Insertion of Alkynes into Ni−H Bonds: Synthesis of Novel Vinyl Nickel(II) and Dinuclear Vinyl Nickel(II) Complexes Containing a [P, S]-Ligand

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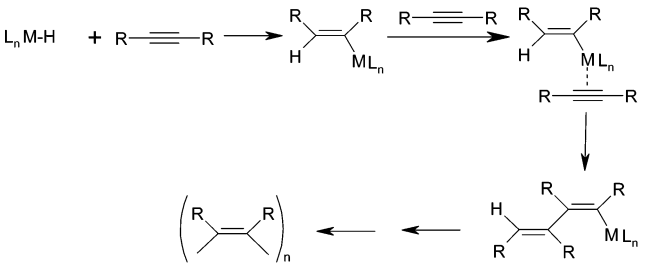
Reactions of alkynes with nickel hydride complexes bearing a [P, S]-ligand and supported by trimethylphosphine were investigated. Tetracoordinate vinyl nickel(II) complexes **3**, **5**, and **6** with square-planar geometry were obtained by reacting phenylacetylene, trimethylsilylacetylene, and 1-hexyne with the hydrido nickel complex **1**. Reaction of 1,4-bis(trimethylsilylethynyl)benzene with complex **1** proceeds as a monoinsertion and afforded complex **7**, while reaction of 1,4-bis(ethynyl)benzene with **1** leads to the dinuclear vinyl nickel(II) complex **8**.

Introduction

Oligomerization and polymerization of alkynes may occur by two different routes: (a) alkyne insertion yielding vinyl complexes; (b) alkyne metathesis via transition-metal carbene complexes. The first pathway is probably more common and is illustrated in a general sense in Scheme 1. In this insertion process the σ-vinyl metal complexes are important intermediates, through which the carbon chain is propagated.[1] However, in most cases the vinyl complexes have not been isolated from the reaction system.

In the commercially significant Shell Higher Olefin Process (SHOP)[2] hydrido nickel(II) complexes containing [P, O]-chelate ligands are considered as the active species.[3] Therefore studies on the reactivity of [Ni−H] units are of great importance. Some reports on 2-(diphenylphosphino)thiophenole as a chelating ligand have been published. Most of these studies are concerned with bis- and tris-chelate complexes of 3d, 4d, and 5d metals.[4−7] There are few examples of stable mono[P, S]-chelate complexes of 4d and 5d elements.[8,9]

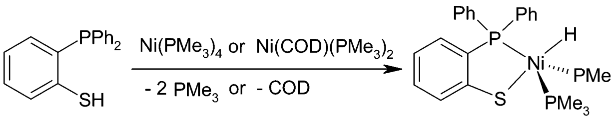
Scheme 1



In this paper, we report the synthesis of hydrido(2-diphenylphosphinyl)thiophenolatobis(trimethylphosphine)nickel(II) (**1**) and its insertion reactions with different alkynes. The studied alkynes include phenylacetylene, trimethylsilylacetylene, 1-hexyne, 1,4-bis(ethynyl)benzene, and 1,4-bis(trimethylsilylethynyl)benzene.

Results and Discussion

1. Synthesis of Hydrido Nickel Complex 1. The reaction of Ni(PMe$_3$)$_4$ or Ni(PMe$_3$)$_2$(COD) with 1 molar equiv of 2-(diphenylphosphino)thiophenol in the presence of excess (5 times) trimethylphosphine gave rise to hydrido(2-diphenylphosphinyl)thiophenolatobis(trimethylphosphine)nickel(II) (**1**) (eq 1).



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(1)

Crystallization at −27 °C afforded a red crystalline solid in 30−40% yield. Complex **1** in the solid state is stable below 65 °C and quickly decomposes at room temperature in solution. In the IR spectrum the (Ni−H) band was found at 1907 cm^{-1}. The resonance of the hydrido hydrogen in the ^{1}H NMR spectrum at room temperature is registered at −19.9 ppm as a doublet with the coupling constant ^2J(P, H) = 41 Hz. At 203 K the ligand exchange is decelerated so as to split up the one doublet of triplets with the coupling constant ^2J(P$_{\text{phenyl}}$, H) = 45 Hz and ^2J(P$_{\text{methyl}}$, H) = 9 Hz. This multiplicity accords with a

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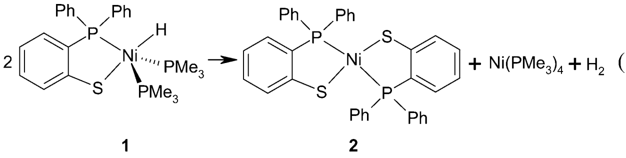
trigonal bipyramidal coordination geometry. In the ^{31}P NMR spectrum this conjecture is proved through a double doublet for the chelating phosphorus atom at 57.5 ppm with a coupling constant $^2J(P, P) = 9$ Hz and a double doublet for the two trimethylphosphine phosphorus atoms at −14.4 ppm with the same coupling constants.

