Inorg. Chem. **2008**, *47*, 749–758

Nickel(II) Complexes Containing Bidentate Amido Phosphine Ligands Derived from α-Iminophosphorus Ylides: Synthesis and Structural Characterization

Pei-Ying Lee and Lan-Chang Liang*

Department of Chemistry and Center for Nanoscience and Nanotechnology, National Sun Yat-sen University, Kaohsiung 80424, Taiwan

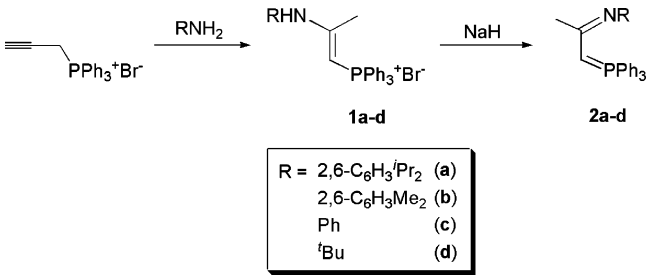
Received September 17, 2007

The reactions of prop-2-ynyltriphenylphosphonium bromide with a series of primary aromatic or aliphatic amines in refluxing acetonitrile generated the corresponding 2-hydrocarbylaminoprop-1-enyltriphenylphosphonium bromide $[RNHC(Me)=CHPPh_3]^+Br^-$ (R = 2,6-$C_6H_3{}^iPr_2$ (**1a**), 2,6-$C_6H_3Me_2$ (**1b**), Ph (**1c**), *t*-Bu (**1d**)) as crystalline solids. Deprotonation of **1a**–**d** with NaH in THF at –35 °C afforded the α-iminophosphorus ylides $RN=C(Me)CH=PPh_3$ (**2a**–**d**) in high yield. Spectroscopic and crystallographic data of **2** suggest a strong intramolecular interaction between the imino nitrogen and the phosphorus atom. In contrast to N-arylated **2a**–**c**, the *N-tert*-butyl-derived **2d** is extremely moisture-sensitive. Hydrolysis of **2d** led to elimination of benzene and generated concomitantly the phosphine oxide **3d** that contains an ene-amine functionality. The reactions of **2a**–**c** with $Ni(COD)_2$ in the presence of an excess amount of pyridine in toluene produced the divalent nickel complexes of the type [κ^2-$RNC(Me)=CHPPh_2$]-Ni(Ph)(Py) (**4a**–**c**). The solution and solid-state structures of these new compounds are presented.

Introduction

Functionalized phosphorus ylides are appealing as they facilitate the preparation of not only functionalized olefinic molecules but also coordination and organometallic complexes that may serve as catalytic initiators for specific chemical transformations.[1−6] One remarkable precedent in this regard is the nickel(II)-based catalysts for the Shell higher olefin process (SHOP) derived from α-ketophosphorus ylides $Ph_3P=CRC(O)R'$.[7,8] It has been shown that the oxidative addition of zero-valent nickel species such as $Ni(COD)_2$ (COD = cycloocta-1,5-diene) with $Ph_3P=CRC(O)R'$ in the presence of a two-electron donor (L; e.g., PPh_3) generated divalent nickel complexes $[Ph_2PCR=C(R')O]$-NiPh(L) that contain a monoanionic bidentate phosphine enolate ligand. Extensive research has subsequently been directed to the development of new SHOP-type catalysts by modifying the monoanionic bidentate ligands.[9] Representative examples reminiscent of that of $[Ph_2PCR=C(R')O]NiPh(L)$ include $[O-N]^-$,[10−19] $[N-N]^-$,[20−26] $[N-P]^-$,[27−33] and modified $[O-P]^-$,[34−43] etc.

Scheme 1



We are currently investigating the exploratory chemistry involving metal complexes of chelating amido phosphine ligands.[44−50] In particular, a series of nickel(II) alkyl complexes supported by bidentate diarylamido phosphine ligands have been synthesized and structurally characterized.[51] The incorporation of the rigid and robust *o*-phenylene backbone in the ligand design is beneficial in view of the

* To whom correspondence should be addressed. E-mail: lcliang@mail.nsysu.edu.tw. Fax: +886-7-5253908.

(1) Johnson, A. W. *Ylides and Imines of Phosphorus*; John Wiley: New York, 1993.
(2) Schmidbaur, H. *Acc. Chem. Res.* **1975**, *8*, 62−70.
(3) Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 907−927.
(4) Kaska, W. C. *Coord. Chem. Rev.* **1983**, *48*, 1−58.
(5) Belluco, U.; Michelin, R. A.; Mozzon, M.; Bertani, R.; Facchin, G.; Zanotto, L.; Pandolfo, L. *J. Organomet. Chem.* **1998**, *557*, 37−68.
(6) Serrano, E.; Valles, C.; Carbo, J. J.; Lledos, A.; Soler, T.; Navarro, R.; Urriolabeitia, E. P. *Organometallics* **2006**, *25*, 4653−4664.
(7) Keim, W.; Kowaldt, F. H.; Goddard, R.; Kruger, C. *Angew. Chem., Int. Ed.* **1978**, *17*, 466−467.
(8) Keim, W. *Angew. Chem., Int. Ed.* **1990**, *29*, 235−244.

10.1021/ic701836j CCC: $40.75
Published on Web 12/15/2007

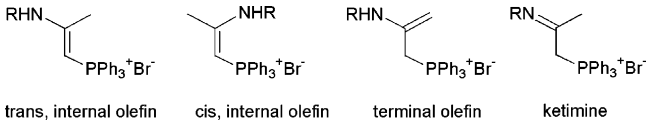
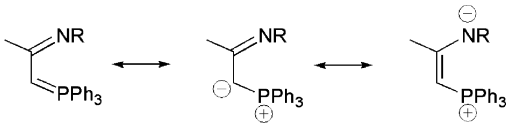


Figure 1. Possible isomeric structures of 2-aminoprop-1-enyltriphenylphosphonium bromide (**1a**−**d**).

enhanced thermal stability of the derived metal complexes.[52−55] In an effort to expand the territory of amido phosphine chemistry and our general interests in metal-mediated chemical transformations, we aim to prepare transition metal complexes that contain an olefinic linkage to connect the amido nitrogen and the phosphorus donors. The sp^2-hybridized olefinic carbon atoms should in principle offer the rigidity similar to that of the *o*-phenylene counterparts. Our strategy to prepare such complexes of divalent nickel involves oxidative addition of $Ni(COD)_2$ with α-iminophosphorus ylides, in analogy with that of the established SHOP catalysts. To this end, we have set out to prepare a series of N-substituted α-iminophosphorus ylides and explore their subsequent reactivity with $Ni(COD)_2$. Remarkably, the spectroscopic and crystallographic data of these functionalized phosphorus ylides are all indicative of a strong intramolecular, noncovalent interaction between the imino nitrogen and the phosphorus atom. In this Article, we describe the preparation and structural characterization of these α-iminophosphorus ylides and the divalent nickel complexes derived thereafter. Spectroscopic data and molecular structures of these compounds are discussed.

Scheme 2



2a-d

Results and Discussion

Preparation and Characterization of N-Substituted α-Iminophosphorus Ylides. Scheme 1 summarizes the synthetic protocol. The starting material prop-2-ynyltriphenylphosphonium bromide was readily prepared following the literature procedures from the reaction of triphenylphosphine with propargyl bromide in the presence of aqueous hydrobromic acid in 1,4-dioxane at room temperature.[56,57] Subsequent reactions with a number of primary aromatic or aliphatic amines in refluxing acetonitrile generated high yield of the corresponding 2-hydrocarbylaminoprop-1-enyltriphenylphosphonium bromide $[RNHC(Me)=CHPPh_3]^+Br^-$ (R = 2,6-$C_6H_3{}^iPr_2$ (**1a**), 2,6-$C_6H_3Me_2$ (**1b**), Ph (**1c**), *t*-Bu (**1d**)) as crystalline solids. The hydroamination reactions are highly

