980 *Organometallics* **2001,** *20,* 980−989

Preparation and Reactivity of Nickel(0) Complexes with η^2-Coordinated Alkynylphosphines

Martin A. Bennett,* Jeffrey Castro, Alison J. Edwards, Mike R. Kopp,
Eric Wenger, and Anthony C. Willis

*Research School of Chemistry, Australian National University,
Canberra, Australian Central Territory 0200, Australia*

Received October 18, 2000

The η^2-alkynylphosphine complexes [Ni(η^2-Ph$_2$PC≡CR)(dcpe)] (R = Me (**1a**), CO$_2$Me (**1b**), Ph (**1c**)), which are formed by displacement of ethylene from [Ni(C$_2$H$_4$)(dcpe)] by the corresponding alkynylphosphine, react with HCl (1 equiv) to give five-coordinate nickel(II) complexes, [NiCl{C(=CHR)PPh$_2$-κP,C^1}(dcpe)] (R = Me (**2a**), CO$_2$Me (**2b**), Ph (**2c**)), which contain a coordinated methylenephosphanickelacyclopropane fragment. In the case of **1a**, the proton adds regiospecifically at the carbon atom bearing the methyl group. This mode of addition is favored for **1b**,**c**, but small amounts of the addition products [NiCl{η^1-*C*(*R*)=CH(PPh$_2$)}(dcpe)] (R = CO$_2$Me (**3b**), Ph (**3c**)), arising from addition at the PPh$_2$-bearing carbon atoms, are also formed. Unsaturated molecules such as CS$_2$ and CO$_2$ insert into the Ni−P bonds of complexes **2a**,**c** to give five-membered nickelacycles. Complexes **1a**, **2a**,**c**, and **3c** have been structurally characterized by X-ray diffraction analysis.

Introduction

As potentially bifunctional ligands, (alkynyl)diphenylphosphines of general formula Ph$_2$PC≡CR have been used extensively in organometallic and coordination chemistry, especially for the formation of polynuclear metal complexes.[1] In general, P-donor coordination of (alkynyl)diphenylphosphines is favored kinetically. In the case of bis(diphenylphosphino)acetylene (dppa),[2] this property has been used to prepare numerous complexes or clusters in which dppa acts as a bridging ligand through its phosphorus atoms.[3] Alkynylphosphines are also known to react with polymetallic species by cleavage of the phosphorus−carbon bond.[4]

Only a few compounds are known in which alkyne coordination is favored over P-donor coordination, e.g. [Co$_2$(CO)$_6${μ-η^2-(C$_6$F$_5$)$_2$PC≡CR}] (R = Me, Ph),[1a] [(CpNi)$_2$-(μ-η^2-Ph$_2$PC≡C-^{t}Bu)],[1b] and [W(CO)(η^2-Ph$_2$PC≡CPPh$_2$)-(S$_2$CNEt$_2$)$_2$];[5] more commonly the Ph$_2$PC≡CR ligands bridge a pair of metal atoms via phosphorus and the triple bond, as in [Ni$_2$(CO)$_2$(μ-η^1:η^2-Ph$_2$PC≡C-^{t}Bu)].[6] Recently, however, complexes having Ph$_2$PC≡CPh η^2-coordinated to a NiP$_2$ fragment were identified as byproducts of the double-insertion reactions of this alkynylphosphine with benzyne− and 4,5-difluorobenzyne−nickel(0) complexes.[7]

It was therefore of interest to investigate nickel(0) complexes containing η^2-coordinated alkynylphosphines in more detail. In this paper we report the preparation, characterization, and some reactions of several complexes of this type.

Results

Treatment of [Ni(C$_2$H$_4$)(dcpe)] with 1 equiv of Ph$_2$PC≡CR (R = Me, CO$_2$Me) at 0 °C in diethyl ether gives initially orange solutions, which are believed to contain P-coordinated NiL$_3$ species. When the reaction of [Ni(C$_2$H$_4$)(dcpe)] with Ph$_2$PC≡CMe is monitored by ^{31}P NMR spectroscopy at 0 °C, a broad triplet at δ 1.4

---

[1] Selected references: (a) Patel, H. A.; Carty, A. J.; Hota, N. K. *J. Organomet. Chem.* **1973**, *50*, 247. (b) Carty, A. J.; Paik, H. N.; Ng, T. W. *J. Organomet. Chem.* **1974**, *74*, 279. (c) Carty, A. J.; Jacobson, S. E.; Simpson, R. J.; Taylor, N. J. *J. Am. Chem. Soc.* **1975**, *97*, 7254. (d) Taylor, N. J.; Carty, A. J. *J. Chem. Soc., Dalton Trans.* **1976**, 799. (e) Carty, A. J. *Pure Appl. Chem.* **1982**, *54*, 113. (f) Sappa, E.; Predieri, G.; Tiripicchio, A.; Camellini, M. T. *J. Organomet. Chem.* **1985**, *297*, 103. (g) Nucciarone, D.; MacLaughlin, S. A.; Taylor, N. J.; Carty, A. J. *Organometallics* **1988**, *7*, 106. (h) Charkas, A. A.; Randall, L. H.; MacLaughlin, S. A.; Mott, G. N.; Taylor, N. J.; Carty, A. J. *Organometallics* **1988**, *7*, 969. (i) Sappa, E.; Pasquinelli, G.; Tiripicchio, A.; Camellini, M. T. *J. Chem. Soc., Dalton Trans.* **1989**, 601. (j) Braga, D.; Benvenutti, M. H. A.; Grepioni, F.; Vargas, M. D. *J. Chem. Soc., Chem. Commun.* **1990**, 730. (k) Lang, H.; Zsolnai, L. *Chem. Ber.* **1991**, *124*, 259. (l) Forniés, J.; Lalinde, E.; Martín, A.; Moreno, M. T.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1995**, 1333. (m) Moldes, I.; Ros, J. *Inorg. Chim. Acta* **1995**, *232*, 75. (n) Louattani, E.; Suades, J.; Alvarez-Larena, A.; Piniella, J. F.; Germain, G. *J. Organomet. Chem.* **1996**, *506*, 121. (o) Dickson, R. S.; de Simone, T.; Parker, R. J.; Fallon, G. D. *Organometallics* **1997**, *16*, 1531. (p) Ara, I.; Falvello, L. R.; Fernández, S.; Forniés, J.; Lalinde, E.; Martín, A.; Moreno, M. T. *Organometallics* **1997**, *16*, 5923.

[2] Abbreviations: dcpe = bis(dicyclohexylphosphino)ethane, Cy$_2$PCH$_2$CH$_2$PCy$_2$; dppm = bis(diphenylphosphino)methane, Ph$_2$PCH$_2$PPh$_2$; dppa = bis(diphenylphosphino)acetylene, Ph$_2$PC$_2$PPh$_2$.

[3] (a) Orama, O. *J. Organomet. Chem.* **1986**, *314*, 273 and references therein. (b) Hogarth, G.; Norman, T. *Polyhedron* **1996**, *15*, 2859 and references therein. (c) Sappa, E. *J. Organomet. Chem.* **1988**, *352*, 327.

[4] (a) Bruce, M. I.; Williams, M. L.; Patrick, J. M.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1985**, 1229. (b) Daran, J.-C.; Cabrera, E.; Bruce, M. I.; Williams, M. L. *J. Organomet. Chem.* **1987**, *319*, 239. (c) Bruce, M. I.; Liddell, M. J.; Tiekink, E. R. T. *J. Organomet. Chem.* **1990**, *391*, 81.

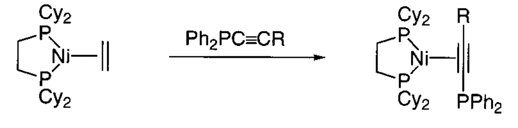
[5] (a) Ward, B. C.; Templeton, J. L. *J. Am. Chem. Soc.* **1980**, *102*, 1532. (b) Nickel, T. M.; Wau, S. Y. W.; Went, M. J. *J. Chem. Soc., Chem. Commun.* **1989**, 775. (c) Powell, A. K.; Went, M. J. *J. Chem. Soc., Dalton Trans.* **1992**, 439.

[6] Paik, H. N.; Carty, A. J.; Dymock, K.; Palenik, G. J. *J. Organomet. Chem.* **1974**, *70*, C17.

[7] Bennett, M. A.; Cobley, C. J.; Rae, A. D.; Wenger, E.; Willis, A. C. *Organometallics* **2000**, *19*, 1522.