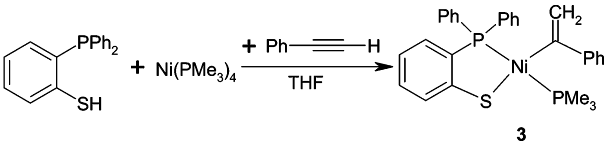
Complex **1** in solution is very unstable and decomposes to bis-chelated complex **2** within several minutes (eq 2). The decomposition mechanism is proposed.[10] Therefore in this paper



(2)

all of the reactions with complex **1** were carried out without isolation of complex **1**.

2. Reaction with Phenylacetylene. Hydrido nickel complex **1**, which is in situ generated in THF through the reaction of $Ni(PMe_3)_4$ with 2-(diphenylphosphino)thiophenole, in the presence of phenylacetylene afforded tetracoordinate vinyl nickel(II) complexes **3** (eq 3). Complex **3** was fully characterized by



(3)

IR and NMR spectroscopy. In the IR spectra the typical (Ni−H) absorption at 1907 cm^{-1} of the hydrido nickel complex **1** is absent. The ^1H NMR spectrum (in $CDCl_3$) revealed two vinyl protons at 4.7 and 5.79 ppm as singlets, respectively, indicating that Markovnikov addition of the Ni−H bond to phenylethyne has occurred.[11] In the ^{31}P NMR spectrum doublets at −12.8 and 51.2 ppm are assigned to the trimethylphosphine ligand and to the diphenylphosphanyl group, respectively. The large coupling constant ($^2J(PP) = 280$ Hz) implies a *trans*-orientation of these two P nuclei in solution. The molecular structure of complex **3** was confirmed for the crystal by an X-ray diffraction analysis.

The molecular structure of complex **3** is shown in Figure 1. The nickel atom displays a square-planar geometry with two P-donor atoms lying in *trans*-positions. The vinyl group is oriented perpendicular to the coordination plane, and the Ni1−C20 bond length of 1.918(6) Å is almost the same as that the Ni−C$_{vinyl}$ bond (1.916 Å) in *trans*-$[Ni(C_6Cl_5)(PMe_3)_2\{C(OMe)=CH_2\}]$[12] and falls in the typical range for σ-vinyl complexes of cobalt(III).[13]

The reaction (eq 3) is better carried out in a polar medium (THF), giving less byproduct **2** than in pentane. Complex **3** is stable at room temperature. If 1 equiv of trimethylphosphine is added to a solution of complex **3**, the color below − 80 °C changes from yellow to red; otherwise the solution remains yellow. According to our early observation about the equilibrium between a pentacoordinate vinyl cobalt(III) complex and a hexacoordinate vinyl cobalt(III) complex,[13] we suggest an equilibrium between tetracoordinate complex **3** and pentacoordinate complex **4** at low temperature (eq 4). Our efforts to isolate complex **4** were not successful.

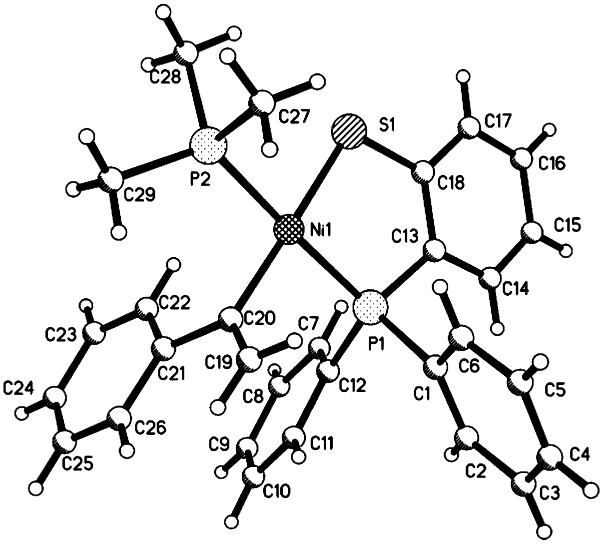
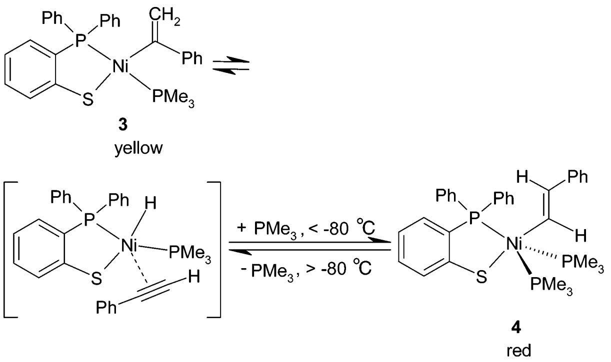
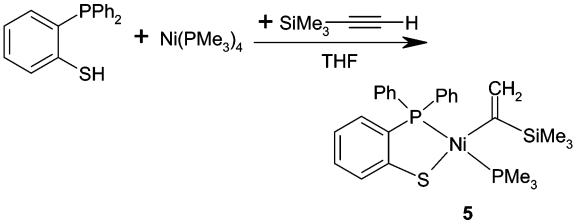