(9) Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169−1203.
(10) Younkin, T. R.; Connor, E. F.; Henderson, J. I.; Friedrich, S. K.; Brubbs, R. H.; Bansleben, D. A. *Science* **2000**, *287*, 460−462.
(11) Wang, C.; Friedrich, S.; Younkin, T. R.; Li, R. T.; Grubbs, R. H.; Bansleben, D. A.; Day, M. W. *Organometallics* **1998**, *17*, 3149−3151.
(12) Hicks, F. A.; Brookhart, M. *Organometallics* **2001**, *20*, 3217−3219.
(13) Hicks, F. A.; Jenkins, J. C.; Brookhart, M. *Organometallics* **2003**, *22*, 3533−3545.
(14) Jenkins, J. C.; Brookhart, M. *Organometallics* **2003**, *22*, 250−256.
(15) Bauers, F. M.; Mecking, S. *Angew. Chem., Int. Ed.* **2001**, *40*, 3020−3022.
(16) Zhang, D.; Jin, G.-X. *Organometallics* **2003**, *22*, 2851−2854.
(17) Shim, C. B.; Kim, Y. H.; Lee, B. Y.; Dong, Y.; Yun, H. *Organometallics* **2003**, *22*, 4272−4280.
(18) Sun, W.-H.; Yang, H.; Li, Z.; Li, Y. *Organometallics* **2003**, *22*, 3678−3683.
(19) Rojas, R. S.; Wasilke, J.-C.; Wu, G.; Ziller, J. W.; Bazan, G. C. *Organometallics* **2005**, *24*, 5644−5653.
(20) Domhover, B.; Klaui, W.; Kermer-Aach, A.; Bell, R.; Mootz, D. *Angew. Chem., Int. Ed.* **1998**, *37*, 3050−3052.
(21) Kogut, E.; Zeller, A.; Warren, T. H.; Strassner, T. *J. Am. Chem. Soc.* **2004**, *126*, 11984−11994.
(22) Bellabara, R. M.; Gomes, P. T.; Pascu, S. I. *J. Chem. Soc., Dalton Trans.* **2003**, 4431−4436.
(23) Lee, B. Y.; Bazan, G. C.; Vela, J.; Komon, Z. J. A.; Bu, X. *J. Am. Chem. Soc.* **2001**, *123*, 5352−5353.
(24) Lee, B. Y.; Bu, X.; Banzan, G. C. *Organometallics* **2001**, *20*, 5425−5431.
(25) Kim, Y. H.; Kim, T. H.; Lee, B. Y.; Woodmansee, D.; Bu, X.; Bazan, G. C. *Organometallics* **2002**, *21*, 3082−3084.
(26) Diamanti, S. J.; Ghosh, P.; Shimizu, F.; Bazan, G. C. *Macromolecules* **2003**, *36*, 9731−9735.
(27) Ansell, C. W. G.; Cooper, M. K.; Duckworth, P. A.; McPartlin, M.; Tasker, P. A. *Inorg. Chim. Acta* **1983**, *76*, L135.
(28) Rachita, M. J.; Huff, R. L.; Bennett, J. L.; Brookhart, M. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 4627−4640.
(29) Braunstein, P.; Pietsch, J.; Chauvin, Y.; Mercier, S.; Saussine, L.; DeCian, A.; Fischer, J. *J. Chem. Soc., Dalton Trans.* **1996**, 3571−3574.
(30) Braunstein, P.; Pietsch, J.; Chauvin, Y.; Decian, A.; Fischer, J. *J. Organomet. Chem.* **1997**, *529*, 387−393.
(31) Pietsch, J.; Braunstein, P.; Chauvin, Y. *New J. Chem.* **1998**, 467−472.
(32) Guan, Z.; Marshall, W. J. *Organometallics* **2002**, *21*, 3580−3586.
(33) Keim, W.; Killat, S.; Nobile, C. F.; Suranna, G. P.; Englert, U.; Wang, R.; Mecking, S.; Schroder, D. L. *J. Organomet. Chem.* **2002**, *662*, 150−171.
(34) Miiller, U.; Keim, W.; Kriiger, C.; Betz, P. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1011−1013.
(35) Fryzuk, M. D.; Gao, X.; Rettig, S. J. *Can. J. Chem.* **1995**, *73*, 1175−1180.
(36) Komon, Z. J. A.; Bu, X.; Bazan, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 12379−12380.
(37) Komon, Z. J. A.; Bu, X.; Bazan, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 1830−1831.
(38) Komon, Z. J. A.; Bazan, G. C.; Fang, C.; Bu, X. *Inorg. Chim. Acta* **2003**, *345*, 95−102.
(39) Soula, R.; Broyer, J. P.; Llauro, M. F.; Tomov, A.; Spitz, R.; Claverie, J.; Drujon, X.; Malinge, J.; Saudemont, T. *Macromolecules* **2001**, *34*, 2438−2442.
(40) Kalamarides, H. A.; Iyer, S.; Lipian, J.; Rhodes, L. F. *Organometallics* **2000**, *19*, 3983−3990.
(41) Doherty, M. D.; Trudeau, S.; White, P. S.; Morken, J. P.; Brookhart, M. *Organometallics* **2007**, *26*, 1261−1269.
(42) Braunstein, P. *Chem. Rev.* **2006**, *106*, 134−159.
(43) Braunstein, P.; Chauvin, Y.; Mercier, S.; Saussine, L. *C. R. Chim.* **2005**, *8*, 31−38.
(44) Liang, L.-C. *Coord. Chem. Rev.* **2006**, *250*, 1152−1177.
(45) Liang, L.-C.; Lee, W.-Y.; Hung, C.-H. *Inorg. Chem.* **2003**, *42*, 5471−5473.
(46) Liang, L.-C.; Chien, P.-S.; Huang, Y.-L. *J. Am. Chem. Soc.* **2006**, *128*, 15562−15563.
(47) Liang, L.-C.; Lin, J.-M.; Lee, W.-Y. *Chem. Commun.* **2005**, 2462−2464.
(48) Lee, W.-Y.; Liang, L.-C. *Dalton Trans.* **2005**, 1952−1956.
(49) Chien, P.-S.; Liang, L.-C. *Inorg. Chem.* **2005**, *44*, 5147−5151.
(50) Liang, L.-C.; Huang, M.-H.; Hung, C.-H. *Inorg. Chem.* **2004**, *43*, 2166−2174.
(51) Liang, L.-C.; Lee, W.-Y.; Yin, C.-C. *Organometallics* **2004**, *23*, 3538−3547.
(52) Huang, M.-H.; Liang, L.-C. *Organometallics* **2004**, *23*, 2813−2816.
(53) Liang, L.-C.; Chien, P.-S.; Huang, M.-H. *Organometallics* **2005**, *24*, 353−357.
(54) Liang, L.-C.; Chien, P.-S.; Lin, J.-M.; Huang, M.-H.; Huang, Y.-L.; Liao, J.-H. *Organometallics* **2006**, *25*, 1399−1411.
(55) Liang, L.-C.; Lin, J.-M.; Hung, C.-H. *Organometallics* **2003**, *22*, 3007−3009.
(56) Schweizer, E. E.; Goff, S. D.; Murray, W. P. *J. Org. Chem.* **1977**, *42*, 200−205.
(57) Schweizer, E. E.; Goff, S. D. *J. Org. Chem.* **1978**, *43*, 2972−2976.

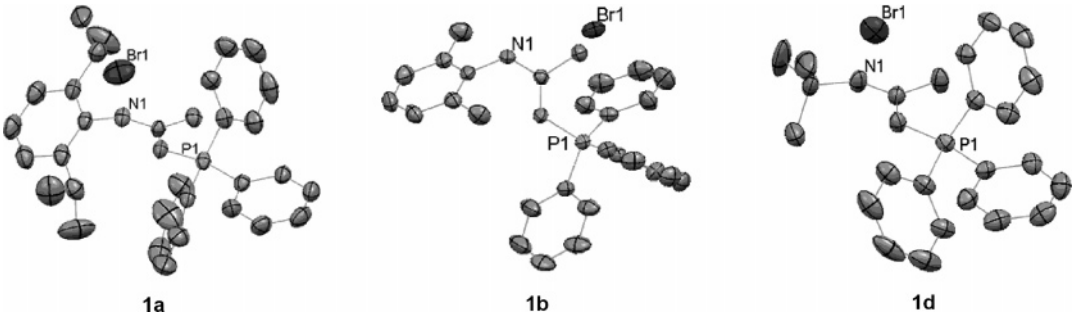


Figure 2. Molecular structures of **1a**, **1b**, and **1d** with thermal ellipsoids drawn at the 35% probability level. Selected bond distances and angles are listed in Supporting Information.

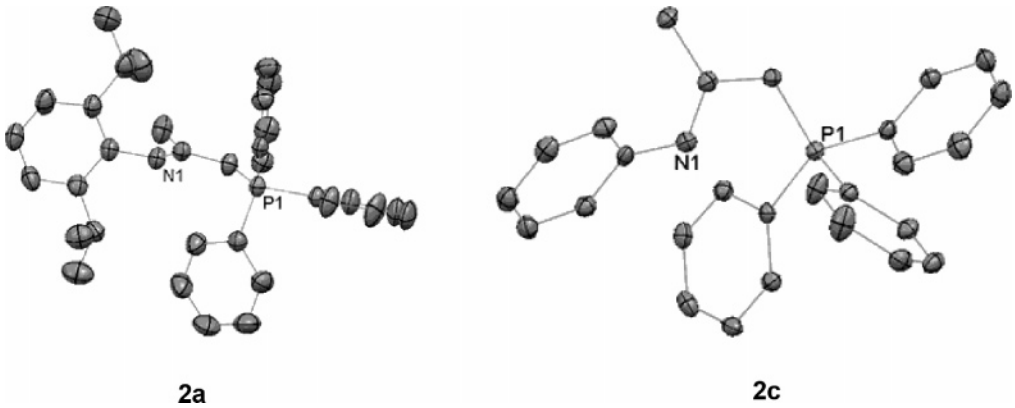


Figure 3. Molecular structures of **2a** and **2c** with thermal ellipsoids drawn at the 35% probability level. Selected bond distances and angles are listed in Supporting Information.