10.1021/om000895o CCC: $20.00

Scheme 1



1a: R = Me
1b: R = CO$_2$Me
1c: R = Ph

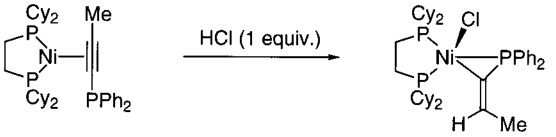
assigned to the P-coordinated alkynylphosphine of [Ni(η^1-Ph$_2$PC≡CMe)(dcpe)] and a multiplet at δ_P 40.0−40.9 due to coordinated dcpe are observed initially. After 30 min at room temperature, these signals disappear and the reaction mixtures turn yellow, owing to the quantitative formation of the corresponding [Ni(η^2-Ph$_2$PC≡CR)(dcpe)] complexes (R = Me (**1a**), CO$_2$Me (**1b**)) (Scheme 1). Although **1a** is stable in solution in the absence of air, the isolated solid decomposes on storage, even at −20 °C in the absence of light. The carboxylate analogue **1b** is more stable and can be stored at room temperature under N$_2$ for several weeks. The ^{31}P NMR spectrum of **1a** resembles closely that of the similarly prepared phenyl analogue [Ni(η^2-Ph$_2$PC≡CPh)(dcpe)] (**1c**),[7] consisting of three doublets of doublets, at ca. δ 72 for the phosphorus atom of the dcpe ligand trans to the alkyne carbon atom bearing the PPh$_2$ group (C^1), at ca. δ 68 for the other phosphorus atom of dcpe, and at ca. δ −15 for the diphenylphosphino group; the shielding of the last signal shows clearly that the PPh$_2$ moiety is not coordinated. In **1b**, the phosphorus atoms of dcpe are slightly less shielded and the coupling constants are slightly smaller than in **1a**.

The ^{13}C NMR chemical shifts of the quaternary carbons of the triple bond of Ph$_2$PC^1≡C^{2}R are deshielded by ca. 40 ppm compared with those of the free alkynylphosphines,[7,8] showing that these carbon atoms are coordinated to the metal center. The signals appear as doublets of doublets of doublets at δ_C 120.42 (**1a**), 136.43 (**1b**), and 140.38 (**1c**)[9] for C^1 and at δ_C 146.63 (**1a**), 140.62 (**1b**), and 150.27 (**1c**) for C^2. The assignments of C^1 and C^2 are based on the observation that the coupling observed for J(C^{1}P) (20−45 Hz) is greater than J(C^{2}P) (18−19 Hz). The coupling constants between the two alkynyl carbons and the phosphorus atoms of the dcpe ligand are similar to the values reported for other unsymmetrical alkynes coordinated to a Ni^{0}P$_2$ fragment.[10]

Evidence for coordination of the triple bond comes also from the infrared spectra, which show a band due to C≡C stretching for **1a** at 1758 cm^{-1} and for **1b** at 1735 cm^{-1}. The structure of complex **1a** has been confirmed by single-crystal X-ray diffraction (see below).

Unsaturated molecules such as dimethyl acetylenedicarboxylate or CO displace the alkynylphosphine from **1a**, there being no evidence for insertion into the Ni−C bond. The reaction of **1b** with CO also causes decomposition to give [Ni(CO)$_2$(dcpe)] and [Ni(dcpe)$_2$], but in this case no free Ph$_2$PC≡CCO$_2$Me was observed. Monitoring by ^{31}P NMR spectroscopy indicates the presence of other unidentified phosphorus-containing species.

Scheme 2



1a

2a

The main product from the reaction of [Ni(η^2-Ph$_2$PC≡CMe)(dcpe)] (**1a**) with 1 equiv of HCl in diethyl ether is a thermally sensitive red solid whose ^{31}P NMR spectrum shows a highly shielded doublet of doublets at δ_P −100.2 ppm in addition to two doublets of doublets in the region of δ 73.0−77.0 due to coordinated dcpe. Some [NiCl$_2$(dcpe)], identified by its ^{31}P NMR singlet at ca. δ 82.2, is also formed; this is the main nickel-containing product if an excess of HCl is used. The signals of the red solid are broad in benzene, diethyl ether, or thf but sharp in CD$_2$Cl$_2$. The associated P−P coupling constants of 181.9 and 29.9 Hz are characteristic of trans and cis ^2J(PP) couplings, respectively, with dcpe, showing clearly that the phosphorus atom of PPh$_2$ is now coordinated. The ^{1}H and ^{13}C NMR spectra (see Experimental Section) show the presence of a vinylic CH group, resulting from protonation of the alkynyl function, and a quaternary carbon atom bound to nickel, while the FAB mass spectrum shows the highest mass peak at m/z 705 similar to that observed in the FAB mass spectrum of **1a**. All these data are consistent with a Ni(dcpe) complex containing a vinylphosphine group that is formed by protonation of **1a** at C^2 and is coordinated via both phosphorus and the carbon atom C^1. They do not, however, establish whether the complex is the chloride salt of a four-coordinate cation or a five-coordinate complex with a labile chloride. The formulation of the complex as five-coordinate [NiCl{C(=CHMe)-PPh$_2$-$\kappa P,C^1$}(dcpe)] (**2a**) (Scheme 2) has been confirmed by single-crystal X-ray analysis (see below).

Complex **2a** is fairly air-stable as a solid or in solution up to 50 °C in dry aprotic solvents. In the presence of moisture, decomposition occurs more rapidly to form the (Z)-vinylphosphine Ph$_2$PCH=CHMe. This compound is also obtained, together with [NiCl$_2$(dcpe)], after addition of more HCl to **2a**, or it can be isolated in 65% overall yield, based on [Ni(C$_2$H$_4$)(dcpe)], after in situ reaction of **1a** with HCl (2 equiv). The product has been fully characterized, and the spectroscopic data are identical with those reported for (Z)-Ph$_2$PCH=CHMe.[11,12] The protonation of the triple bond is apparently irreversible: complex **2a** is inert toward bases such as NHEt$_2$ and CaH$_2$.

The alkynylphosphine complex **1c** reacts analogously with HCl to give [NiCl{C(=CHPh)PPh$_2$-$\kappa P,C^1$}(dcpe)] (**2c**) as the main product, which has been isolated as air-stable red crystals and its structure confirmed by X-ray crystallography (see below) (Scheme 3). The NMR data are similar to those of **2a**, but the ^{31}P NMR signals are broad at room temperature. Cooling to −20 °C was required to obtain a well-resolved spectrum (see Ex-

---

[8] Louattani, E.; Lledós, A.; Suades, J.; Alvarez-Larena, A.; Piniella, J. F. *Organometallics* **1995**, *14*, 1053.

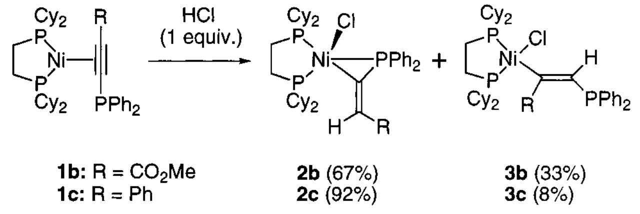
[9] The previously reported ^{13}C chemical shift for C^1 of **1b**[7] was misassigned. The correct ^{13}C NMR data are given in the Experimental Section.

[10] Bartik, T.; Happ, B.; Iglewsky, M.; Bandmann, H.; Boese, R.; Heimbach, P.; Hoffmann, T.; Wenschuh, E. *Organometallics* **1992**, *11*, 1235.

[11] Grim, S. O.; Molenda, R. P.; Mitchell, J. D. *J. Org. Chem.* **1980**, *45*, 250.

[12] Duncan, M.; Gallagher, M. J. *Org. Magn. Reson.* **1981**, *15*, 37.

