)_2(\eta^1(N)PhCH_2N=CMe_2)]BPh_4 \cdot CH_2Cl_2$. (0.520 g, 70%). One of these crystals was used for the X-ray characterization. Anal. Calcd for $C_{71}H_{102}NBPn_2Cl_2$: C, 72.76; H, 8.77; N, 1.19; Ni, 5.01; P, 5.29. Found: C, 73.10; H, 9.02; N, 1.15; Ni, 4.89; P, 4.93. IR (Nujol, KBr disks, cm^{-1}): 1980 (ν_{N-H} , m-w), 1638 ($\nu_{C=N}$, m), 1578 (m), 1477 (m), 1448 (m-s), 1425 (m), 1264 (m), 1174 (m), 1135 (m), 1030 (m), 1002 (m), 887 (m), 848 (m-s), 745 (m-s), 732 (s), 703 (s), 611 (m-s), 511 (m). 1H NMR (CD_2Cl_2 , 200 MHz, 293 K): δ -24.41 (t, 1 H, NiH, $J_{HP} = 76.73$ Hz), 1.1–1.9 (Cy protons), 2.13 (s, 3 H, Me), 2.79 (s, 3 H, Me), 4.99 ($PhCH_2$), 6.88 (t, 4 H, H_{para,BPh_4} , $J = 7$ Hz), 7.04 (t, 8 H, H_{meta,BPh_4} , $J = 7$ Hz), 7.11 ($PhCH_2$), 7.33 (m, 8 H, H_{ortho,BPh_4}), 7.41 ($PhCH_2$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2 , 125.76 MHz, 293 K): δ 22.01 (s, Me), 25.84 (s, C_{δ,PCy_3}), 27.12 (virtual t, C_{γ,PCy_3} and C_{γ',PCy_3} , $J = 5.09$ Hz), 29.72 and 29.83 (singlets, C_{β,PCy_3} and C_{β',PCy_3}), 32.90 (s, Me), 34.83 (virtual t, C_{α,PCy_3} , $J = 10.37$ Hz),

58.86 (s, $PhCH_2$), 121.37 (C_{para,BPh_4}), 125.28 (C_{meta,BPh_4}), 127.39 ($PhCH_2$), 128.21 ($PhCH_2$), 128.84 ($PhCH_2$), 133.98 ($C_{ipso,PhCH_2}$), 135.60 (C_{ortho,BPh_4}), 163.75 (q, C_{ipso,BPh_4} , $^1J_{CB} = 49.2$ Hz), 179.49 (s, $Me_2C=N$). ^{31}P NMR (CH_2Cl_2 , 81 MHz, 293 K): δ 28.64 (d, $J_{HP} = 76.53$ Hz).

X-ray Data Collection, Structure Determination, and Refinement for $[trans-(H)Ni(PCy_3)_2(\eta^1(N)PhCH_2N=CMe_2)]BPh_4 \cdot CH_2Cl_2$ (3**· CH_2Cl_2).** The crystals for the X-ray analysis were obtained by recrystallization from dichloromethane solutions. All crystals were of very small size; one of them, having dimensions $0.15 \times 0.18 \times 0.21$ mm, was used for data collection on a Siemens AED diffractometer at room temperature. Crystallographic data are summarized in Table 2. A total of 5554 unique reflections were measured with θ in the range 3–60°; only 1819 of them, having $I > 2\sigma(I)$, were used in the refinement. One standard reflection was monitored every 100 measurements; no significant decay was noticed over the time of data collection. Intensities were corrected for Lorentz and polarization effects. No correction for absorption was applied.

The structure was solved by Patterson and Fourier methods and refined first by full-matrix least-squares procedures with isotropic thermal parameters and then by full-matrix least-squares procedures with anisotropic thermal parameters in the last cycles of refinement for the non-hydrogen atoms, except for the carbons of the cyclohexyl groups. In the crystals dichloromethane molecules of solvation were found. The hydride was clearly localized in the final ΔF map and refined isotropically; all other hydrogen atoms were placed at their geometrically calculated positions ($C-H = 0.96$ Å) and refined "riding" on the corresponding carbon atoms, isotropically. Since the space group $P2_12_12_1$ leads to a chiral configuration in the structure, a refinement of the non-hydrogen atoms with anisotropic thermal parameters was carried out using the coordinates $-x, -y, -z$, an increasing in the R and R_w values was obtained ($R(x,y,z) = 0.0642$, $R_w(x,y,z) = 0.0761$; $R(-x, -y, -z) = 0.0666$, $R_w(-x, -y, -z) = 0.0790$). The former model was selected, and the reported data refer to this model. The final cycles of refinement were carried out on the basis of 407 variables; after the last cycles, no parameters shifted by more than 0.8 esd. The highest remaining peak in the final difference map was equivalent to about $0.27 e/\text{\AA}^3$. In the final cycles of refinement the weighting scheme $w = K[\sigma^2(F_o) + gF_o^2]^{-1}$ was used; at convergence the K and g values were 0.733 and 0.003. Final R and R_w values were 0.0642 and 0.0761, respectively. The analytical scattering factors, corrected for the real and imaginary parts of anomalous dispersion, were taken from ref 40. All calculations were carried out on the Gould Powernode 6040 and Encore 91 computers of the "Centro di Studio per la Strutturistica Diffraattometrica" del CNR, Parma, Italy, using the SHELX-76 and SHELXS-86 systems of crystallographic computer programs.⁴¹

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Supporting Information Available: Tables of final values of atomic coordinates for the non-hydrogen atoms, calculated coordinates and isotropic thermal parameters for the hydrogen atoms, anisotropic thermal parameters for some of the non-hydrogen atoms, and all bond distances and angles for **3** (7 pages). Ordering information is given on any current masthead page.

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