Figure 1. Molecular structure of **3** and selected bond distances (Å) and angles (deg): Ni1−C20 1.918(6), Ni1−P1 2.1618(17), Ni1−P2 2.181(2), Ni1−S1 2.1994(18), S1−C18 1.755(6), P1−C13 1.812(5), C19−C20 1.329(8); C20−Ni1−P1 90.54(19), C20−Ni1−P2 89.26(19), P1−Ni1−P2 174.72(8), C20−Ni1−S1 177.5(2), P1−Ni1−S1 89.59(6), P2−Ni1−S1 90.84(7), C18−S1−Ni1 106.56(19), C13−P1−C12 105.6(2), C13−P1−C1 104.2(3), C12−P1−C1 106.4(3), C13−P1−Ni1 108.25(19), C12−P1−Ni1 115.51(19), C1−P1−Ni1 115.8(2).



(4)

3. Reaction with Trimethylsilylacetylene. When trimethylsilylethyne is used instead of phenylethyne, an analogous four-coordinate vinyl nickel(II) complex, **5**, is directly obtained from ether solution as orange rhombic crystals (eq 5). At room temperature complex **5** is stable in the air for several hours.



(5)

In the ^1H NMR spectrum (in C_6D_6), the two vinyl protons appear as singlets at 5.78 and 6.13 ppm, respectively. When compared with the vinyl protons in complex **3**, the signals are shifted downfield by the electron-donating trimethylsilyl group. Two ^{31}P NMR doublets at −14.2 and 46.8 ppm with $^2J(PP) = 280$ Hz indicate a *trans*-arrangement of the two phosphorus nuclei.

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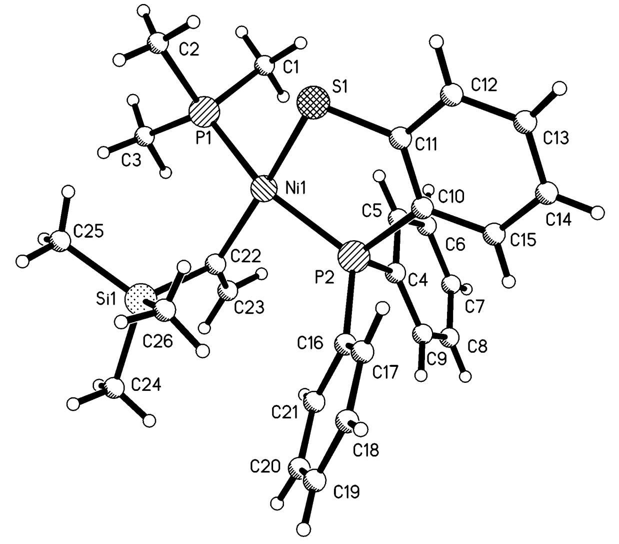
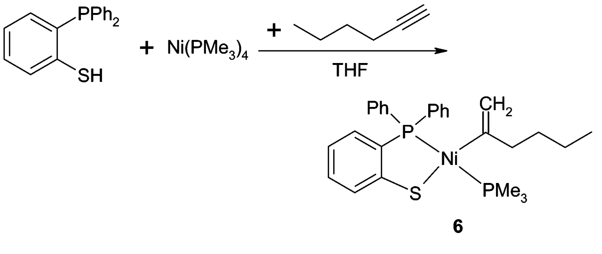


Figure 2. Molecular structure of **5** and selected distances (Å) and angles (deg): S1−Ni1 2.2117(9), Ni1−C22 1.911(3), Ni1−P2 2.1546(8), Ni1−P1 2.1819(9), S1−C11 1.769(3), P2−C10 1.815(3), C22−C23 1.336(4); C11−S1−Ni1 105.47(9), C22−Ni1−P2 90.06(8), C22−Ni1−P1 93.51(9), P2−Ni1−P1 155.77(3), C22−Ni1−S1 168.86(9), P2−Ni1−S1 90.10(4), P1−Ni1−S1 90.90(4).

An X-ray diffraction study reveals that complex **5** attains a molecular structure (Figure 2) that is closely related with complex **3**. The bulky trimethylsilyl group renders the angle P2−Ni1−P1 (155.77(3)°) significantly smaller than that in complex **3** (174.72(8)°).