Scheme 3

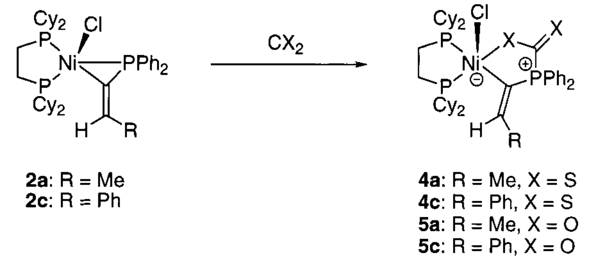


1b: R = CO_2Me
1c: R = Ph

2b (67%)
2c (92%)

3b (33%)
3c (8%)

Scheme 4

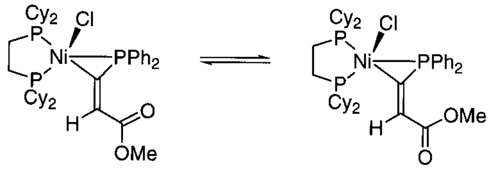


2a: R = Me
2c: R = Ph

4a: R = Me, X = S
4c: R = Ph, X = S
5a: R = Me, X = O
5c: R = Ph, X = O

perimental Section). However, the protonation is not as regiospecific as for **2a**. A second product (**3c**) is formed in ca. 5% yield whose ^{31}P NMR spectrum shows doublets of doublets at δ_P 62.0 and 66.5 for the dcpe ligand and a doublet of doublets at δ_P −28.8 for the remaining phosphorus atom. The chemical shift of the latter signal is in the range expected for an uncoordinated vinyldiphenylphosphine,[11,12] which could result from protonation at C^1. Unfortunately, the ^1H and ^{13}C NMR spectra are very broad and uninformative, although there is a doublet of doublets at δ_H 6.36 in the ^1H NMR spectrum corresponding to a vinylic proton. An X-ray crystallographic study has shown that **3c** is indeed $[NiCl\{\eta^1\text{-}C(Ph){=}CH(PPh_2)\}(dcpe)]$ (see below).

Similar reaction of **1b** with HCl yields a mixture of two species in a 3:2 ratio, which are believed to be $[NiCl\{C({=}CHCO_2Me)PPh_2\text{-}\kappa P,C^1\}(dcpe)]$ (**2b**) and $[NiCl\{\eta^1\text{-}C(CO_2Me){=}CH(PPh_2)\}(dcpe)]$ (**3b**), respectively. The structural assignments are based on the ^{31}P NMR spectrum of the mixture, as the compounds could not be separated. The signals of **3b** are sharp and well-defined and are similar to those of **3c**, whereas those of **2b** are very broad: one at δ_P −97.1 for P^1 and two at δ_P 68.0−69.1 for coordinated dcpe in CD_2Cl_2 at room temperature. The peaks sharpen on warming to +60 °C, leading to a well-defined triplet for P^1. The signals of **2b** split when the solution is cooled to −90 °C, showing that two distinct species are present. The parameters for the predominant species are very similar to those of **2c**, i.e., a broad doublet at δ_P −92.5 and broad signals for the dcpe phosphorus atoms in the region 73.0−78.0 ppm, whereas the ^{31}P NMR chemical shifts for the minor species are more shielded, e.g. δ_P −105.0 for P^1 and δ_P 65.0−70.0 for dcpe. This behavior is indicative of a fast exchange between two isomers, which may arise from syn and anti arrangements of the C=C and C=O bonds of the α,β-unsaturated carboxylate group (eq 1).



(1)

The reactions of complexes **2a**,**c** with small molecules have been investigated briefly. Complex **2a** reacts rapidly with CO and with dimethyl acetylenedicarboxylate at room temperature to give uncharacterizable mixtures of products but is unreactive toward diphenylacetylene, methyl 2-butynoate, and 3-(diphenylphosphino)-2-propyne under the same conditions. The reactions of **2a** and **2c** with CO_2 and CS_2 give insertion products, as shown by ^{31}P NMR spectroscopy, but are accompanied by considerable decomposition. Thus, addition of CS_2 to a solution of **2a** causes replacement of the resonance due to P^1 at δ_P −100.2 by a doublet of doublets at δ_P 30.3 and a small shift for the dcpe resonances. The small coupling constants observed between P^1 and the dcpe phosphorus atoms (5.7 and 2.2 Hz) suggest that P^1 is no longer coordinated; moreover, its chemical shift is outside the range of δ_P 45.0−50.0 that is characteristic of five-membered phosphanickelacycles[13−15] but is similar to the values reported for cationic phosphinodithiocarboxylato complexes that arise from insertion of CS_2 into nickel−, palladium−, or platinum−phosphine bonds.[16−18] These data suggest that CS_2 has inserted into the Ni−P rather than the Ni−C bond of the three-membered nickelacycle, leading to the zwitterionic species **4a** (Scheme 4).[19] The ^{13}C resonance of the inserted CS_2 group appears as a doublet of doublets at δ_C 236.45, with a coupling constant of 71.4 Hz to the adjacent phosphorus atom of PPh_2. The ^{13}C and $^2J(PC)$ values are almost identical with those of the zwitterionic five-membered zirconacycle obtained by reaction of CS_2 with the zirconaindene $[Cp_2Zr\{o\text{-}C_6H_4CH{=}C(PPh_2)\}]$,[20] thus providing further support for the suggested structure.

The reaction of CS_2 with the phenyl analogue **2c** is very slow, and after 5 days at 28 °C, the yield of the corresponding insertion product is only 40%, as estimated by ^{31}P NMR spectroscopy. In addition, the solution contains starting material, $[NiCl_2(dcpe)]$, and other decomposition products; therefore, the insertion compound could not be isolated. Complexes **2a**,**c** also react slowly with technical grade CO_2 at room temperature, but the reactions are not clean and the products are unstable. For example, a solution of the adduct prepared from **2c** decomposed overnight, releasing CO_2, as shown by ^{13}C NMR spectroscopy. The main products are believed to be the nickelacycles $[NiCl\{C({=}CHR)\text{-}PPh_2C(O)O\}(dcpe)]$ (R = Me (**5a**), Ph (**5c**)) (Scheme 4), since their ^{31}P NMR spectra are similar to those of **4a**,**c**: i.e., one doublet of doublets at ca. δ_P 32.0 for P^1 and two others in the region δ_P 62.0−69.5 for dcpe. Surprisingly, similar reactions attempted with dry $^{13}CO_2$ did not give any insertion products, which suggests that water or

---

(13) Carty, A. J.; Johnson, D. K.; Jacobson, S. E. *J. Am. Chem. Soc.* **1979**, *101*, 5612.

(14) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229.

(15) Muller, G.; Panyella, D.; Rocamora, M.; Sales, J.; Font-Bardia, M.; Solans, X. *J. Chem. Soc., Dalton Trans.* **1993**, 2959.

(16) Werner, H.; Bertleff, W. *Chem. Ber.* **1980**, *113*, 267.

(17) Bertleff, W.; Werner, H. *Z. Naturforsch.* **1982**, *37B*, 1294.

(18) Usón, R.; Forniés, J.; Navarro, R.; Usón, M. A.; Garcia, M. P.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1984**, 345.

(19) For a review on the reactions of CS_2 and CO_2 with organometallic complexes, see: Pandey, K. K. *Coord. Chem. Rev.* **1995**, *140*, 37.

(20) Cadierno, V.; Zablocka, M.; Donnadieu, B.; Igau, A.; Majoral, J.-P. *Organometallics* **1999**, *18*, 1882.

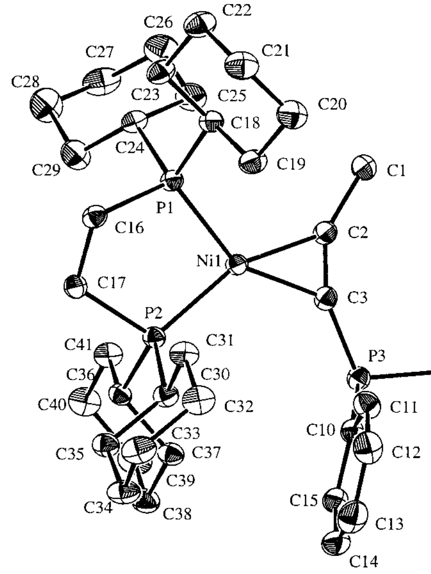


Figure 1. Molecular structure of **1a** with selected atom labeling. Thermal ellipsoids show 30% probability levels; hydrogen atoms have been omitted for clarity.

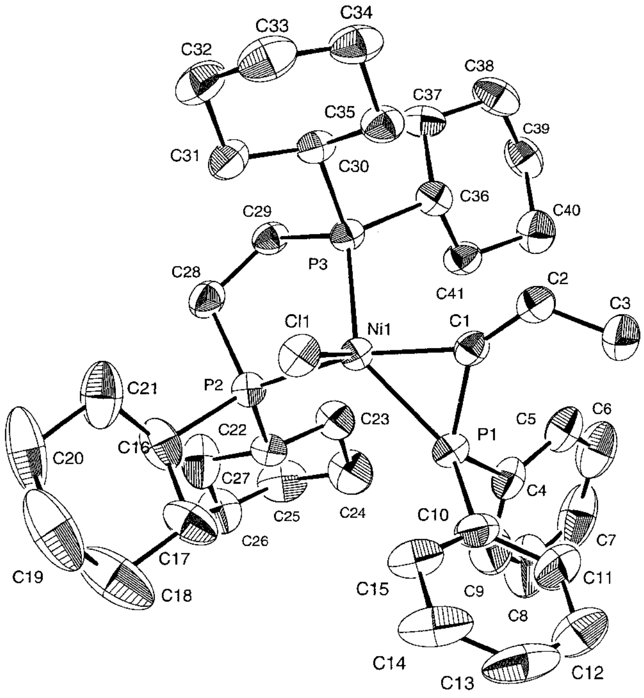


Figure 2. Molecular structure of **2a** with selected atom labeling. Thermal ellipsoids show 50% probability levels; hydrogen atoms have been omitted for clarity.

oxygen, both present in technical grade CO_2, may catalyze the insertion.