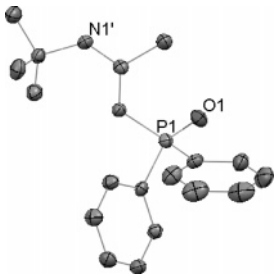
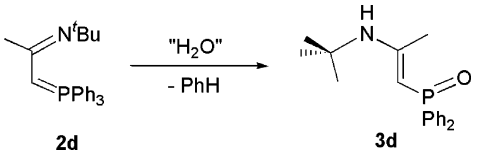


Figure 4. Molecular structure of ^{t}BuNHC(Me)=CHP(O)Ph$_2$ (**3d**) with thermal ellipsoids drawn at the 35% probability level. Selected bond distances and angles are listed in Supporting Information.

regioselective, leading to the exclusive formation of 2-amino-substituted derivatives. No other regioisomer was detected. The NMR spectroscopic data of **1a**−**d** are all indicative of the presence of an internal C=C moiety instead of an isomeric terminal olefin or ketimine functionality (Figure 1). The diagnostic olefinic hydrogen atom is observed in the ^{1}H NMR spectra of **1a**−**d** as a doublet resonance at ca. 3.5 ppm ($^2J_{HP}$ = 16 Hz) and the acidic NH proton at ca. 8−10 ppm ($^4J_{HP}$ = 4 Hz). The allylic CH_3 atoms appear as a singlet resonance at ca. 2.1 ppm. The ^{31}P{^{1}H} NMR spectra exhibit a singlet resonance at ca. 17 ppm for these molecules. The relatively low $^3J_{CP}$ of ca. 5 Hz observed in the ^{13}C{^{1}H} NMR spectra for the phosphorus atom and the allylic carbon is suggestive of a cis geometry for these nuclei with respect to the C=C bond, consistent with what would be anticipated for steric reasons. The ^{1}H and ^{13}C NMR spectroscopic data

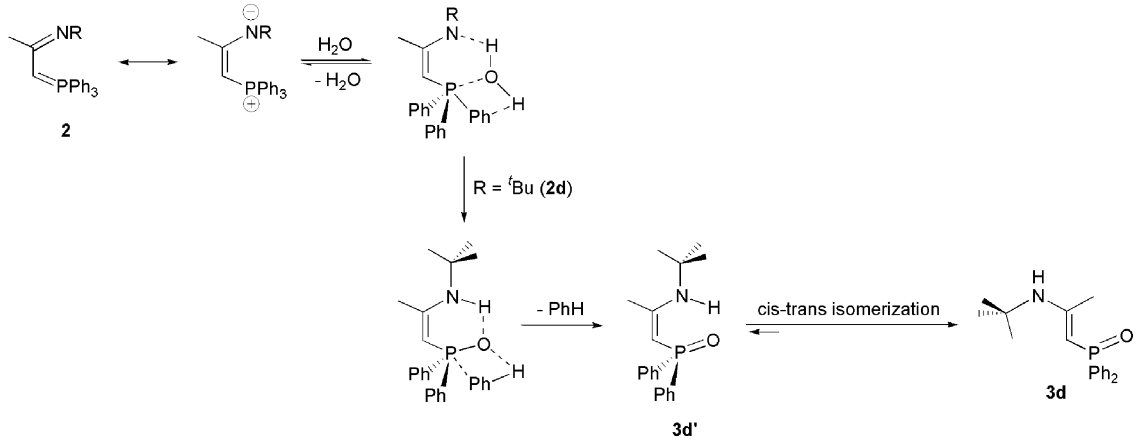
Scheme 3



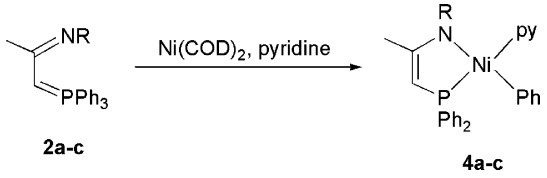
of **1a** and **1b** indicate that the *o*-alkyl groups are chemically equivalent. The isopropylmethyl groups in **1a** are observed as two doublet resonances in the ^{1}H NMR spectrum. The solid-state structures of **1a**, **1b**, and **1d** were also confirmed by X-ray diffraction studies, which revealed a trans geometry for the two hetero substituents in these internal olefins (Figure 2), consistent with that deduced from the solution NMR spectroscopic data. Though not observed spectroscopically, the terminal olefinic isomer (Figure 1) is presumably the kinetic product that subsequently transforms into internal **1a**−**d** thermodynamically.

Deprotonation of **1a**−**d** with NaH in THF at −35 °C produce the desired α-iminophosphorus ylides **2a**−**d**. The ^{1}H NMR spectra of these molecules reveal a doublet resonance at ca. 3.0 ppm for the characteristic ylidic proton CH=PPh$_3$ with $^2J_{HP}$ of ca. 26 Hz, a coupling constant that is notably larger than those corresponding to the olefinic methine moiety in **1a**−**d**. The ^{31}P chemical shifts of ca. 13 ppm found for **2a**−**d** are relatively upfield as compared to those of **1a**−**d**. Interestingly, the $^3J_{CP}$ coupling constants of ca. 16 Hz between the phosphorus atom and the methyl carbon α to the imino group are significantly large as

Scheme 4



Scheme 5



compared to the corresponding values in **1a**−**d** (vide supra), suggesting that these two nuclei are positioned mutually trans in a cisoid heterobutadiene molecule. As a result, the two sterically demanding hetero substituents in **2a**−**d** are mutually cis. Such geometry is apparently unusual in view of the steric hindrance imposed by these bulky substituents but likely indicative of a strong 1,4-intramolecular, noncovalent interaction between the imino nitrogen and the phosphorus atom due to the zwitterionic nature arising from the delocalization of π electrons in these heterobutadiene molecules as illustrated in Scheme 2. The discrepancy in the geometric preferences found for **2a**−**d** and **1a**−**d**, respectively, highlights particularly the presence of such intramolecular interaction in the former. The absence of the 1,4-N···P interaction in **1a**−**d** is presumably ascribed to the relatively insufficient electronegative nature of the amine nitrogen atom as compared to that of imine and the profound electrostatic interaction of the cationic phosphorus atom with the anionic bromide rather than the neutral amine. Similar to what has been observed for **1a**, the two isopropyl substituents of the *N*-aryl ring in **2a** are chemically equivalent and the isopropylmethyl groups are observed as two doublet resonances in the ^{1}H NMR spectrum.

The solid-state structures of **2a** and **2c** were established by X-ray diffraction analysis. As depicted in Figure 3, the imino and the phosphorus ylidic functionalities are mutually cis with respect to the $C_{sp2}-C_{sp2}$ bond, consistent with the result derived from the solution NMR studies. The $C_{sp2}-C_{sp2}$ distances of **2a** (1.412(4) Å) and **2c** (1.418(4) Å) are relatively shorter than the typical value of 1.478 Å for a $C_{sp2}-C_{sp2}$ single bond,[58] but comparatively longer than the corresponding distances of **1** (ca. 1.36 Å) and a typical $C_{sp2}=C_{sp2}$ double bond distance (1.34 Å).[59] The C−N distances of **2** (ca. 1.30 Å) are slightly shorter than those of **1** (ca. 1.34 Å), so are the C−P lengths (**2**, ca. 1.70 Å; **1**, ca. 1.74 Å). These results are consistent with what we formulate in Scheme 2, in which the π electrons delocalize throughout the heterobutadiene backbone. Consistently, the $N-C_{sp2}-C_{sp2}-P$ atoms are nearly coplanar as evidenced by the mean deviation value of 0.0115 Å for **2a** and 0.0069 Å for **2c**. Notably, the N−P distances of 3.013 Å for **2a** and 2.832 Å for **2c** are smaller than the sum of the van der Waals radius of N and P of 3.40 Å,[60] indicating a noncovalent interaction between the two heteroatoms. Similar observation has also been reported for α-carbonyl-functionalized phosphorus ylides[61] and an ester-functionalized iminophosphorus ylide.[62] Consistent with the steric hindrance of the N-substituents, the $N-C_{sp2}-C_{sp2}$ and $C_{sp2}-C_{sp2}-P$ bond angles of **2a** are both wider than those of **2c** by ca. 4°, and the N−P distance of the former is longer than that of the latter. The *N*-aryl ring of **2a** is approximately perpendicular to the $N-C_{sp2}-C_{sp2}-P$ mean plane with the dihedral angle of 89.6°; however, that of **2c** is tilted with respect to the $N-C_{sp2}-C_{sp2}-P$ mean plane with the dihedral angle of 52.9° due likely to the absence of sterically demanding *o*-alkyl substituents.

Unlike **2a**−**c**, the *N*-*tert*-butyl-derived **2d** is viscous oil and tends to be more sensitive to moisture. Attempts to crystallize this compound from a variety of solvents were not successful. Instead, it reacts with the trace amount of moisture present in the solvents employed for crystallization to produce in low yield a crystalline solid **3d** that is characteristic of an ene-amine-functionalized phosphine oxide (Scheme 3). The ^{31}P{^{1}H} NMR spectrum of this molecule exhibits a singlet resonance at 21.4 ppm, a value that is shifted relatively downfield from those of **1d** and **2d**. The ^{1}H NMR spectrum displays a doublet resonance at 4.66 ppm with $^2J_{HP}$ of 19 Hz for the olefinic proton and a broad singlet resonance at 5.37 ppm for NH. The relatively low inter-

(58) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, *685*, S1−S19.
(59) Zumdahl, S. S. *Chemical Principles*, 5th ed.; Houghton Mifflin Company, 2006.
(60) Bondi, A. *J. Chem. Phys.* **1964**, *68*, 441.
(61) Lledos, A.; Carbo, J. J.; Urriolabeitia, E. P. *Inorg. Chem.* **2001**, *40*, 4913−4917.
(62) Falvello, L. R.; Gines, J. C.; Carbo, J. J.; Lledos, A.; Navarro, R.; Soler, T.; Urriolabeitia, E. P. *Inorg. Chem.* **2006**, *45*, 6803−6815.