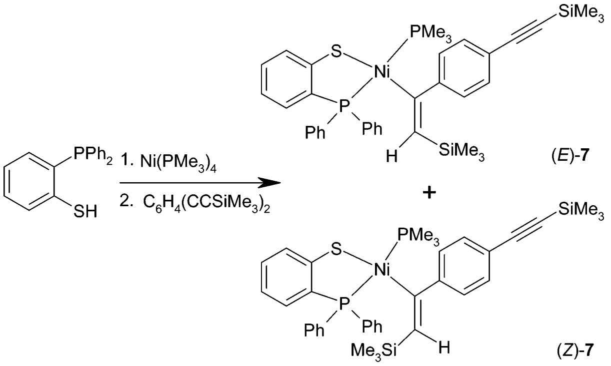
It is known that ligands containing a C(sp^2)−Si bond can be very sensitive to water.[13,14] Hydrolysis is expected to give rise to a C(sp^2)−H bond along with Me_3SiOH and/or $(Me_3Si)_2O$ as byproducts. However, IR and ^{1}H NMR spectroscopic data confirmed that there was no reaction in THF/water solution of complex **5**. Hydrolysis appears to require special conditions, and the mechanism is not fully understood.[15]

4. Reaction with 1-Hexyne. Insertions of phenylethyne and trimethylsilylethyne into the Ni−H bond preferentially gave branched vinyl nickel complexes. In order to better understand the regioselectivity of the insertion reaction and the influence of both steric and electron effects upon the reaction products, 1-hexyne was introduced. In this case a branched vinyl nickel complex **6** was also obtained. The ^{1}H NMR spectrum (in $CDCl_3$) of complex **6** reveals two vinyl protons at 4.50 and 5.07 ppm as singlets, which were coincident with that of complexes **3** and **5**. The coupling constant (^2J(PP) = 278 Hz) in the ^{31}P NMR spectrum is almost as large as that for complexes **3** and **5** (^2J(PP) = 280 Hz), indicating a *trans*-orientation of the two phosphorus atoms.



(6)

5. Reaction with 1,4-Bis(trimethylsilylethynyl)benzene. When 1,4-bis(trimethylsilylethynyl)benzene was added to tetrakis(trimethylphosphine)nickel(0) and 2-diphenylphosphinothiophenole in diethyl ether, the dark red solution rapidly turned yellow-brown. Complex **7** was isolated as a 4:1 ((*Z*)-**7**:(*E*)-**7**) mixture of isomers from diethyl ether at −20 °C as a yellow powder in 76% yield (eq 7).



(7)

A strong infrared absorption at 2152 cm^{-1} indicates the presence of a C≡C bond. In the ^{1}H NMR spectrum, the two trimethylsilyl groups appear as singlets at 0.22 and −0.15 ppm, indicating different chemical surroundings after a monoinsertion reaction. A signal for the vinyl protons is observed as a singlet at 6.78 ppm. The ^{13}C NMR data clearly show resonances of both C=C bonds (141.7 and 157.1 ppm) and C≡C bonds (93.6 and 105.7 ppm).

In the ^{31}P NMR spectrum four doublet signals were found, which can be divided into two groups for the two isomers. Each group consists of a doublet for the trimethylphosphine ligand and a doublet for the diphenylphosphino group. The observed multipicity is consistent with the presence of *Z* and *E* isomers of complex **7** in solution. The larger coupling constant [$J(PMe_3-PPh_2)$ = 345 Hz] is assigned to (*E*)-**7**. The bulky trimethylsilyl group appears to favor a *trans*-orientation with respect to the nickel center as a result of repulsion with the diphenylphosphino group of the chelate ligand. These effects cause a smaller angle P−Ni−P in (*Z*)-**7** and consequently a smaller coupling constant [$J(PMe_3-PPh_2)$ = 280 Hz] in (*Z*)-**7**. The ratio of (*Z*)-**7** and (*E*)-**7** in $CDCl_3$ at 295 K is 4:1.

In order to generate a dinuclear nickel vinyl compound, complex **7** was added to a solution of tetrakis(trimethylphosphine)nickel(0) and 2-(diphenylphosphino)thiophenole. Spectroscopic examination of the reaction mixture verified the generation of a nickel hydride. However, the expected double insertion reaction did not occur, presumably because the bulky trimethylsilyl group prevents an insertion reaction of the second (C≡C) group. Similar results have been reported before.[16]

6. Reaction with 1,4-Bis(ethynyl)benzene. Addition of 1,4-bis(ethynyl)benzene to a solution of $Ni(PMe_3)_4$ and 2-(diphenylphosphino)thiophenole in THF afforded a yellow-brown solution. Complex **8** was obtained from pentane at −20 °C as yellow-brown microcrystals. In the IR spectrum the absence of a (C≡C) band around 2100 cm^{-1} indicates the formation of the dinickel complex **8** (eq 8). The NMR data are consistent with two square-planar nickel units in complex **8**. In the ^{1}H NMR spectrum four vinyl protons appear as two singlets at 5.11 (2 H) and 6.03 ppm (2 H). The ^{13}C NMR and ^{31}P NMR spectra

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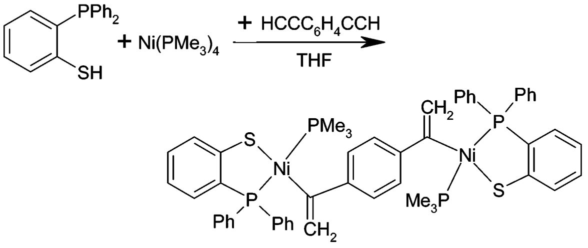
clearly confirm the dinuclear nature of the vinyl nickel(II) complex **8**. The quality of single crystals was not sufficient for an X-ray analysis.