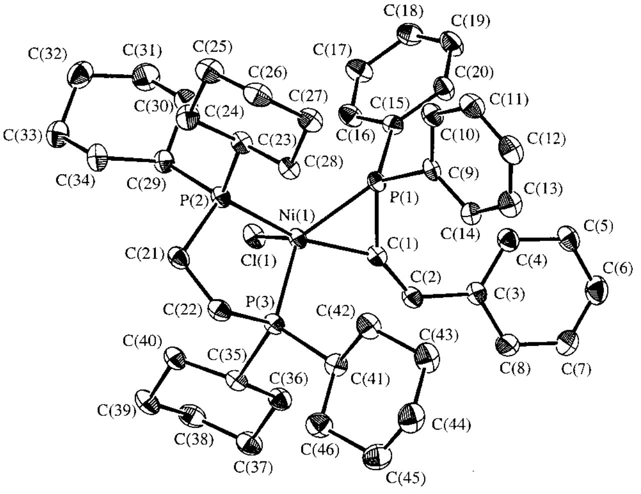


Figure 3. Molecular structure of **2c** with selected atom labeling. Thermal ellipsoids show 30% probability levels; hydrogen atoms have been omitted for clarity.

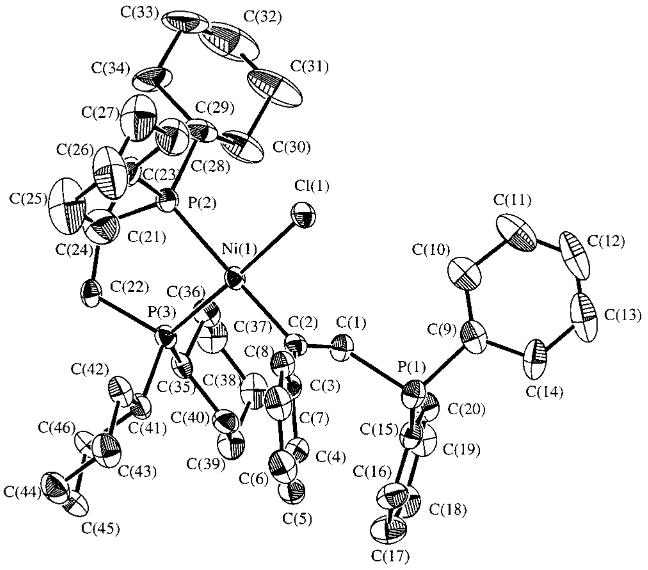


Figure 4. Molecular structure of **3c** with selected atom labeling. Thermal ellipsoids show 30% probability levels; hydrogen atoms have been omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for 1a

Ni(1)−P(1)	2.1478(8)	Ni(1)−P(2)	2.1613(9)
Ni(1)−C(2)	1.869(3)	Ni(1)−C(3)	1.913(3)
C(1)−C(2)	1.489(5)	C(2)−C(3)	1.280(4)
P(3)−C(3)	1.763(3)		
P(1)−Ni(1)−P(2)	91.46(3)	P(1)−Ni(1)−C(2)	110.2(1)
P(2)−Ni(1)−C(3)	118.8(1)	C(1)−C(2)−C(3)	147.6(3)
P(3)−C(3)−C(2)	154.9(3)	Ni(1)−C(3)−C(2)	68.4(2)

Molecular Structures of [Ni(η^2-$Ph_2PC{\equiv}CMe$)(dcpe)] (1a), [NiCl{C(=CHMe)PPh_2-$\kappa P,C^1$}(dcpe)] (2a), [NiCl{C(=CHPh)PPh_2-$\kappa P,C^1$}(dcpe)] (2c), and [NiCl{η^1-C(Ph)=CH(PPh_2)}(dcpe)] (3c). The molecular geometries of **1a**, **2a**,**c**, and **3c** are shown, together with the atom labeling, in Figures 1−4, respectively; corresponding selected interatomic distances and angles are listed in Tables 1−4. The coordination of complex **1a** is trigonal planar with the C≡C bond and its two substituents laying in the NiP_2 plane, as expected for nickel(0)−alkyne complexes bearing chelating diphosphine ligands.[10,21,22] The deviations from the coordination plane of the alkynyl carbon atoms C(2) and C(3) are only −0.016 and −0.076 Å, respectively. The Ni−C distances, 1.869(3) and 1.913(3) Å, the slightly elongated bond length for the coordinated triple bond with respect to that of a free alkyne, and the angles of the alkynyl substituents, 147.6° for C(1)−C(2)−C(3) and 154.9° for

---

(21) Bonrath, W.; Pörschke, K. R.; Wilke, G.; Angermund, K.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 833.

(22) Edelbach, B. L.; Lachicotte, R. J.; Jones, W. D. *Organometallics* **1999**, *18*, 4660.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for 2a

Ni(1)−P(1)	2.1862(11)	Ni(1)−P(2)	2.2272(11)
Ni(1)−P(3)	2.1699(11)	Ni(1)−Cl(1)	2.4220(10)
Ni(1)−C(1)	1.903(4)	P(1)−C(1)	1.747(4)
C(1)−C(2)	1.324(5)	C(2)−C(3)	1.500(6)
P(1)−Ni(1)−P(2)	112.63(4)	P(1)−Ni(1)−C(1)	49.98(11)
P(1)−Ni(1)−P(3)	136.24(5)	P(2)−Ni(1)−P(3)	88.88(4)
P(2)−Ni(1)−C(1)	158.70(12)	C(1)−C(2)−C(3)	125.8(4)
P(1)−C(1)−C(2)	137.4(3)	Ni(1)−C(1)−C(2)	148.5(3)
Cl(1)−Ni(1)−P(2)	101.04(4)	Cl(1)−Ni(1)−C(1)	95.62(11)
Cl(1)−Ni(1)−P(3)	110.19(4)	Cl(1)−Ni(1)−P(1)	102.68(4)
Ni(1)−P(1)−C(1)	56.6(2)	Ni(1)−C(1)−P(1)	73.5(2)

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for 2c

Ni(1)−P(1)	2.1734(8)	Ni(1)−P(2)	2.2300(9)
Ni(1)−P(3)	2.1952(9)	Ni(1)−Cl(1)	2.4119(8)
Ni(1)−C(1)	1.903(3)	P(1)−C(1)	1.751(3)
C(1)−C(2)	1.328(5)	C(2)−C(3)	1.478(4)
P(1)−Ni(1)−P(2)	112.49(3)	P(1)−Ni(1)−C(1)	50.34(9)
P(1)−Ni(1)−P(3)	135.96(4)	P(2)−Ni(1)−P(3)	88.62(3)
P(2)−Ni(1)−C(1)	161.28(9)	C(1)−C(2)−C(3)	129.2(3)
P(1)−C(1)−C(2)	142.8(2)	Ni(1)−C(1)−C(2)	144.3(2)
Cl(1)−Ni(1)−P(2)	98.07(3)	Cl(1)−Ni(1)−C(1)	94.78(9)
Cl(1)−Ni(1)−P(3)	108.44(3)	Cl(1)−Ni(1)−P(1)	106.24(3)
Ni(1)−P(1)−C(1)	56.79(10)	Ni(1)−C(1)−P(1)	72.87(12)

Table 4. Selected Bond Lengths (Å) and Bond Angles (deg) for 3c

P(1)−C(1)	1.823(7)	Ni(1)−P(2)	2.212(2)
Ni(1)−P(3)	2.148(2)	Ni(1)−Cl(1)	2.230(2)
Ni(1)−C(2)	1.944(7)	C(1)−C(2)	1.322(9)
C(2)−C(3)	1.50(1)		
P(2)−Ni(1)−P(3)	88.73(8)	P(2)−Ni(1)−Cl(1)	89.68(8)
P(2)−Ni(1)−C(2)	177.3(2)	Ni(1)−C(2)−C(3)	116.8(5)
P(1)−C(1)−C(2)	126.2(6)	Ni(1)−C(2)−C(1)	119.5(6)
C(1)−C(2)−C(3)	123.3(7)	Cl(1)−Ni(1)−C(2)	89.7(2)

C(2)−C(3)−P(3), are in the normal range for such complexes.