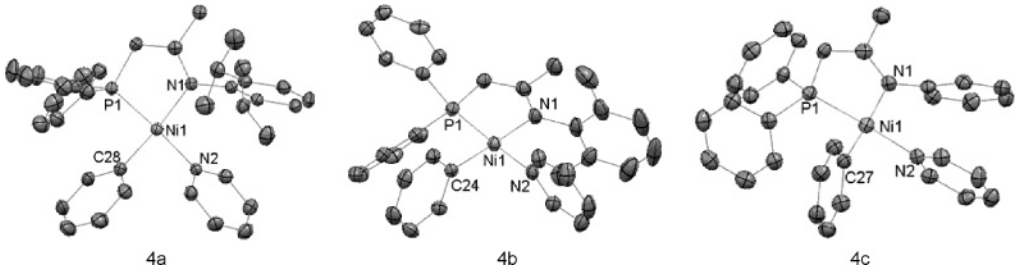


Figure 5. Molecular structures of **4a**, **4b**, and **4c** with thermal ellipsoids drawn at the 35% probability level. Selected bond distances and angles are listed in Supporting Information.

nuclear coupling constant of 7 Hz between the phosphorus atom and the allylic carbon atom is suggestive of a cis geometry for these two nuclei with respect to the C═C bond in this molecule, reminiscent of what has been observed for **1d** rather than **2d**. The amino group is thus trans to the phosphine oxide functionality in this olefinic molecule. Consistent with this result, an X-ray diffraction study of **3d** (Figure 4) also verified the trans relationship between the *N*-*tert*-butyl group and the O═PPh_2 moiety. The C═C bond distance of 1.371 (5) Å in **3d** is similar to those found for **1a**, **1b**, and **1d**. With the presence of both NH and O═PPh_2 functionalities, intermolecular hydrogen bonding is found in the lattice of **3d**.

Scheme 4 illustrates a plausible mechanism for the transformation of **2d** to **3d**. With the zwitterionic characteristic, the α-iminophosphorus ylides **2** should be prone to association with a water molecule as a result of intermolecular dipole−dipole interaction. The water adduct thus formed, though in low concentration due to the limited availability of moisture present in the solvents employed, is presumably in equilibrium with the α-iminophosphorus ylides **2**. In contrast to the N-arylated **2a**−**c**, the *N*-*tert*-butyl-derived **2d** is nucleophilic/basic enough to react irreversibly with water as a consequence of the enhanced electron-releasing nature of the *N*-*tert*-butyl group in the latter. A concerted process is presumably involved in the water adduct of **2d** for the cleavage of P−Ph and O−H bonds as well as the formation of N−H, P═O, and Ph−H bonds, leading to the concomitant generation of a benzene molecule and the presumed kinetic product **3d′**, which subsequently isomerizes to the thermodynamically more favorable **3d** for steric reasons. The identity of the liberated benzene was confirmed by GC, and the yield (relative to *m*-xylene as an internal standard) was virtually equivalent to the (sub)stoichiometry of the water added in controlled experiments. Perhaps phenomenal in this process is the water-mediated P−Ph bond activation under extremely mild conditions.[63,64]

Reactions of N-Substituted α-Iminophosphorus Ylides with Ni(COD)$_2$. In contrast to what has been reported for the SHOP catalysts derived from Ph_3P═CRC(O)R′,[7,8] attempts to prepare divalent nickel complexes from the reactions of **2** with Ni(COD)$_2$ in the presence of a number of phosphines such as PPh_3 or PMe_3 led to the formation of a complicated mixture, from which no desired product could be effectively purified. Similar results have also been reported for systems employing PhN═C(Ph)CH═PPh_3,[29] which led unexpectedly to the formation of the ylidic complex [κ^2-Ph_2-PCH═C(Ph)(NPh)]Ni(Ph)[PhN═C(Ph)CH═PPh_3] regardless of the identity of the Lewis base (e.g., PPh_3, PMe_3, pyridine, etc.) involved. Interestingly, addition of an excess amount of pyridine to a mixture of **2a**−**c** and Ni(COD)$_2$ in toluene effectively generated red crystals of the corresponding divalent nickel complexes [κ^2-RNC(Me)═CHPPh_2]Ni(Ph)-(Py) (**4a**−**c**) (Scheme 5). Though it seems not atypical in view of the established SHOP chemistry, the phenyl group transfer from the phosphorus atom in **2a**−**c** to nickel is somewhat analogous, at least in part, to that from **2d** to the acidic proton as illustrated in Scheme 4. No ylidic complex similar to [κ^2-Ph_2PCH═C(Ph)(NPh)]Ni(Ph)[PhN═C(Ph)-CH═PPh_3][29] was detected. Parallel experiments employing **2d**, however, gave intractable materials that could not be identified.

The $^{31}P\{^1H\}$ NMR spectra of **4a**−**c** exhibit a singlet resonance at ca. 31 ppm, which is relatively downfield shifted from those of the corresponding **1** and **2** but comparable to those of diarylamido phosphine complexes of nickel(II) such as [^{i}Pr−NP]NiPh(PMe_3) (33 ppm; [^{i}Pr−NP]$^-$ = *N*-(2-diphenylphosphinophenyl)-2,6-diisopropylanilide).[51] The olefinic proton of **4a**−**c** is observed as a doublet resonance at ca. 3.8 ppm with $^2J_{HP}$ of ca. 2 Hz. Consistent with the anticipated trans geometry of the allylic carbon with respect to the phosphorus donor, the $^3J_{CP}$ values of ca. 17 Hz for these molecules are considerably large and similar to those of the corresponding **2** rather than **1**. Analogous to those of **1a** and **2a**, the isopropyl groups in **4a** are chemically equivalent and the isopropylmethyl moieties are observed as two doublet resonances in the ^{1}H NMR spectrum.

Figure 5 illustrates the molecular structures of **4a**−**c**. As anticipated, the C_{sp2}−C_{sp2} distances of ca. 1.36 Å found in the backbone of **4a**−**c** are comparable to those of the corresponding **1** rather than **2**, so are the C−N and C−P bond lengths. The nickel center lies virtually on the square plane defined by the four donor atoms with the slight displacement of nickel from the mean coordination plane by 0.0262 Å for **4a**, 0.0206 Å for **4b**, and 0.0094 Å for **4c**. Reminiscent of that of the SHOP catalyst [Ph_2PCH═C(Ph)O]-Ni(Ph)(PPh_3),[7,8] the phenyl group is cis to the phosphorus donor with the P−Ni−C_{ipso} angles of 88.39(12)° (**4a**), 90.64-(14)° (**4b**), and 92.02(14)° (**4c**). The coordinated pyridine

(63) Marinetti, A.; Mathey, F. *Organometallics* **1984**, *3*, 456−461.
(64) Watson, W. H.; Wu, G.; Richmond, M. G. *Organometallics* **2006**, *25*, 930−945.

and the amido nitrogen donor in **3a**−**c** are thus mutually cis. The N_{amide}−Ni−P binding angles of ca. 85° are similar to those of the nickel derivatives featuring a five-membered metallacycle such as [^{i}Pr−NP]NiCl(PMe$_3$) (85.21(9)°),[51] [^{i}Pr−NP]NiMe(PMe$_3$) (85.0(1)°),[51] [^{i}Pr−NP]NiPh(PMe$_3$) (85.9(2)°),[51] [(*o*-Ph$_2$PC$_6$H$_4$NHMe)NiCl(PMe$_3$)]PF$_6$ (87.0(1)°),[65] and [Ph$_2$PCH═C(Ph)O]Ni(Ph)(PPh$_3$) (86.5°).[7] The Ni−N_{amide}, Ni−P, and Ni−Ph distances of **4a**−**c** are also comparable to the corresponding values found for nickel(II) complexes of [^{i}Pr−NP]$^-$.[51] In **4a**−**c**, the coordination plane coincides virtually with the backbone N−C_{sp2}−C_{sp2}−P plane with small dihedral angles of 3.0° (**4a**), 2.5° (**4b**), and 7.6° (**4c**). The *N*-aryl ring of **4b** is approximately perpendicular to the coordination plane (dihedral angle 93.1°), whereas those of **4a** and **4c** are tilted severely (dihedral angle 77.1° and 65.9°, respectively) from the ideal orthogonal geometry. As a result, the pyridine and phenyl ligands are also tilted accordingly with respect to the coordination plane in order to minimize the steric repulsion between these ligands.

Table 1. Crystallographic Data for **1a**, **1b**, **1d**, **2a**, **2c**, **3d**, **4a**, **4b**, and **4c**

compd	{[(2,6-^{i}Pr$_2$C$_6$H$_3$)NHC(Me)═CHPPh$_3$]$^+$Br$^-$}(CH$_2$Cl$_2$)(H$_2$O) (**1a**)	{[(2,6-Me$_2$C$_6$H$_3$)NHC(Me)═CHPPh$_3$]$^+$Br$^-$}(CH$_2$Cl$_2$) (**1b**)	[^{i}BuNHC(Me)═CHPPh$_3$]$^+$Br$^-$ (**1d**)
formula	$C_{34}H_{41}BrCl_2NOP$	$C_{30}H_{31}BrCl_2NP$	$(C_{25}H_{29}BrNP)_2(H_2O)$
fw	661.492	587.34	926.76
D_{calc} (g cm^{-3})	1.292	1.324	1.265
cryst syst	Triclinic	monoclinic	orthorhombic
space group	$P\bar{1}$	$C2/c$	$Pbca$
a (Å)	9.8565(3)	21.3127(4)	19.127(4)
b (Å)	11.3286(3)	10.0835(3)	13.562(3)
c (Å)	15.5802(5)	16.2680(3)	37.528(7)
α (deg)	79.602(1)	90	90
β (deg)	83.649(1)	122.569(2)	90
γ (deg)	88.124(2)	90	90
V (Å^3)	1700.47(9)	2946.3(1)	9735(3)
Z	2	4	8
T (K)	298	293(2)	293(2)
diffractometer	Kappa CCD	Kappa CCD	SMART CCD
radiation, λ (Å)	Mo Kα, 0.71073	Mo Kα, 0.71073	Mo Kα, 0.71073
$2\theta_{max}$ (deg)	50.10	50.06	52.14
total reflns	11881	9073	53108
independent reflns	5940	4345	9585
R_{int}	0.044	0.0375	0.0721
abs coeff (mm^{-1})	1.439	1.650	1.767
data/restraints/params	5940/0/361	4345/2/316	9585/0/522
GOF	2.232	1.118	0.872
final R indices [$I > 2\sigma(I)$]	R1 = 0.1146 wR2 = 0.3181	R1 = 0.0380 wR2 = 0.0962	R1 = 0.0526 wR2 = 0.1438
R indices (all data)	R1 = 0.1519 wR2 = 0.3463	R1 = 0.0448 wR2 = 0.1219	R1 = 0.1220 wR2 = 0.1676