(8)

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Conclusion

In situ reactions of alkynes with a nickel hydride complex bearing a [P, S]-ligand and supported with trimethylphosphine were investigated. Tetracoordinate vinyl nickel(II) complexes **3**, **5**, and **6** with square-planar geometry were obtained through formal insertion reactions of phenylacetylene, trimethylsilylacetylene, and 1-hexyne with an intermediate hydrido nickel complex, **1**. The reaction of 1,4-bis(trimethylsilylethynyl)benzene afforded the monoinsertion complex **7**, while the reaction of 1,4-bis(ethynyl)benzene leads to the dinuclear vinyl nickel(II) complex **8**. This reaction will open up access to bimetallic, oligomeric, or polymeric organonickel compounds with conjugated bridges, which have interesting potential as molecular conductors.[17]

Investigation of the catalytic properties of complexes **3**, **5**, and **6** is in progress.

Experimental Section

General Procedures and Materials. Standard vacuum techniques were used in manipulations of volatile and air-sensitive materials. Tetrakis(trimethylphosphine)nickel(0),[18] 2-(diphenylphosphino)benzenethiol,[19] phenylethyne,[20] trimethylsilylethyne,[21] 1,4-bis(timethylsilylethynyl)benzene,[22] and 1,4-bis(ethynyl)benzene[23] were synthesized according to literature procedures. Infrared spectra (4000−400 cm^{-1}), as obtained from Nujol mulls between KBr disks, were recorded on a Nicolet 5700. ^{1}H, ^{13}C, and ^{31}P NMR (300, 75, and 121 MHz, respectively) spectra were recorded on a Bruker Avance 300 spectrometer. ^{13}C and ^{31}P NMR resonances were obtained with broadband proton decoupling. Elemental analyses were carried out on an Elementar Vario EL III. Melting points were measured in capillaries sealed under argon and are uncorrected.

Hydrido(2-diphenylphosphino)thiophenolato-[*P,S*]-bis(trimethylphosphine)nickel(II) (1). To the solution of tetrakis(trimethylphosphine)nickel(0) (1.30 g, 3.60 mmol) in 80 mL of pentane was added 2-diphenylphosphinothiophenole (1.05 g, 3.60 mmol) in the presence of excess trimethylphosphine (1.80 g, 18.4 mmol). After stirring at room temperature for 16 h the reaction solution was filtrated. Crystallization of the filtrate at −27 °C afforded hydrido nickel(II) complex **1** as light red, small, thin plates. Yield: 0.67 g of **1** (37.0%), mp (dec) > 65 °C. Anal. Calcd for $C_{24}H_{33}NiP_3S$ (505.20 g/mol): C, 57.06; H, 6.58; P, 18.39. Found: C, 57.80; H, 6.95; P, 17.91. IR (Nujol): $\nu = 1907$ (Ni−H) cm^{-1}. ^{1}H NMR (300 MHz, d_8-THF, 203 K, ppm): δ (C*H*), 7.71−7.64 (m, 4H); δ (C*H*), 7.44−7.32 (m, 7H), δ (C*H*), 7.09 (m, 2H), δ (C*H*), 6.86 (m, 1H), δ (PCH_3), 1.15 (s, 18H), δ (Ni*H*) −19.9 (dt, ^{2}J(PH) = 45 Hz, ^{2}J(PH) = 9 Hz, 1H). ^{31}P NMR (81 MHz, d_8-THF, 203 K, ppm): δ (*P*Ph$_2$), 57.5 (dd, ^{2}J(PphPme) = 154 Hz, ^{2}J(PphPme) = 18 Hz, 1P); δ (*P*Me$_3$), −14.4 (dd, ^{2}J(PmePph) = 154 Hz, ^{2}J(PmePph) = 18 Hz, 2P).