The molecular structure of the five-coordinated complex **2a** shows a distorted-trigonal-bipyramidal arrangement around the nickel(II) center, the carbon atom C(1) being −0.437 Å from the trigonal plane defined by Ni(1)−Cl(1)−P(2). The molecule contains a three-membered phosphametallacycle formed by Ni(1), P(1), and C(1). The vinylic carbon atom C(2) and its methyl substituent C(3) are only 0.118 and 0.248 Å, respectively, out of the plane of the three-membered ring. The Ni−C(1) distance of 1.903(4) Å is slightly shorter than the range of 1.92−1.95 Å reported for Ni−aryl or Ni−vinyl bonds in metallacycles, and the P(1)−C(1) distance (1.747(4) Å) is also short compared to the average P−C distance of 1.85 Å; these shortenings are probably a consequence of the strain in the three-membered ring. The Ni−P(1) distance (2.1862(11) Å) is similar to that of the two other Ni−P bonds in the molecule. Several phosphametallacyclopropane complexes have been structurally characterized (see examples in Table 5). Two complexes with group 10 metals have been reported, but none with nickel. They show the P−C bond lengths in the metallacycle to be quite similar to that measured in **2a** (or in **2c**, see below): i.e., 1.76 Å in [$\overline{\text{Pt(CH(Ph)}}$-$\overline{\text{PBz}_2)}$(PBz$_3$)(2-Me-1,2-B$_{10}C_2H_{10}$)]^{23} or 1.754 Å in the dimer [$\overline{\text{PdCl\{CH(}\mu\text{-C}_6\text{H}_4\text{C}_6\text{H}_4\text{N)P}}$Me(C$_6H_2{}^tBu_3$)}]$_2$.[24] The angles in the metallacycles of the latter complexes are, however, quite different from those in **2a**, due to the absence of an sp^2 carbon atom (see Discussion).

Structural analogies with a nickelaphosphacyclopropane are provided by nickel(0) complexes with η^2-phosphaalkene groups. These species have P−C distances similar to those of **2a** (1.83 Å for [Ni{η^2-P(2,6-Me$_2$C$_6$H$_3$)═CPh$_2$}(bipy)][25,26] and 1.77 Å for [Ni{η^2-P(CH(SiMe$_3$)$_2$)═C(SiMe$_3$)$_2$}(PMe$_3$)$_2$][27,28]), values which are closer to a single rather than a double bond between the phosphorus and the carbon atoms of the coordinated phosphaalkenes. These species, however, have Ni−P and Ni−C distances longer than those of **2a**. The bond lengths of C(1)−C(2) (1.324(5) Å) and C(2)−C(3) (1.500(6) Å) are typical of double and single bonds, respectively, and the vinylic character of C(1)−C(2) is confirmed by the C(1)−C(2)−C(3) angle of 125.8°. The Ni−Cl distance of 2.4220(10) Å lies in the middle of the range known for the limited number of structurally characterized pentacoordinate chloronickel(II) tertiary phosphine complexes. They range from 2.169 Å for the trigonal-bipyramidal [NiCl{(Ph$_2$PCH$_2$CH$_2$)$_3$N}]PF$_6$[29] to 2.699 Å for the square-pyramidal complex [NiCl{CH$_2$(PPhCH$_2$CH$_2$NH$_2$)$_2$}]PF$_6$.[30,31]

Apart from the substituent on C(2), the molecular structure of **2c** is practically identical with that of **2a**. The phenyl substituent is cis to the PPh$_2$ group, with contact distances between the two groups indicative of steric interactions.

Complex **3c** shows a conventional square-planar environment around the nickel atom, including the η^1-vinyl ligand −C(Ph)═CH(PPh$_2$), in which the PPh$_2$ and Ph groups are mutually cis. The Ni−P distances to Cy$_2$PCH$_2$CH$_2$PCy$_2$ are 2.212(2) Å (trans to the vinyl group) and 2.148(2) Å (trans to Cl), reflecting the higher trans influence of the η^1-vinyl ligand. The C═C and C−P distances (1.322(9) and 1.823(9) Å, respectively) are unexceptional. The phosphorus atom bonded to carbon C(1) of the vinyl group is completely enclosed by the

---

[23] Bresadola, S.; Bresciani-Pahor, N.; Longato, B. *J. Organomet. Chem.* **1979**, *179*, 73.

[24] van der Sluis, M.; Beverwijk, V.; Termaten, A.; Bickelhaupt, F.; Kooijman, H.; Spek, A. L. *Organometallics* **1999**, *18*, 1402.

[25] van der Knaap, T. A.; Jenneskens, L. W.; Meeuwissen, H. J.; Bickelhaupt, F.; Walther, D.; Dinjus, E.; Uhlig, E.; Spek, A. L. *J. Organomet. Chem.* **1983**, *254*, C33.

[26] Spek, A. L.; Duisenberg, A. J. M. *Acta Crystallogr., Sect. C* **1987**, *43*, 1216.

[27] Cowley, A. H.; Jones, R. A.; Stewart, C. A.; Stuart, A. L.; Atwood, J. L.; Hunter, W. E.; Zhang, H.-M. *J. Am. Chem. Soc.* **1983**, *105*, 3737.

[28] Cowley, A. H.; Jones, R. A.; Lasch, J. G.; Norman, N. C.; Stewart, C. A.; Stuart, A. L.; Atwood, J. L.; Hunter, W. E.; Zhang, H. M. *J. Am. Chem. Soc.* **1984**, *106*, 7015.

[29] Di Vaira, M.; Sacconi, L. *J. Chem. Soc., Dalton Trans.* **1975**, 493.

[30] Scanlon, L. G.; Tsao, Y.-Y.; Toman, K.; Cummings, S. C.; Meek, D. W. *Inorg. Chem.* **1982**, *21*, 2707.

[31] Most of the Ni−Cl bond lengths in five-coordinate tris- or tetrakis(tertiary phosphine) complexes fall in the range 2.23−2.48 Å; see for example: (a) Font-Bardía, M.; González-Platas, J.; Muller, G.; Panyella, D.; Rocamora, M.; Solans, X. *J. Chem. Soc., Dalton Trans.* **1994**, 3075. (b) Manojlovic-Muir, L.; Mirza, H. A.; Sadiq, N.; Puddephatt, R. J. *Inorg. Chem.* **1993**, *32*, 117. (c) Kyba, E. P.; Davis, R. E.; Fox, M. A.; Clubb, C. N.; Liu, S.-T.; Reitz, G. A.; Scheuler, V. J.; Kashyap, R. P. *Inorg. Chem.* **1987**, *26*, 1647. (d) Fox, M. A.; Chandler, D. A.; Kyba, E. P. *J. Coord. Chem.* **1992**, *25*, 1. (e) Powell, H. M.; Chui, K. M. *J. Chem. Soc., Dalton Trans.* **1976**, 1301. (f) Wartchow, R. *Z. Kristallogr.— New Cryst. Struct.* **1998**, *213*, 191. (g) Airey, A. L.; Hockless, D. C. R.; Swiegers, G. F.; Wild, S. B. *Z. Kristallogr.* **1996**, *211*, 939. (h) Arbuckle, B. W.; Musker, W. K. *Polyhedron* **1991**, *10*, 415. (i) Baxley, G. T.; Miller, W. K.; Lyon, D. K.; Miller, B. E.; Nieckarz, G. F.; Weakley, T. J. R.; Tyler, D. R. *Inorg. Chem.* **1996**, *35*, 6688.