compd	[(2,6-^{i}Pr$_2$C$_6$H$_3$)N═C(Me)CH═PPh$_3$] (**2a**)	PhN═C(Me)CH═PPh$_3$ (**2c**)	[^{i}BuNHC(Me)═CHP(O)Ph$_2$]$_2$(C$_6$H$_6$) (**3d**)
formula	$C_{33}H_{36}NP$	$C_{27}H_{24}NP$	$C_{44}H_{54}N_2O_2P_2$
fw	477.632	393.44	704.876
D_{calc} (g cm^{-3})	1.143	1.218	1.169
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a (Å)	9.7036(6)	14.7550(3)	11.3747(3)
b (Å)	15.480(1)	17.6120(4)	16.4104(4)
c (Å)	18.628(1)	17.5880(4)	21.9760(7)
α (deg)	90	90	90
β (deg)	97.413(2)	110.168(1)	102.379(1)
γ (deg)	90	90	90
V (Å^3)	2774.8(3)	4290.3(2)	4006.7(2)
Z	4	8	4
T (K)	298	100(2)	298
diffractometer	Kappa CCD	Kappa CCD	Kappa CCD
radiation, λ (Å)	Mo Kα, 0.71073	Mo Kα, 0.71073	Mo Kα, 0.71073
$2\theta_{max}$ (deg)	50.10	50.08	50.12
total reflns	13889	28392	33766
independent reflns	4849	7575	7078
R_{int}	0.0682	0.0923	0.075
abs coeff (mm^{-1})	0.120	0.141	0.146
data/restraints/params	4849/0/316	7575/0/523	7078/0/451
GOF	1.008	1.070	1.177
final R indices [$I > 2\sigma(I)$]	R1 = 0.0598 wR2 = 0.1481	R1 = 0.0580 wR2 = 0.1415	R1 = 0.0673 wR2 = 0.1597
R indices (all data)	R1 = 0.1223 wR2 = 0.1849	R1 = 0.0989 wR2 = 0.1693	R1 = 0.1298 wR2 = 0.2143

Table 1. Continued

compd	[(^{i}Pr$_2$C$_6$H$_3$)NC(Me)═CHPPh$_2$]NiPh(py) (**4a**)	[Me$_2$C$_6$H$_3$)NC(Me)═CHPPh$_2$]NiPh(py) (**4b**)	[PhNC(Me)═CHPPh$_2$]NiPh(py) (**4c**)
formula	$C_{38}H_{41}N_2NiP$	$C_{34}H_{33}N_2NiP$	$C_{32}H_{29}N_2NiP$
fw	615.41	576.35	531.25
D_{calc} (g cm^{-3})	1.266	1.281	1.321
cryst syst	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$	$P2_1/n$
a (Å)	9.5170(2)	9.1790(2)	10.2380(4)
b (Å)	12.1780(2)	14.1900(3)	9.7480(5)
c (Å)	15.0260(4)	23.1820(6)	26.779(1)
α (deg)	70.647(1)	90	90
β (deg)	84.281(1)	98.271(1)	91.737(2)
γ (deg)	79.506(1)	90	90
V (Å^3)	1614.15(6)	2988.1(1)	2671.3(2)
Z	2	4	4
T (K)	200(2)	200(2)	200(2)
diffractometer	Kappa CCD	Kappa CCD	Kappa CCD
radiation, λ (Å)	Mo Kα, 0.71073	Mo Kα, 0.71073	Mo Kα, 0.71073
$2\theta_{max}$ (deg)	50.00	50.00	50.06
total reflns	21802	20834	13566
independent reflns	5646	5250	4291
R_{int}	0.0925	0.0924	0.0828
abs coeff (mm^{-1})	0.679	0.729	0.809
data/restraints/params	5646/0/380	5250/0/344	4291/0/325
GOF	1.070	1.144	1.057
final R indices [$I > 2\sigma(I)$]	R1 = 0.0554 wR2 = 0.1196	R1 = 0.0690 wR2 = 0.1481	R1 = 0.0617 wR2 = 0.1372
R indices (all data)	R1 = 0.0962 wR2 = 0.1450	R1 = 0.1270 wR2 = 0.1960	R1 = 0.1099 wR2 = 0.1619

Conclusions

In summary, we have prepared and characterized a series of N-arylated and N-alkylated α-iminophosphorus ylides **2a**−**d** and studied the reactivity of these molecules with Ni(COD)$_2$. Interestingly, a strong 1,4-intramolecular, noncovalent interaction is found for these α-iminophosphorus ylides as evidenced by solution NMR spectroscopic and solid-state X-ray crystallographic studies. Unexpectedly, the *N-tert*-butyl-derived **2d** reacts with water to generate an eneamine-functionalized phosphine oxide **3d**, a transformation that presumably involves concomitant bond cleavage of P−Ph and O−H and bond formation of N−H, P═O, and Ph−H. The P−Ph bond activation mediated by water under extremely mild conditions is intriguing.[63,64] Upon reactions with Ni(COD)$_2$ in the presence of pyridine, the N-arylated α-iminophosphorus ylides **2a**−**c** are transformed to bidentate amido phosphine ligands in which the two donor atoms are connected by an olefinic backbone. The nickel-bound phenyl group in **4a**−**c** is cis to the phosphorus donor as verified by X-ray crystallography.

Experimental Section

General Procedures. Unless otherwise specified, all experiments were performed under nitrogen using standard Schlenk or glovebox techniques. All solvents were reagent grade or better and purified by standard methods. The NMR spectra were recorded on Varian Unity or Bruker AV instruments. Chemical shifts (δ) are listed as parts per million downfield from tetramethylsilane, and coupling constants (J) are in hertz. ^{1}H NMR spectra are referenced using the residual solvent peak at δ 7.16 for C_6D_6 and δ 7.27 for $CDCl_3$. ^{13}C NMR spectra are referenced using the residual solvent peak at δ 128.39 for C_6D_6, and δ 77.23 for $CDCl_3$. The assignment of the carbon atoms is based on the DEPT ^{13}C NMR spectroscopy. ^{31}P NMR spectra are referenced externally using 85% H_3PO_4 at δ 0. Routine coupling constants are not listed. All NMR spectra were recorded at room temperature in specified solvents unless otherwise noted. Elemental analysis was performed on a Heraeus CHN−O Rapid analyzer.

Materials. Compound prop-2-ynyltriphenylphosphonium bromide[56,57] was prepared according to the literature procedures. All other chemicals were obtained from commercial vendors and used as received.

X-ray Crystallography. Table 1 summarizes the crystallographic data for **1a**, **1b**, **1d**, **2a**, **2c**, **3d**, **4a**, **4b**, and **4c**. Data were collected on a Bruker-Nonius Kappa CCD diffractometer or a SMART CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.7107 Å). Structures were solved by direct methods and refined by full-matrix least-squares procedures against F^2 using WinGX crystallographic software package or SHELXL-97. All full-weight non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions.

Synthesis of 2-(2,6-Diisopropylanilino)-prop-1-enyltriphenylphosphonium Bromide (1a). A solution of 2,6-dimethylaniline (505 mg, 2.62 mmol) in acetonitrile (10 mL) was added via a syringe to a Schlenk flask containing solid prop-2-ynyltriphenylphosphonium bromide (1.0 g, 2.62 mmol) under nitrogen. The reaction solution was stirred and heated to reflux overnight. After being cooled to room temperature, the solution was evaporated to dryness under reduced pressure. The solid thus obtained was dissolved in a minimal amount of CH_2Cl_2 (15 mL), and ethyl acetate (10 mL) was added. The solution was stirred at room temperature for 30 min, resulting in the formation of white precipitate, which was collected on a frit by filtration and dried in vacuo; yield 1.26 g (86%). Colorless crystals suitable for X-ray diffraction analysis were grown from a concentrated CH_2Cl_2 solution at room temperature; yield 1.16 g (79%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 10.16 (br d, 1, J_{HP} = 4 Hz, NH), 7.69 (t, 3, Ar), 7.57 (m, 6, Ar), 7.45 (m,

(65) Crociani, L.; Tisato, F.; Refosco, F.; Bandoli, G.; Corain, B. *Eur. J. Inorg. Chem.* **1998**, 1689−1697.

6, Ar), 7.25 (t, 1, Ar), 7.15 (d, 2, Ar), 3.41 (d, 1, $^2J_{HP}$ = 16 Hz, MeC=C*H*), 3.24 (septet, 2, C*H*Me$_2$), 2.16 (s, 3, *Me*C=CH), 1.25 (d, 6, J_{HH} = 7 Hz, CH*Me*$_2$), 1.16 (d, 6, J_{HH} = 7 Hz, CH*Me*$_2$). ^{31}P{^{1}H} NMR (CDCl$_3$, 202.31 MHz) δ 17.10. ^{13}C{^{1}H} NMR (CDCl$_3$, 125.5 MHz) δ 167.63 (d, $^2J_{CP}$ = 15.44 Hz, Me*C*=CH), 146.40 (s, ortho-NAr), 133.90 (d, $^4J_{CP}$ = 2.76 Hz, para-P*C*$_6$H$_5$), 132.62 (d, $^3J_{CP}$ = 9.92 Hz, meta-P*C*$_6$H$_5$), 129.95 (d, $^2J_{CP}$ = 12.68 Hz, ortho-P*C*$_6$H$_5$), 128.63 (s, para-NAr), 123.94 (s, meta-NAr), 123.34 (d, $^1J_{CP}$ = 91.62, ipso-P*C*$_6$H$_5$), 56.62 (d, $^1J_{CP}$ = 121.36 Hz, MeC=*C*H), 28.56 (s, *C*HMe$_2$), 24.73 (s, CH*Me*$_2$), 23.81 (s, CH*Me*$_2$), 21.66 (d, $^3J_{CP}$ = 5.40 Hz, *Me*C=CH). Anal. Calcd for C$_{33}$H$_{37}$BrNP: C, 70.96; H, 6.68; N, 2.51. Found: C, 70.63; H, 6.68; N, 2.57.