[(1-Phenylethenyl)[(2-diphenylphosphino)thiophenyl(*S,P*)]-trimethylphosphine]nickel(II) (3). Tetrakis(trimethylphosphine)nickel(0) (2.36 g, 6.40 mmol) was dissolved in 40 mL of THF. To this solution was added 2-(diphenylphosphino)benzenethiole (1.93 g, 6.56 mmol) in 20 mL of THF at −80 °C. The mixture was stirred and turned dark red when warmed to 20 °C. Phenylethyne (2.75 g, 26.96 mmol) was injected into the mixture, which rapidly turned brown. After 18 h, the color changed to yellow-brown. Filtration and evaporation of the filtrate in vacuo followed by washing with pentane resulted in a yellow powder, which was crystallized from diethyl ether at −27 °C. Complex **3** formed yellow cubic crystals suitable for X-ray diffraction analysis. Yield: 1.40 g of **3** (47.0%), mp (dec) > 135 °C. Anal. Calcd for $C_{29}H_{30}NiP_2S$ (531.24 g/mol): C, 65.57; H, 5.70. Found: C, 65.60; H, 5.95. IR (Nujol): $\nu = 1587$, 1570, 1549 (C=C) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, 294 K, ppm): δ [P (CH_3)$_3$], 1.29 (d, ^{2}J(PH) = 9 Hz, 9H); δ (Ni−C−CH_2), 4.74 (s, 1H), 5.79 (s, 1H); δ (CH_{arom}), 6.77−7.97 (m, 19H). ^{13}C NMR (75 MHz, $CDCl_3$, 297 K, ppm): δ (P*C*H_3), 14.15 (d, ^{1}J(PC) = 27.7 Hz); δ (Ni-C-*C*H_2),117.3; δ (Ni-*C*-CH$_2$), 163.1 (t, $|^{1}J(PC) + {}^{3}J(PC)| = 59$ Hz); δ (*C*-S), 157; δ (CH$_2$-C-*C*), 145.2; δ (C_{arom}), 121.9, 125.3, 126.9, 127.4, 128.3, 129.3, 130.2, 130.8, 132.0, 132.9, 133.4. ^{31}P NMR (121 MHz, $CDCl_3$, 295 K, ppm): δ (*P*CH$_3$), −12.8 (d, ^{2}J(PP) = 280 Hz, 1P); δ (*P*Ph$_2$), 51.2 (d, ^{2}J(PP) = 280 Hz, 1P).

[(1-(Trimethylsilyl)ethenyl)[(2-diphenylphosphino)thiophenyl-(*S,P*)]trimethylphosphan]nickel(II) (5). Adding a solution of 2-(diphenylphosphino)benzenethiol (1.27 g, 4.32 mmol) in 20 mL of THF to a solution of tetrakis(trimethylphosphine)nickel(0) (1.57 g, 4.32 mmol) in 40 mL of THF at −80 °C afforded a dark red solution. Trimethylsilylethyne (0.80 g, 8.16 mmol) was injected into the mixture, and a dark red suspension formed rapidly. After stirring for 18 h at room temperature, a brown suspension was obtained. The filtrate was evaporated in vacuo, and the residue was extracted with pentane/diethyl ether (1:1). Crystallization in diethyl ether at −27 °C afforded complex **5** as orange rhombus crystals suitable for X-ray diffraction analysis. Yield: 1.16 g (51.0%), mp (dec) > 122 °C. Anal. Calcd for $C_{26}H_{34}NiP_2SSi$ (527.33 g/mol): C, 59.22; H, 6.50. Found: C, 59.48; H, 6.85. IR (Nujol): $\nu = 1571$, 1547 (C=C) cm^{-1}. ^{1}H NMR (300 MHz, C_6D_6, 294 K, ppm): δ (SiCH_3), 0.20 (s, 9H); δ (PCH$_3$), 1.33 (d, ^{2}J(PH) = 8.7 Hz, 9H); δ (Ni-C-CH_2), 5.78 (s, 1H), 6.13 (s, 1H); δ (CH_{arom}), 6.78−8.34 (m, 14H). ^{13}C NMR (75 MHz, C_6D_6, 297 K, ppm): δ (Si*C*H$_3$), 1.0; δ (P*C*H$_3$), 15.0 (d, ^{1}J(PC) = 27 Hz); δ (Ni-C-*C*H$_2$), 121.3 (d, ^{3}J(PC) = 5 Hz); δ (Ni-*C*-CH$_2$), 159 (dd, ^{2}J(PC) = 16 Hz, ^{2}J(PC) = 38 Hz); δ (C_{arom}), 128.3, 129.4, 129.9, 130.7, 132.0, 132.3, 133.9, 135.5. ^{31}P NMR (121 MHz, C_6D_6, 295 K, ppm): δ (*P*CH$_3$), −14.2 (d, ^{2}J(PP) = 280 Hz, 1P); δ (*P*Ph$_2$), 46.8 (d, ^{2}J(PP) = 280 Hz, 1P).