Table 5. ^{31}P NMR Chemical Shifts and Corresponding M−P−C Bond Angles for Selected Three-Membered Phosphametallacycles

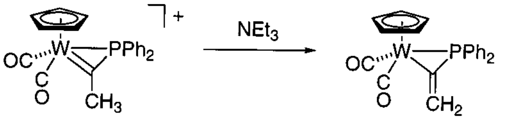
entry	complex	δ_P	M−P−C (deg)	ref
1	$[Ni(CH_2PMe_2)(PMe_3)_3]^+$	−27.1		36
2	$[NiCl\{C({=}CHMe)PPh_2\}(dcpe)$ (**2a**)	−100.2	56.6	this work
3	$[NiCl\{C({=}CHPh)PPh_2\}(dcpe)$ (**2c**)	−88.6	56.8	this work
4	$[Pt\{CH_2PPh_2)(PPh_2Me)(2\text{-}Ph\text{-}1,2\text{-}B_{10}C_2H_{10})]$	−17.7		37
5	$[Pt(CH(Ph)PBz_2)(PBz_2)(2\text{-}Me\text{-}1,2\text{-}B_{10}C_2H_{10})]$	−22.7	63.9	23
6	$[Mn(CH_2PPh_2)(CO)_4]$	13.0	65.2	38
7	$[(CO)_2Fe(\mu\text{-}Ph_2PCHPPh_2)(\mu\text{-}H)Fe(CO)_3]$	13.5	63.4/65.5	39
8	$[(CO)_2Fe(\mu\text{-}Ph_2PC{=}CH_2)(\mu\text{-}PPh_2)Fe(CO)_3]$	−44.6	56.3	40
9	$[Mo(CH_2PPh_2)(CO)_2(Cp)]$	1.3	66.5	41
10	$[(Cp)(Cl)Mo(\mu\text{-}Ph_2PC{=}CHPh)(\mu\text{-}PPh_2)W(Cl)(Cp)]$	−233.4		42
11	$[(Cp)(Cl)Mo(\mu\text{-}Ph_2PC{=}CHMe)(\mu\text{-}PPh_2)Mo(Cl)(Cp)]$	−243.3	58.8	43
12	$[W\{C(Me)(PMe_3)PPh_2\}(CO)(Cp)(PMe_3)]PF_6$	−1.6	66.8	33
13	$[W\{C(p\text{-}C_6H_4Me)(CO)PPh_2\}(Cp)(PMe_3)(NCMe)]BF_4$	−27.0	67.8	44
14	$[W\{C({=}CH_2)PPh_2\}(CO)_2(Cp)]$	−124.1		33
15	$[(Cp)(Cl)W(\mu\text{-}Ph_2PC{=}CHPh)(\mu\text{-}PPh_2)Mo(Cl)(Cp)]$	−241.1	58.4	42

surrounding phenyl rings and therefore cannot bind to the nickel atoms of neighboring molecules in the lattice.

Discussion

The reaction of alkynylphosphines with $[Ni(\eta^2\text{-}C_2H_4)(dcpe)]$ gives mononuclear, trigonally coordinated η^2-alkyne complexes $[Ni(\eta^2\text{-}Ph_2PC{\equiv}CR)(dcpe)]$. The strong π-donor ability of the electron-rich Ni(dcpe) fragment probably is an important factor that favors η^2-alkyne over P-coordination. The reactions of alkynylphosphines with $[Ni(CO)_4]$ generally give P-donor substitution products[32] and, as noted in the Introduction, η^2-alkyne coordination to nickel has been observed previously only in dinuclear nickel complexes. In our case, P-coordinated species are observed as the kinetically favored products, but they rearrange rapidly to the corresponding η^2-coordinated complexes.

Protonation of **1a**−**c** generates a substituted η^2-methylenenickelaphosphacyclopropane, a ligand system that, to the best of our knowledge, has never been structurally characterized in a monometallic complex. Such a ligand has been observed in the neutral tungsten complex $[W\{C({=}CH_2)PPh_2\}(CO)_2(Cp)]$, which has been generated by deprotonation of a cationic phosphinocarbene complex (entry 14 of Table 5 and eq 2).[33]



(2)

Binuclear complexes containing a methylenemetallaphosphacyclopropane unit have been described in which the ligand is coordinated through its double bond to the second metal atom (see examples in Table 5, entries 8, 10, 11, and 15).

A notable feature of complexes **2a**−**c** is the shielding of the phosphorus atom P^1 (δ −100.2, −97.1, and −88.6, respectively), which is in the same region as that observed in phosphiranes. It is far greater than that found in three-membered metallacycles of the type $M(CR_2PPh_2)$, which usually have values ranging from δ_P +15.0 to −60.0, e.g. δ_P +13.0 and +13.5 for Mn and Fe species, respectively (Table 5, entries 6 and 7), and δ_P −57.4 for $[W\{C(Me)(SMe)PPh_2\}(Cp)(PMe_3)(CO)]PF_6$.[33] Somewhat higher shieldings occur in analogous dimethylphosphino complexes of 5d elements; e.g., for $[Os(CH_2PMe_2)(H)(PMe_3)_3]$ the δ value is −71.0.[34] However, a pronounced shielding occurs when the carbon atom of the phosphametallacyclopropane is part of a double bond. This was also observed for the mononuclear complex $[W\{C({=}CH_2)PPh_2\}(CO)_2(Cp)]$, whose ^{31}P resonance is shielded by more than 100 ppm relative to those of analogous tungsten complexes where C^1 is sp^3 hybridized (see Table 5, entries 12−14). The effect is even more marked for dinuclear complexes in which the ligand bridges the two metal atoms via its double bond. Shieldings of ca. 50 ppm are observed for iron (entry 8) and up to 240 ppm for 4d and 5d elements (entries 10, 11, and 15). Although the reasons for this shielding are not well understood, it seem to correlate with the M−P−C angle, which decreases from ca. 65 to 57° when the hybridization of C^1 changes from sp^3 to sp^2 (see Table 5), thus bending the M−C bond further away from the ideal tetrahedral geometry. A similar angle dependence of chemical shift tensors, measured by ^{31}P solid-state NMR spectroscopy, has been reported.[35]

The protonation of **1a**−**c** probably occurs by initial oxidative addition of HCl to the metal atoms and

---

[32] Hengefeld, A.; Nast, R. *J. Organomet. Chem.* **1983**, *252*, 375.

[33] Ostermeier, J.; Hiller, W.; Kreissl, F. R. *J. Organomet. Chem.* **1995**, *491*, 283.

[34] Werner, H.; Gotzig, J. *Organometallics* **1983**, *2*, 547.

[35] Lindner, E.; Fawzi, R.; Mayer, H. A.; Eichele, K.; Hiller, W. *Organometallics* **1992**, *11*, 1033.

subsequent hydride migration to carbon atom C^2 to give a η^1-vinyl that is stabilized by coordination of the adjacent PPh_2 group to the metal atom. The first step is similar to that proposed for the addition of acids to the platinum(0)−alkyne complexes $[Pt(RC{\equiv}CR)(PPh_3)_2]$.[45] The second step would give rise to a cis arrangement of the substituent on C^2 and the PPh_2 group in the resulting vinylic double bond, as is observed in **2a**,**c**. The reaction of HCl with **1c** is not as regiospecific as that with **1a**, as shown by the formation of a small amount of **3c**, which results from addition of the hydrogen atom to C^1. This small decrease in regioselectivity can be correlated with the difference in chemical shifts of the acetylenic carbon atoms in **1a**,**c**. In **1a**, C^2 is 26 ppm less shielded than C^1, whereas the difference in **1c** is only 10 ppm. Thus, in **1c**, the electron deficiency at C^2 is less than that in **1a**; hence, the migration of the hydride shows less discrimination. In **1b**, the difference in chemical shift between the acetylenic carbons is even smaller (4 ppm) and, correspondingly, the regioselectivity is poorer.

In conclusion, the nickel(0)−dcpe fragment shows the ability to form unusual η^2-coordinated alkynylphosphine complexes, which can be protonated to give bidentate three-membered vinylphosphine species. Although the organometallic chemistry of the latter complexes seems to be limited, their reactions with a further 1 equiv of HCl provide an entry into the formation of (*Z*)-vinylphosphines. The overall reaction can be seen as a mild cis hydrogenation of alkynylphosphines, which could provide a route to a range of substituted vinylphosphines that would not otherwise be easily accessible.

Experimental Section

General Procedures. All experiments, unless otherwise specified, were carried out under argon with use of standard Schlenk techniques. All solvents were dried and degassed before use. NMR spectra were recorded on a Varian XL-200E (^1H at 200 MHz, ^{13}C at 50.3 MHz, ^{31}P at 81.0 MHz), a Varian Gemini 300BB (^1H at 300 MHz, ^{13}C at 75.4 MHz, ^{31}P at 121.4 MHz), or a Varian Inova-500 instrument (^1H at 500 MHz, ^{13}C at 125.7 MHz) at 298 K unless otherwise specified. The chemical shifts (δ) for ^1H and ^{13}C are given in ppm relative to residual signals of the solvent and to external 85% H_3PO_4 for ^{31}P. The spectra of all nuclei (except ^1H) were ^1H-decoupled. The coupling constants (J) are given in Hz with an estimated error of ±0.2 Hz unless otherwise stated. The numbering scheme used in the description of the ^{13}C NMR data is $Ph_2PC^1{\equiv}C^2R$. Infrared spectra were measured on a Perkin-Elmer Spectrum One instrument. Mass spectra were obtained on a ZAB-2SEQ spectrometer by the fast-atom bombardment (FAB) technique or on a Micromass Tof Spec 2E instrument by the MALDI/TOF technique. Unfortunately, attempts to obtain satisfactory elemental analyses for the new compounds described here were unsuccessful. Although stable in solution in the absence of air, the nickel(0) complexes **1a**,**c** decomposed on storage. The stable solid HCl adducts **2a**,**c** and **3c** were thermally sensitive and also tenaciously retained solvents, which could not be removed in vacuo without decomposition of the sample. The presence of solvents was confirmed by X-ray crystallography in two cases (see below).