Synthesis of 2-(2,6-Dimethylanilino)-prop-1-enyltriphenylphosphonium Bromide (1b). A solution of 2,6-dimethylaniline (318 mg, 2.62 mmol) in acetonitrile (10 mL) was added via a syringe to a Schlenk flask containing solid prop-2-ynyltriphenylphosphonium bromide (1.0 g, 2.62 mmol) under nitrogen. The reaction solution was stirred and heated to reflux overnight. After being cooled to room temperature, the solution was evaporated to dryness under reduced pressure. The solid thus obtained was dissolved in a minimal amount of CH_2Cl_2 (10 mL), and ethyl acetate (15 mL) was added. The solution was stirred at room temperature for 30 min, resulting in the formation of white precipitate, which was collected on a frit by filtration and dried in vacuo; yield 1.087 g (83%). Colorless crystals suitable for X-ray diffraction analysis were grown by slow evaporation of a concentrated CH_2Cl_2 solution at room temperature; yield 1.054 g (80%). ^{1}H NMR (CDCl$_3$, 500 MHz) δ 10.26 (br d, 1, J_{HP} = 4.0 Hz, NH), 7.70 (t, 3, Ar), 7.59 (m, 6, Ar), 7.50 (m, 6, Ar), 7.08 (m, 3, Ar), 3.47 (d, 1, $^2J_{PH}$ = 16.5 Hz, MeC=C*H*), 2.39 (s, 6, ArC*H*$_3$), 2.20 (s, 3, *Me*C=CH). ^{31}P{^{1}H} NMR (CDCl$_3$, 202.31 MHz) δ 17.23. ^{13}C{^{1}H} NMR (CDCl$_3$, 125.5 MHz) δ 166.27 (d, $^2J_{CP}$ = 15.44 Hz, Me*C*=CH), 135.96 (s, ortho-NAr), 135.23 (s, ipso-NAr), 133.89 (s, para-P*C*$_6$H$_5$), 132.76 (d, $^3J_{CP}$ = 9.92, meta-P*C*$_6$H$_5$), 129.99 (d, $^2J_{CP}$ = 12.68, ortho-P*C*$_6$H$_5$), 128.51 (s, meta-NAr), 127.80 (s, para-NAr), 123.61 (d, $^1J_{CP}$ = 91.62, ipso-P*C*$_6$H$_5$), 55.24 (d, $^1J_{CP}$ = 122.36 Hz, MeC=*C*H), 21.86 (d, $^3J_{CP}$ = 4.52 Hz, *Me*C=CH), 18.61 (s, Ar*Me*). Anal. Calcd for C$_{29}$H$_{29}$BrNP: C, 69.33; H, 5.82; N, 2.79. Found: C, 69.02; H, 5.84; N, 2.74.

Synthesis of 2-Anilinoprop-1-enyltriphenylphosphonium Bromide (1c). A solution of aniline (244 mg, 2.62 mmol) in acetonitrile (10 mL) was added via a syringe to a Schlenk flask containing solid prop-2-ynyltriphenylphosphonium bromide (1.0 g, 2.62 mmol) under nitrogen. The reaction solution was stirred and heated to reflux overnight. After being cooled to room temperature, the solution was evaporated to dryness under reduced pressure. The solid thus obtained was dissolved in a minimal amount of CH_2Cl_2 (8 mL), and ethyl acetate (15 mL) was added. The solution was stirred at room temperature for 30 min, resulting in the formation of white precipitate, which was collected on a frit by filtration and dried in vacuo; yield 560 mg (90%). ^{1}H NMR (CDCl$_3$, 200 MHz) δ 10.36 (br s, 1, NH), 7.02−7.36 (m, 15, Ar), 6.77−6.98 (m, 5, Ar), 4.38 (d, 1, CH), 1.23 (s, 3, CH$_3$). ^{31}P{^{1}H} NMR (CDCl$_3$, 80.95 MHz) δ 17.32. The NMR spectroscopic data are identical to those reported previously.[56]

Synthesis of 2-(*tert*-Butylamino)-prop-1-enyltriphenylphosphonium Bromide (1d). A solution of *tert*-butylamine (0.28 mL, 2.62 mmol) in acetonitrile (10 mL) was added via a syringe to a Schlenk flask containing solid prop-2-ynyltriphenylphosphonium bromide (1.0 g, 2.62 mmol) under nitrogen. The reaction solution was stirred and heated to reflux overnight. After being cooled to room temperature, the solution was evaporated to dryness under reduced pressure. The solid thus obtained was dissolved in a minimal amount of CH_2Cl_2 (10 mL), and ethyl acetate (15 mL) was added. The solution was stirred at room temperature for 30 min, resulting in the formation of orange precipitate, which was collected on a frit by filtration and dried in vacuo; yield 1.02 g (86%). Orange crystals suitable for X-ray diffraction analysis were grown from a concentrated CH_2Cl_2/Et$_2$O solution at room temperature; yield 0.95 g (80%). ^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.94 (br d, 1, J_{HP} = 4.0 Hz, NH), 7.67 (t, 3, Ar), 7.57 (m, 9, Ar), 7.53 (t, 3, Ar), 3.85 (d, 1, $^2J_{HP}$ = 15.5 Hz, MeC=C*H*), 1.92 (s, 3, *Me*C=CH), 1.47 (s, 9, CMe$_3$). ^{31}P{^{1}H} NMR (CDCl$_3$, 202.31 MHz) δ 16.27. ^{13}C{^{1}H} NMR (CDCl$_3$, 125.5 MHz) δ 164.15 (d, $^2J_{CP}$ = 12.55 Hz, Me*C*=CH), 133.72 (d, $^4J_{CP}$ = 2.64 Hz, para-P*C*$_6$H$_5$), 132.65 (d, $^2J_{CP}$ = 10.67 Hz, meta-P*C*$_6$H$_5$), 129.89 (d, $^3J_{CP}$ = 12.43 Hz, ortho-P*C*$_6$H$_5$), 123.66 (d, $^1J_{CP}$ = 91.11 Hz, ipso-P*C*$_6$H$_5$), 56.23 (d, $^1J_{CP}$ = 121.48 Hz, MeC=*C*H), 52.98 (s, *C*Me$_3$), 28.51 (s, C*Me*$_3$), 24.21 (d, $^3J_{CP}$ = 6.15 Hz, *Me*C=CH). Anal. Calcd for (C$_{25}$H$_{29}$BrNP)$_4$(H$_2$O): C, 65.41; H, 6.48; N, 3.05. Found: C, 65.33; H, 6.43; N, 2.95. Incorporation of water is confirmed by X-ray crystallography. Complete removal of the water molecules from recrystallized samples was not successful.

Deprotonation of 2-(2,6-Diisopropylanilino)-prop-1-enyltriphenylphosphonium Bromide (1a): Synthesis of 2a. Solid NaH (50 mg, 2.08 mmol, 3.9 equiv) was added to a solution of 2-(2,6-diisopropylanilino)-prop-1-enyltriphenylphosphonium bromide (300.4 mg, 0.538 mmol) dissolved in THF (15 mL) at −35 °C. After being stirred at room temperature overnight, the reaction mixture was filtered through a pad of Celite to remove the excess amount of NaH, which was further washed with THF (5 mL) until the washings became colorless. The filtrate and washings were combined, and THF was removed in vacuo. The pale yellow solid residue was extracted with benzene (10 mL). The benzene solution was filtered through a pad of Celite and evaporated to dryness under reduced pressure, affording the product as a pale yellow solid; yield 215 mg (84%). Yellow crystals suitable for X-ray diffraction analysis were grown from a concentrated THF/benzene solution at room temperature. ^{1}H NMR (C$_6$D$_6$, 500 MHz) δ 7.76 (dd, 6, Ar), 7.17 (d, 2, Ar), 6.98−7.09 (m, 10, Ar), 3.05 (d, 1, $^2J_{HP}$ = 25.5 Hz, *H*C=PPh$_3$), 2.92 (septet, 2, $^3J_{HH}$ = 7 Hz, C*H*Me$_2$), 1.92 (d, 3, $^4J_{PH}$ = 2.0 Hz, *Me*C=NAr), 1.20 (d, 6, $^3J_{HH}$ = 7 Hz, CH*Me*$_2$), 0.98 (d, 6, $^3J_{HH}$ = 7 Hz, CH*Me*$_2$). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 202.31 MHz) δ 13.50. ^{13}C{^{1}H} NMR (C$_6$D$_6$, 125.5 MHz) δ 166.39 (d, $^2J_{CP}$ = 3.64 Hz, Me*C*=NAr), 150.89 (s, C), 140.37 (s, C), 133.95 (d, J_{CP} = 10.04 Hz, CH), 131.75 (d, J_{CP} = 2.76 Hz, CH), 130.58 (d, $^1J_{CP}$ = 88.98 Hz, ipso-P*C*$_6$H$_5$), 128.92 (d, J_{CH} = 11.80 Hz, CH), 123.28 (s, CH), 121.99 (s, CH), 40.54 (d, $^1J_{CP}$ = 115.34 Hz, H*C*=PPh$_3$), 28.23 (s, *C*HMe$_2$), 24.87 (s, CH*Me*$_2$), 24.47 (s, CH*Me*$_2$), 22.13 (d, $^3J_{CP}$ = 16.32 Hz, *Me*C=NAr). Anal. Calcd for C$_{33}$H$_{36}$NP: C, 82.99; H, 7.60; N, 2.93. Found: C, 83.00; H, 7.57; N, 2.89.