[(1-*n*-Butylethenyl)[(2-diphenylphosphino)thiophenyl(*S,P*)]-trimethylphosphine]nickel(II) (6). Tetrakis(trimethylphosphine)nickel(0) (1.07 g, 2.95 mmol) was dissolved in 30 mL of THF. To this solution was added 2-(diphenylphosphino)benzenethiol (0.86 g, 2.92mmol) in 20 mL of THF at −80 °C. The mixture was stirred and immediately turned to dark red when it was warmed to 20 °C. 1-Hexyne (0.24 g, 2.92mmol) was injected into the above mixture. After 18 h, the reaction solution turned to brown. After filtration

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and evaporation of the filtrate under vacuum, 70 mL of pentane was employed to dissolve the residue. The filtrate was cooled at −27 °C, and orange crystals were obtained. Yield: 0.96 g (64%), mp (dec) > 97.5 °C. Anal. Calcd for $C_{27}H_{34}NiP_2S$ (511.27 g/mol): C, 63.43; H, 6.70. Found: C, 63.71; H, 6.96. IR (Nujol): $\nu = 1569$, 1548 (C=C) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$, 296 K, ppm): δ [P (CH_3)$_3$], 1.41 (d, ^2J(PH) = 8.7 Hz, 9H); δ (C-CH_2-CH$_2$), 1.75 (m, 2H); δ (C-CH$_2$-CH_2-CH_2), 0.91 (m, 4H); δ (CH$_2$−CH_3), 0.62 (m, 3H); δ (C=CH_2), 4.50 (s, 1H), 5.07 (s, 1H); δ (CH_{arom}), 6.80−8.06 (m, 14H). ^{13}C NMR (75 MHz, CDCl$_3$, 298 K, ppm): δ [P(CH$_3$)$_3$], 13.82 (t, $|^1J$(PC) + ^3J(PC)$|$ = 59 Hz); δ (CH$_2$-CH$_3$), 23.64; δ (C-CH$_2$-CH$_2$-CH$_2$), 30.76; δ (C-CH$_2$-CH$_2$), 39.16; δ (C=CH$_2$),114.0; δ (C=CH$_2$), 160.3; δ (C_{arom}), 121.6, 130.0, 130.9, 132.0, 133.7, 136.3, 137.1. ^{31}P NMR (121 MHz, CDCl$_3$, 296 K, ppm): δ [P(CH$_3$)$_3$], −12.8 (d, ^2J(PP) = 278 Hz, 1P); δ (PhPPh$_2$), 50.8 (d, ^2J(PP) = 278 Hz, 1P).

[(*Z,E*)-(1-(4-(trimethylsilylethenyl)phenyl)-2-(trimethylsilyl)-ethenyl)[(2-diphenylphosphino)thiophenyl(*S,P*)]trimethylphosphine]nickel(II) (7). Tetrakis(trimethylphosphine)nickel(0) (0.96 g, 2.64 mmol), 2-(diphenylphosphino)benzenethiol (0.77 g, 2.62 mmol), and 1,4-bis(timethylsilylethynyl)benzene (0.71 g, 2.63 mmol) were each dissolved in 25 mL of diethyl ether. To tetrakis-(trimethylphosphine)nickel(0) was added 2-(diphenylphosphino)-benzenethiol at −80 °C, giving a dark red suspension at ca. 20 °C. Addition of 1,4-bis(timethylsilylethynyl)benzene to this solution formed a brown suspension. After 18 h diethyl ether was removed in vacuo, and the residue was extracted with pentane/diethyl ether. From the pentane extract at −27 °C complex **7** was isolated as a yellow powder. Yield: 1.38 g (76%), mp (dec) > 120 °C. Anal. Calcd for $C_{31}H_{42}NiP_2SSi_2$ (623.53 g/mol): C, 59.72; H, 6.79. Found: C, 60.10; H, 6.95. IR (Nujol): $\nu = 2153$ (C≡C); 1597, 1569, 1524 (C=C) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$, 294 K, ppm): δ (SiCH_3), −0.158 (s, 9H), 0.230 (s, 9H); δ (PCH_3), 1.48 (d, ^2J(PH) = 8.4 Hz, 9H); δ (Ni-C-CH), 6.78 (s, 1H); δ (CH_{arom}), 6.81−8.18 (m, 18H). ^{13}C NMR (75 MHz, CDCl$_3$, 296 K, ppm): δ (SiCH$_3$), −0.34, 1.77; δ (PCH$_3$), 15.3 (d, ^1J(PC) = 26 Hz); δ (Ni-C-CH), 141.7 (dd, ^3J(PC) = 23 Hz, ^3J(PC) = 7.5 Hz); δ (Ni-C-CH), 157.0; δ (Ph-C≡C), 105.7; δ (Ph−C≡C), 93.6; δ (CH$_{\mathrm{arom}}$), 126.6, 128.0, 128.4, 129.4, 130.3, 130.7, 131.4, 132.0, 133.4, 133.8. ^{31}P NMR (121 MHz, CDCl$_3$, 295 K, ppm): δ (PCH$_3$)$_{(E)}$, −14.5 (d, ^2J(PP) = 345 Hz, 0.19P); δ (PCH$_3$)$_{(Z)}$, −12.9 (d, ^2J(PP) = 280 Hz, 0.81P); δ (PPh$_2$)$_{(E)}$, 49.0 (d, ^2J(PP) = 345 Hz, 0.19P); δ (PPh$_2$)$_{(Z)}$, 47.1 (d, ^2J(PP) = 280 Hz, 0.81P).