Starting Materials. The complexes $[Ni(\eta^2\text{-}C_2H_4)(dcpe)]$[46] and $[Ni(\eta^2\text{-}Ph_2PC{\equiv}CPh)(dcpe)]$[7] and the (alkynyl)diphenylphosphines $Ph_2PC{\equiv}CR$ (R = Me, Ph, CO_2Me)[47−49] were prepared by published procedures.

Preparation of $[Ni(\eta^2\text{-}Ph_2PC{\equiv}CMe)(dcpe)]$ (1a). $Ph_2PC{\equiv}CMe$ (55 mg, 0.25 mmol) was added at 0 °C to a stirred suspension of $[Ni(C_2H_4)(dcpe)]$ (126 mg, 0.247 mmol) in diethyl ether (10 mL). After 30 min, ^{31}P NMR monitoring of the yellow solution indicated that the reaction was complete, and the solution was evaporated in vacuo to dryness to obtain **1a** quantitatively as a pale yellow powder. Yellow crystals suitable for X-ray analysis were obtained from pentane at 0 °C.

IR (Nujol): 2923 (vs), 2854 (vs), 2725 (w), 2666 (w), 1758 (s, C≡C), 1584 (w), 1569 (w), 1461 (s), 1377 (s), 1168 (m), 1026 (m), 1001 (m), 856 (m), 735 (m), 695 (m), 655 (m), 511 (m) cm^{-1}. ^1H NMR (300 MHz, C_6D_6): δ 1.05−2.05 (m, 48H, CH_2 and CH of dcpe), 2.59 (d, 3H, $J_{HP} = 6.7$, CH_3), 7.03−7.16 (m, 6H, H^{arom}), 7.86 (t, 4H, $J_{HH} = 6.9$, H^{arom}). $^{13}C\{^1H\}$ NMR (125.7 MHz, C_6D_6): δ 17.69 (ddd, $J_{CP} = 12.4, 6.9, 2.3$, CH_3), 22.25 (t, $J_{CP} = 19.4$, CH_2), 22.79 (t, $J_{CP} = 19.1$, CH_2), 25.90−30.12 (m, CH_2 of C_6H_{11}), 34.99 (dd, $J_{CP} = 15.6, 4.1$, CH of C_6H_{11}), 35.40 (dd, $J_{CP} = 16.5, 4.1$, CH of C_6H_{11}), 120.42 (ddd, $J_{CP} = 47.1, 42.6, 4.8$, C^1), 127.75 (s, CH^{Ph}), 128.22 (d, $J_{CP} = 6.7$, CH^{Ph}) (coupling constant obtained from APT experiment at 75.4 MHz), 133.88 (d, $J_{CP} = 20.2$, CH^{Ph}), 142.76 (dd, $J_{CP} = 15.6, 4.1$, C^{Ph}), 146.63 (ddd, $J_{CP} = 41.5, 18.3, 6.2$, C^2). $^{31}P\{^1H\}$ NMR (80.96 MHz, C_6D_6): δ −15.4 (dd, $^3J_{PP} = 37.0, 24.0$), 67.6 (dd, $^2J_{PP} = 46.3$, $^3J_{PP} = 24.0$), 72.9 (dd, $^2J_{PP} = 46.3$, $^3J_{PP} = 37.0$). FAB-MS (tetraglyme, $C_{41}H_{61}NiP_3$): *m*/*z* 705 (MH^+).

Preparation of $[Ni(\eta^2\text{-}Ph_2PC{\equiv}CCO_2Me)(dcpe)]$ (1b). $Ph_2PC{\equiv}CCO_2Me$ (44 mg, 0.16 mmol) was added at 0 °C to a stirred suspension of $[Ni(C_2H_4)(dcpe)]$ (83 mg, 0.16 mmol) in diethyl ether (10 mL). After 2 h, ^{31}P NMR monitoring of the yellow solution indicated that the reaction was complete and quantitative. Cooling of the solution to 0 °C yielded **1b** as a yellow crystalline solid.

IR (Nujol) 2924 (vs), 2854 (vs), 2723 (w), 2666 (w), 1735 (m, C≡C), 1665 (m, C═O), 1583 (w), 1460 (s), 1376 (m), 1194 (m), 1177 (w), 748 (w), 733 (w), 700 (w) cm^{-1}. ^1H NMR (300 MHz, C_6D_6): δ 1.05−2.12 (m, 48H, CH_2 and CH of dcpe), 3.46 (s, 3H, CH_3), 7.01 (m, 2H, H^{arom}), 7.09 (m, 4H, H^{arom}), 7.80 (m, 4H, H^{arom}). $^{13}C\{^1H\}$ NMR (125.7 MHz, C_6D_6): δ 22.09 (t, $J_{CP} = 18.7$, CH_2), 22.30 (t, $J_{CP} = 20.5$, CH_2), 26.49−30.00 (m, CH_2 of C_6H_{11}), 34.83 (dd, $J_{CP} = 17.9, 3.2$, CH of C_6H_{11}), 35.18 (dd, $J_{CP} = 18.3, 3.2$, CH of C_6H_{11}), 50.64 (s, OCH_3), 128.11 (s, CH^{Ph}), 128.26 (d, $J_{CP} = 6.9$, CH^{Ph}), 134.02 (d, $J_{CP} = 20.4$, CH^{Ph}), 136.43 (ddd, $J_{CP} = 56.6, 44.6, 6.5$, C^1), 140.62 (ddd, $J_{CP} = 39.8, 18.7, 5.9$, C^2), 141.15 (dd, $J_{CP} = 12.9, 3.8$, C^{Ph}), 171.93 (m, C═O). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6): δ −13.7 (dd, $^3J_{PP} = 34.3, 19.0$), 72.9 (dd, $^2J_{PP} = 31.5$, $^3J_{PP} = 19.0$), 74.4 (app. t, $J = 33.2$). FAB-MS ($C_{42}H_{61}NiO_2P_3$, tetraglyme): *m*/*z* 749 (MH^+), 663.

$[Ni(\eta^2\text{-}Ph_2PC{\equiv}CPh)(dcpe)]$ (1c).[9] $^{13}C\{^1H\}$ NMR (125.7 MHz, C_6D_6): δ 21.99 (t, $J_{CP} = 19.5$, CH_2), 22.59 (t, $J_{CP} = 19.4$,

---

(36) Karsch, H. H. *Chem. Ber.* **1984**, *117*, 783.

(37) Bresadola, S.; Longato, B.; Morandini, F. *J. Organomet. Chem.* **1977**, *128*, C5.

(38) Lindner, E.; Starz, K. A.; Eberle, H.-J.; Hiller, W. *Chem. Ber.* **1983**, *116*, 1209.

(39) Dawkins, G. M.; Green, M.; Jeffery, J. C.; Sambale, C.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1983**, 499.

(40) Grist, N. J.; Hogarth, G.; Knox, S. A. R.; Lloyd, B. R.; Morton, D. A. V.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1988**, 673.

(41) Lindner, E.; Küster, E. U.; Hiller, W.; Fawzi, R. *Chem. Ber.* **1984**, *117*, 127.

(42) Acum, G. A.; Mays, M. J.; Raithby, P. R.; Solan, G. A. *J. Chem. Soc., Dalton Trans.* **1995**, 3049.

(43) Conole, G.; Hill, K. A.; McPartlin, M.; Mays, M. J.; Morris, M. J. *J. Chem. Soc., Chem. Commun.* **1989**, 688.

(44) Lehotkay, T.; Wurst, K.; Jaitner, P.; Kreissl, F. J. *J. Organomet. Chem.* **1998**, *553*, 103.

(45) Hartley, F. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, U.K., 1982; Vol. 6, p 702.

(46) Bennett, M. A.; Hambley, T. W.; Roberts, N. K.; Robertson, G. B. *Organometallics* **1985**, *4*, 1992.

(47) Charrier, C.; Chodkiewicz, W.; Cadiot, P. *Bull. Soc. Chim. Fr.* **1966**, 1002.

(48) Carty, A. J.; Hota, N. K.; Ng, T. W.; Patel, H. A.; O'Connor, T. J. *Can. J. Chem.* **1971**, *49*, 2706.