Deprotonation of 2-(2,6-Dimethylanilino)-prop-1-enyltriphenylphosphonium Bromide (1b): Synthesis of 2b. Solid NaH (108 mg, 4.51 mmol, 7.4 equiv) was added to a solution of 2-(2,6-dimethylanilino)-prop-1-enyltriphenylphosphonium bromide (307.6 mg, 0.61 mmol) dissolved in THF (15 mL) at −35 °C. After being stirred at room temperature for 4 h, the reaction mixture was filtered through a pad of Celite to remove the excess amount of NaH, which was further washed with THF (4 mL) until the washings became colorless. The filtrate and washings were combined, and THF was removed in vacuo. The pale yellow solid residue was extracted with benzene (10 mL). The benzene solution was filtered through a pad of Celite and evaporated to dryness under reduced pressure, affording the product as a pale yellow solid; yield 235 mg (91%). Yellow crystals suitable for X-ray diffraction analysis were grown from a concentrated THF/benzene solution at room temperature.

^{1}H NMR (C_6D_6, 500 MHz) δ 7.81 (dd, 6, Ar), 7.10 (d, 2, Ar), 7.06 (d, 2, Ar), 7.00 (m, 7, Ar), 6.89 (t, 1, Ar), 3.11 (d, 1, $^2J_{HP}$ = 26.5 Hz, *H*C═PPh$_3$), 1.96 (s, 6, ArC*H*$_3$), 1.88 (d, 3, $^4J_{HP}$ = 1.5 Hz, *Me*C═NAr). ^{31}P{^{1}H} NMR (C_6D_6, 202.31 MHz) δ 13.75. ^{13}C{^{1}H} NMR (C_6D_6, 125.5 MHz) δ 165.36 (d, $^2J_{CP}$ = 4.02 Hz, Me*C*═NAr), 153.85 (s, C), 134.08 (d, J_{cp} = 10.04 Hz, CH), 131.67 (d, J_{cp} = 2.76 Hz, CH), 130.10 (d, $^1J_{cp}$ = 89.98 Hz, ipso-P*C*$_6$H$_5$), 129.84 (s, C), 128.78 (d, J_{cp} = 11.80 Hz, CH), 128.30 (s, CH), 120.95 (s, CH), 39.64 (d, $^1J_{cp}$ = 116.21 Hz, H*C*═PPh$_3$), 21.70 (d, $^3J_{cp}$ = 16.82 Hz, *Me*C═NAr), 19.52 (s, ArMe). Anal. Calcd for $C_{29}H_{28}NP$: C, 82.63; H, 6.70; N, 3.32. Found: C, 82.39; H, 6.73; N, 3.26.

Deprotonation of 2-Anilinoprop-1-enyltriphenylphosphonium Bromide (1c): Synthesis of 2c. Solid NaH (12 mg, 0.5 mmol, 1.58 equiv) was added to a solution of 2-anilinoprop-1-enyltriphenylphosphonium bromide (150 mg, 0.316 mmol) dissolved in THF (10 mL) at −35 °C. After being stirred at room temperature for 4 h, the reaction mixture was filtered through a pad of Celite to remove the excess amount of NaH, which was further washed with THF (2 mL) until the washings became colorless. The filtrate and washings were combined, and THF was removed in vacuo. The pale yellow solid residue was extracted with benzene (10 mL). The benzene solution was filtered through a pad of Celite and evaporated to dryness under reduced pressure, affording the product as a pale yellow solid; yield 66 mg (53%). Yellow crystals suitable for X-ray diffraction analysis were grown from a concentrated THF/benzene solution at room temperature. ^{1}H NMR (C_6D_6, 500 MHz) δ 7.79 (dd, 6, Ar), 7.20 (t, 2, Ar), 7.02 (m, 9, Ar), 6.87 (t, 1, Ar), 6.75 (d, 2, Ar), 3.12 (d, 1, $^2J_{HP}$ = 28.5 Hz, *H*C═PPh$_3$), 2.13 (d, 3, $^4J_{HP}$ = 2.5 Hz, *Me*C═NAr). ^{31}P{^{1}H} NMR (C_6D_6, 202.31 MHz) δ 14.01. ^{13}C{^{1}H} NMR (C_6D_6, 125.5 MHz) δ 166.00 (s, Me*C*═NPh), 155.33 (s, C), 133.89 (d, J_{CP} = 9.41 Hz, CH), 131.58 (s, CH), 130.09 (d, J_{CP} = 90.74 Hz, ipso-P*C*$_6$H$_5$), 129.01 (s, CH), 128.84 (s, CH), 123.23 (s, CH), 120.56 (s, CH), 43.06 (d, $^1J_{CP}$ = 115.34 Hz, H*C*═PPh$_3$), 20.49 (d, $^3J_{CP}$ = 16.06 Hz, *Me*C═NPh). LRMS (EI) calcd for $C_{27}H_{24}NP$ *m*/*z* 393, found *m*/*z* 393. Anal. Calcd for ($C_{27}H_{24}NP$)$_3$(C_4H_8O): C, 81.50; H, 6.44; N, 3.36. Found: C, 81.36; H, 6.11; N, 3.02.

Deprotonation of 2-(*tert*-Butylamino)-prop-1-enyltriphenylphosphonium Bromide (1d): Synthesis of 2d. Solid NaH (43 mg, 1.69 mmol, 4.0 equiv) was added to a solution of 2-(*tert*-butylamino)-prop-1-enyltriphenylphosphonium bromide (191.8 mg, 0.422 mmol) dissolved in THF (10 mL) at −35 °C. After being stirred at room temperature for 4 h, the reaction mixture was filtered through a pad of Celite to remove the excess amount of NaH, which was further washed with THF (2 mL) until the washings became colorless. The filtrate and washings were combined, and THF was removed in vacuo. The orange, oily residue was extracted with benzene (10 mL). The benzene solution was filtered through a pad of Celite and evaporated to dryness under reduced pressure, affording the product as reddish orange viscous oil; yield 142 mg (90%). ^{1}H NMR (C_6D_6, 500 MHz) δ 7.80 (dd, 6, Ar), 7.03−7.09 (m, 9, Ar), 2.79 (d, 1, $^2J_{HP}$ = 31.5 Hz, *H*C═PPh$_3$), 2.14 (d, 3, $^4J_{HP}$ = 3.0 Hz, *Me*C═NCMe$_3$), 1.14 (s, 9, C*Me*$_3$). ^{31}P{^{1}H} NMR (C_6D_6, 202.31 MHz) δ 11.64. ^{13}C{^{1}H} NMR (C_6D_6, 125.5 MHz) δ 164.25 (d, $^2J_{CP}$ = 2.76 Hz, Me*C*═NCMe$_3$), 133.82 (d, J_{CP} = 9.54 Hz, CH), 132.03 (d, $^1J_{CP}$ = 90.36 Hz, ipso-P*C*$_6$H$_5$), 131.00 (d, J_{CP} = 2.76 Hz, CH), 128.48 (d, J_{CP} = 11.80 Hz, CH), 54.00 (s, *C*Me$_3$), 41.18 (d, $^1J_{CP}$ = 120.36 Hz, H*C*═PPh$_3$), 32.34 (s, CMe$_3$), 21.79 (d, $^3J_{CP}$ = 16.32 Hz, *Me*C═NCMe$_3$). HRMS (EI) calcd for $C_{25}H_{28}NP$ *m*/*z* 373.1959, found *m*/*z* 373.1956.

Synthesis of 3d. Attempts to crystallize the oily **2d** from a concentrated diethyl ether/benzene solution at room temperature led to colorless cubes of **3d** suitable for X-ray diffraction analysis. Alternatively, hydrolysis of **2d** in THF at room temperature also afforded **3d** on the basis of NMR studies. ^{1}H NMR (C_6D_6, 500 MHz) δ 8.06 (m, 4, Ar), 7.09 (m, 6, Ar), 5.37 (br s, 1, NH), 4.66 (d, 1, $^2J_{HP}$ = 19, MeC═C*H*), 2.18 (s, 3, *Me*C═CH), 1.17 (s, 9, CMe$_3$). ^{31}P{^{1}H} NMR (C_6D_6, 202.31 MHz) δ 21.39. ^{13}C{^{1}H} NMR (C_6D_6, 125.5 MHz) δ 158.10 (d, $^2J_{CP}$ = 19.8 Hz, Me*C*═CH), 140.06 (d, $^1J_{CP}$ = 104.4 Hz, ipso-P*C*$_6$H$_5$), 131.73 (d, J_{CP} = 9.0 Hz, CH), 130.85 (d, J_{CP} = 29.1 Hz, CH), 128.88 (d, J_{CP} = 10.8 Hz, CH), 81.18 (d, $^1J_{CP}$ = 128.5 Hz, MeC═*C*H), 51.32 (s, *C*Me$_3$), 29.00 (s, C*Me*$_3$), 22.41 (d, J_{CP} = 7.3 Hz, *Me*C═CH).