[Ni(2-PPh$_2$C$_6$H$_4$S)(*S,P*)(PMe$_3$)]$_2$(μ-C(=CH$_2$)-*p*-C$_6$H$_4$−C(=CH$_2$)−) (8). Addition of 2-(diphenylphosphino)benzenethiol (0.66 g, 2.24 mmol, in 20 mL of THF) to tetrakis(trimethylphosphine)-nickel(0) (0.82 g, 2.26 mmol, in 40 mL of THF) immediately afforded a dark red solution. 1,4-Bis(ethynyl)benzene (0.14 g, 1.11 mmol, in 20 mL of THF) was added to the above solution, and the mixture was stirred 18 h at room temperature. A yellow-brown solution was obtained. After evaporating the volatiles, the residue was extracted with pentane/diethyl ether. From the pentane extract at −20 °C complex **8** was obtained as yellow-brown microcrystals. Yield: 0.34 g (30%), mp (dec) > 130 °C. Anal. Calcd for $C_{52}H_{54}Ni_2P_4S_2$ (984.38 g/mol): C, 63.45; H, 5.53. Found: C, 63.67; H, 5.38. IR (Nujol): $\nu = 1567$, 1544 (C=C) cm^{-1}. ^{1}H NMR (300 MHz, C$_6$D$_6$, 294 K, ppm): δ (PCH_3), 1.09 (d, ^2J(PH) = 7.8 Hz, 18H); δ (Ni-C-CH_2), 5.11 (s, 2H), 6.03 (s, 2H); δ (CH_{arom}), 6.66−8.02 (m, 32H). ^{13}C NMR (75 MHz, C$_6$D$_6$, 298 K, ppm): δ (PCH$_3$), 13.69 (t, $|^1J$(PC) + ^3J(PC)$|$ = 50 Hz); δ (Ni-C-CH$_2$), 111.9; δ (Ni-C-CH$_2$), 164.4 s; δ (C-S), 158.9; δ (CH$_2$-C-C), 146.7; δ (C_{arom}), 119.3, 125.2, 126.7, 132.0, 135.0, 135.8, 136.5, 137.2. ^{31}P NMR (121 MHz, C$_6$D$_6$, 295 K, ppm): δ (PCH$_3$) −13.2 (d, ^2J(PP) = 280 Hz, 2P); δ (Ph-PPh$_2$), 51.5 (d, ^2J(PP) = 280 Hz, 2P).

Crystallographic Data for 3. $C_{29}H_{30}NiP_2S$, $M_r = 531.2$, crystal dimensions 0.24 × 0.22 × 0.20 mm, monoclinic, space group $P2(1)/c$, $a = 18.930(4)$ Å, $b = 9.722(2)$ Å, $c = 15.502(3)$ Å, $\beta = 105.691(4)°$, $V = 2746.6(10)$ Å^3, $T = 294(2)$ K, $Z = 4$, $D_c = 1.285$ g cm^{-3}, $\mu = 0.914$ mm^{-1}. Bruker AXS SMART APEX. A total of 14 953 reflections were collected, 5688 unique ($R_{\mathrm{int}} = 0.0860$), $\theta_{\max} = 26.59°$, multiscan absorption correction. R1 = 0.0643 (for 5688 reflections with $I > 2\sigma(I)$), wR2 = 0.1860 (all data). The structure was solved by direct methods and refined with full-matrix least-squares on all F^2 (SHELXL-97) with non-hydrogen atoms anisotropic.

Crystallographic Data for 5. $C_{26}H_{34}NiP_2SSi$, M_r =527.3, crystal dimensions 0.20 × 0.16 × 0.14 mm, triclinic, space group $P\bar{1}$, $a = 10.589(2)$ Å, $b = 11.128(2)$ Å, $c = 12.139(2)$ Å, $\alpha = 104.4(3)°$, $\beta = 104.69(3)°$, $\gamma = 90.20(3)°$, $V = 1336.7(5)$ Å^3, $T = 273(2)$ K, $Z = 2$, $D_c = 1.310$ g cm^{-3}, $\mu = 0.980$ mm^{-1}. A total of 7761 reflections were collected, 5223 unique (R_{int} =0.0678), $\theta_{\max} = 27.10°$, semiempirical absorption correction. R1 = 0.0437 (for 5223 reflections with $I > 2\sigma(I)$), wR2 = 0.1183 (all data). The structure was solved by direct methods and refined with full-matrix least-squares on all F^2 (SHELXL-97) with non-hydrogen atoms anisotropic.

CCDC-614951 (**3**) and CCDC-614952 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Supporting Information Available: Tables containing full X-ray crystallographic data for **3** and **5**. These materials are available free of charge via the Internet at http://pubs.acs.org.

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