Synthesis of 4a. To a solid mixture of **2a** (320 mg, 0.67 mmol) and Ni(COD)$_2$ (203 mg, 0.74 mmol, 1.1 equiv) was added toluene (10 mL) at room temperature. The reaction mixture was stirred at room temperature for 10 min to allow for the complete dissolution of the starting materials. Pyridine (848 mg, 11 mmol, 16 equiv) was added. The reaction solution was heated to 50 °C for 10 min and then stirred at room temperature for 1 day. After being filtered through a pad of Celite to remove a black insoluble solid, the toluene solution was concentrated under reduced pressure until a red, microcrystalline solid began to deposit. The concentrated toluene solution was cooled to −35 °C to afford the product as red crystals, which were isolated, washed with pentane (1 mL × 3), and dried in vacuo; yield 150 mg (36%). The red crystals thus obtained were suitable for X-ray diffraction analysis. ^{1}H NMR (C_6D_6, 500 MHz) δ 8.22 (d, 2, Ar), 7.83 (t, 4, Ar), 7.43 (d, 2, Ar), 7.17 (m, 6, Ar), 6.95 (m, 1, Ar), 6.90 (m, 2, Ar), 6.76 (m, 2, Ar), 6.70 (m, 1, Ar), 6.33 (t, 1, Ar), 6.03 (t, 2, Ar), 3.86 (septet, 2, $^3J_{HH}$ = 6.5 Hz, C*H*Me$_2$), 3.84 (d, 1, $^2J_{HP}$ = 1.5 Hz, MeC═C*H*), 1.85 (s, 3, *Me*C═CH), 1.28 (d, 6, $^3J_{HH}$ = 6.5 Hz, CH*Me*$_2$), 1.22 (d, 6, $^3J_{HH}$ = 6.5 Hz, CH*Me*$_2$). ^{31}P{^{1}H} NMR (C_6D_6, 202.31 MHz) δ 31.22. ^{13}C{^{1}H} NMR (C_6D_6, 125.5 MHz) δ 175.73 (d, $^2J_{CP}$ = 22.0 Hz, HC═*C*Me), 157.61 (d, $^2J_{CP}$ = 43.9 Hz, NiC), 150.58 (s, CH), 148.92 (s, C), 145.84 (s, C), 138.35 (s, CH), 136.10 (d, J_{CP} = 53.1 Hz, C), 135.48 (s, CH), 133.60 (s, CH), 133.52 (s, CH), 129.57 (s, CH), 126.26 (s, CH), 124.37 (s, CH), 123.42 (s, CH), 123.36 (s, CH), 122.34 (s, CH), 72.02 (d, $^1J_{CP}$ = 55.0 Hz, H*C*═CMe), 28.61 (s, *C*HMe$_2$), 24.92 (s, CH*Me*$_2$), 24.35 (s, CH*Me*$_2$), 21.39 (d, $^3J_{CP}$ = 18.3 Hz, HC═C*Me*). Anal. Calcd for $C_{38}H_{41}N_2NiP$: C, 74.16; H, 6.72; N, 4.55. Found: C, 74.15; H, 6.69; N, 4.47.

Synthesis of 4b. To a solid mixture of **2b** (160 mg, 0.38 mmol) and Ni(COD)$_2$ (115 mg, 0.42 mmol, 1.1 equiv) was added toluene (6 mL) at room temperature. The reaction mixture was stirred at room temperature for 5 min to allow for the complete dissolution of the starting materials. Pyridine (480 mg, 6.08 mmol, 16 equiv) was added. The reaction solution was heated to 50 °C for 10 min and then stirred at room temperature for 1 day. After being filtered through a pad of Celite to remove a black insoluble solid, the toluene solution was evaporated to dryness under reduced pressure. The solid residue was dissolved in diethyl ether (10 mL). The ether solution was filtered through a pad of Celite and concentrated in vacuo to give a red solution which contained yellow crystals of Ni(COD)$_2$. The red diethyl ether solution was separated from the yellow crystals and evaporated to dryness under reduced pressure to give the product as a red crystalline solid. In some cases, repeated extraction of the product with diethyl ether was necessary to ensure the complete removal of Ni(COD)$_2$. Alternatively, yellow crystals of Ni(COD)$_2$ might be manually separated with capillaries from the red crystals of **4b** after complete evaporation of the diethyl ether solutions. Yield 70 mg (33%). Crystals suitable for X-ray diffraction analysis were grown from a concentrated diethyl ether solution at −35 °C. ^{1}H NMR (C_6D_6, 500 MHz) δ 8.21 (d, 2, Ar), 7.85 (dd, 4, Ar), 7.48 (d, 2, Ar), 7.19 (m, 6, Ar), 6.81 (t, 2, Ar), 6.74 (t, 1, Ar),

6.66 (m, 2, Ar), 6.60 (m, 1, Ar), 6.32 (t, 1, Ar), 5.94 (t, 2, Ar), 3.82 (d, 1, $^2J_{HP}$ = 2.5 Hz, *H*C═CMe), 2.40 (s, 6, ArC*H*$_3$), 1.70 (s, 3, HC═C*Me*). ^{31}P{^{1}H} NMR (C_6D_6, 202.31 MHz) δ 32.09. ^{13}C{^{1}H} NMR (C_6D_6, 125.5 MHz) δ 174.60 (d, $^2J_{CP}$ = 23.8 Hz, HC═*C*Me), 157.68 (d, $^2J_{CP}$ = 41.7 Hz, NiC), 151.06 (s, C), 149.49 (s, CH), 138.00 (d, J_{CP} = 1.9 Hz, CH), 136.01 (d, J_{CP} = 53.5 Hz, C), 135.46 (s, CH), 135.37 (s, C), 133.57 (d, J_{CP} = 10.2 Hz, CH), 129.58 (d, J_{CP} = 2.8 Hz, CH), 128.78 (d, J_{CP} = 11.9 Hz, CH), 127.77 (s, CH), 126.23 (d, J_{CP} = 1.8 Hz, CH), 123.28 (s, CH), 123.27 (s, CH), 122.35 (s, CH), 71.53 (d, $^1J_{CP}$ = 56.2 Hz, MeC═*C*H), 20.71 (d, $^3J_{CP}$ = 17.3 Hz, HC═C*Me*), 19.85 (s, Ar*C*H$_3$). Anal. Calcd for $C_{34}H_{33}N_2NiP$: C, 73.01; H, 5.95; N, 5.01. Found: C, 72.98; H, 6.16; N, 4.86.

Synthesis of 4c. To a solid mixture of **2c** (199 mg, 0.51 mmol) and Ni(COD)$_2$ (153 mg, 0.56 mmol, 1.1 equiv) was added toluene (8 mL) at room temperature. The reaction mixture was stirred at room temperature for 5 min to allow for the complete dissolution of the starting materials. Pyridine (640 mg, 8.1 mmol, 16 equiv) was added. The reaction solution was heated to 50 °C for 10 min and then stirred at room temperature for 1 day. After being filtered through a pad of Celite to remove a black insoluble solid, the toluene solution was evaporated to dryness under reduced pressure. The solid residue was dissolved in diethyl ether (13 mL). The ether solution was filtered through a pad of Celite, concentrated in vacuo, and cooled to −35 °C to give the product as red crystals, which were isolated, washed with pentane, and dried in vacuo, yield 200 mg (74%). The red crystals thus obtained were suitable for X-ray diffraction analysis. ^{1}H NMR (C_6D_6, 500 MHz) δ 8.18 (d, 2, Ar), 7.82 (m, 4, Ar), 7.49 (d, 2, Ar), 7.18 (m, 6, Ar), 6.83 (t, 2, Ar), 6.76 (d, 1, Ar), 6.73 (m, 2, Ar), 6.68 (d, 2, Ar), 6.59 (t, 1, Ar), 6.30 (t, 1, Ar), 5.94 (t, 2, Ar), 3.87 (d, 1, $^2J_{HP}$ = 1 Hz, *H*C═CMe), 1.98 (s, 3, HC═C*Me*). ^{31}P{^{1}H} NMR (C_6D_6, 202.31 MHz) δ 31.32. ^{13}C{^{1}H} NMR (C_6D_6, 125.5 MHz) δ 174.39 (d, $^2J_{CP}$ = 23.7 Hz, HC═*C*Me), 157.40 (d, $^2J_{CP}$ = 42.04 Hz, NiC), 153.87 (s, C), 150.39 (s, CH), 138.36 (d, J_{CP} = 1.9 Hz, CH), 135.72 (d, J_{CP} = 53.1 Hz, C), 135.24 (s, CH), 133.64 (d, J_{CP} = 10.0 Hz, CH), 129.67 (d, J_{CP} = 1.9 Hz, CH), 129.22 (s, CH), 128.69 (s, CH), 127.98 (s, CH), 126.34 (d, J_{CP} = 1.9 Hz, CH), 123.73 (s, CH), 122.43 (s, CH), 121.90 (s, CH), 73.50 (d, $^1J_{CP}$ = 54.8 Hz, H*C*═CMe), 21.66 (d, $^3J_{CP}$ = 16.4 Hz, HC═C*Me*). Anal. Calcd for $C_{32}H_{29}N_2NiP$: C, 72.35; H, 5.50; N, 5.27. Found: C, 72.47; H, 5.56; N, 5.20.

Acknowledgment. We thank the National Science Council of Taiwan for financial support (NSC 96-2628-M-110-007-MY3) of this work, Professor Hon Man Lee (National Changhua University of Education) and Mr. Ting-Shen Kuo (National Taiwan Normal University) for assistance with X-ray crystallography, and the National Center for High-performance Computing (NCHC) for computer time and facilities. We also thank the reviewers for insightful comments.

Supporting Information Available: Fully labeled molecular structures of **1a**, **1b**, **1d**, **2a**, **2c**, **3d**, **4a**, **4b**, and **4c** with selected bond distances and angles and X-ray crystallographic data in CIF format for these compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

IC701836J