(49) Montlo, D.; Suades, J.; Dahan, F.; Mathieu, R. *Organometallics* **1990**, *9*, 2933.

CH$_2$), 26.63 (CH$_2$), 27.48−27.74 (m, CH$_2$), 29.15, 29.39 (CH$_2$), 30.02−30.18 (m, CH$_2$), 35.14 (dd, J_{CP} = 16.0, 3.4, CH), 35.71 (dd, J_{CP} = 16.7, 3.8, CH), 124.42 (CH), 127.53, 127.86, 127.91 (CH), 128.20 (d, J_{CP} = 7, CH^{PPh}), 133.96 (d, J_{CP} = 20.1, CH^{PPh}), 140.38 (ddd, J_{CP} = 25.0, 19.5, 5.5, C^1), 141.36 (ddd, J_{CP} = 10.5, 5.0, 3.2, C^{Ph}), 141.95 (dd, J_{CP} = 14.8, 4.0, C^{PPh}), 150.27 (ddd, J_{CP} = 41.0, 19.0, 5.3, C^2).

Reaction of [Ni(η^2-Ph$_2$PC≡CMe)(dcpe)] (1a) with HCl. A solution of [Ni(η^2-Ph$_2$PC≡CMe)(dcpe)], freshly prepared from [Ni(C$_2$H$_4$)(dcpe)] (330 mg, 0.65 mmol) and Ph$_2$PC≡CMe (150 mg, 0.65 mmol) in diethyl ether (20 mL), was cooled to 0 °C. A solution of HCl in diethyl ether (0.65 mmol) was added dropwise. Monitoring by ^{31}P NMR spectroscopy indicated the complete disappearance of [Ni(η^2-Ph$_2$PC≡CMe)(dcpe)] and formation of some [NiCl$_2$(dcpe)]. The orange solution was layered with hexane (20 mL) and set aside at −10 °C. The complex [NiCl(C(=CHMe)PPh$_2$-κP,C^1)(dcpe)] (**2a**; 304 mg, 63%) was obtained as a heat- and moisture-sensitive crystalline solid. Red crystals suitable for X-ray crystallography were obtained from pentane at −10 °C.

IR (CH$_2$Cl$_2$): 3037 (w), 2935 (s), 2855 (m), 1481 (s, br), 1447 (s), 1271 (m), 1260 (m), 865 (w), 489 (w) cm^{-1}. ^{1}H NMR (500 MHz, CD$_2$Cl$_2$): δ 0.90−2.20 (m, 48H, dcpe), 2.11 (dd, 3H, J_{HH} = 6.4, J_{HP} = 2.0, CH$_3$), 6.88 (ddq, 1H, J_{PP} = 32.7, 8.0, $^3J_{HH}$ = 6.4, =CH), 7.40−7.60 (m, 10H, H^{arom}). ^{13}C{^{1}H} NMR (125.7 MHz, CD$_2$Cl$_2$): δ 20.10−20.80 (m, PCH$_2$), 22.90−23.50 (m, PCH$_2$), 25.36 (dd, J_{CP} = 9.8, 6.8, CH$_3$), 25.80−30.40 (m, CH$_2$), 34.91 (d, J_{CP} = 20.7, PCH), 35.53 (d, J_{CP} = 22.0, PCH), 125.36 (d, J_{CP} = 54.9, C^{Ph}), 129.84 (d, J_{CP} = 13.4, CH^{Ph}), 131.58 (d, J_{CP} = 3.7, CH^{Ph}), 133.18 (d, J_{CP} = 12.2, CH^{Ph}), 135.10 (ddd, J_{CP} = 52 ± 0.5, 41 ± 0.5, 11 ± 0.5, Ni−C), 146.78 (dd, J_{CP} = 10.1, 5.2, =CH). ^{31}P{^{1}H} NMR (81.0 MHz, CD$_2$Cl$_2$): δ −100.2 (dd, $^2J_{PP}$ = 181.9, 29.8), 73.5 (dd, $^2J_{PP}$ = 30.0, 4.2), 76.5 (dd, $^2J_{PP}$ = 181.9, 4.2). FAB-MS (3-nitrophenyl octyl ether, C$_{41}$H$_{62}$ClNiP$_3$): *m/z* 705 (M − Cl).

In a similar reaction, a solution of **1a** in diethyl ether (20 mL), freshly prepared from [Ni(C$_2$H$_4$)(dcpe)] (369 mg, 0.72 mmol) and Ph$_2$PC≡CPMe (160 mg, 0.72 mmol), was treated with a solution of HCl in diethyl ether (1.44 mmol) at 0 °C. After the mixture was stirred at room temperature for 1 h, hexane (20 mL) was added and the solid [NiCl$_2$(dcpe)] was removed by filtration through Celite. The oily residue obtained after removal of the solvent was extracted with pentane and chromatographed on acidic alumina. Removal of the solvent yielded pure (*Z*)-Ph$_2$PCH=CHMe (105 mg, 65%), whose ^{1}H, ^{13}C, and ^{31}P NMR data were identical with those reported.[11,12]

Reaction of [Ni(η^2-Ph$_2$PC≡CPh)(dcpe)] (1c) with HCl. A solution of **1c**, prepared from [Ni(C$_2$H$_4$)(dcpe)] (398 mg, 0.78 mmol) and Ph$_2$PC≡CPh (223 mg, 0.78 mmol), in diethyl ether (20 mL) was cooled to 0 °C. Dropwise addition of a solution of HCl in diethyl ether (0.78 mmol) gave an orange precipitate and a deep red solution. The suspension was centrifuged and the solution decanted. The solution was concentrated in vacuo to ca. $^1/_2$ volume, layered with hexane, and set aside at −10 °C to yield 379 mg (61%) of [NiCl(C(=CHPh)PPh$_2$-κP,C^1)(dcpe)] (**2c**). Red crystals suitable for X-ray crystallography were obtained from diethyl ether at −10 °C.

The decanted orange solid was dissolved in CH$_2$Cl$_2$, the solution was filtered through Celite, and the solvent was evaporated in vacuo. Crystallization from toluene gave 30 mg (5%) of yellow [NiCl(η^1-C(Ph)=CH(PPh$_2$)(dcpe)] (**3c**). Crystals suitable for X-ray analysis were obtained by diffusion of pentane into a solution of **3c** in chlorobenzene.

2c. IR (CH$_2$Cl$_2$): 2934 (m), 2856 (w), 1486 (s, br), 1447 (s), 1438 (s), 865 (m), 500 (w) cm^{-1}.^{1}H NMR (200 MHz, CD$_2$Cl$_2$): δ 0.90−2.40 (m, 48H, dcpe), 7.15−7.85 (m, 16H). ^{13}C{^{1}H} NMR (50.3 MHz, CD$_2$Cl$_2$): δ 19.80−21.60 (br m, PCH$_2$), 22.30−23.80 (br m, PCH$_2$), 25.60−30.30 (br m, CH$_2$), 34.60−35.80 (m, PCH), 124.10 (dt, J_{CP} = 55.3, 2.6, C^{PPh}), 128.20 (CH^{Ph}), 129.14 (CH^{Ph}), 129.67 (CH^{Ph}), 129.98 (d, J_{CP} = 12.7, CH^{PPh}), 131.92 (d, J_{CP} = 3.3, CH^{PPh}), 132.94 (d, J_{CP} = 12.6, CH^{PPh}), 135.43 (dd, J = 41.9, 33.3, Ni−C), 136.3 (dt, J_{CP} = 6.6, 3.3, C^{Ph}), 147.0 (m, =CH). ^{31}P{^{1}H} NMR (81.0 MHz, CD$_2$Cl$_2$): δ −88.6 (br dd, $^2J_{PP}$ = 181 ± 1, 30 ± 1), 73.1 (br d, $^2J_{PP}$ = 30 ± 1), 75.5 (br d, $^2J_{PP}$ = 181 ± 1). ^{31}P{^{1}H} NMR (121.4 MHz, CD$_2$Cl$_2$, 253 K): δ −89.3 (dd, $^2J_{PP}$ = 179.0, 32.0), 72.4 dd, $^2J_{PP}$ = 32.0, 3.0), 74.9 (dd, $^2J_{PP}$ = 179.0, 3.0). EI-MS (C$_{41}$H$_{62}$ClNiP$_3$): *m/z* 766 (18, M − Cl), 607 (3), 561 (10), 515 (80), 339 (100), 287 (63), 286 (67).

3c. IR (CH$_2$Cl$_2$): 3020 (w), 2933 (m), 2854 (w), 1479 (s, br), 1446 (s, br), 1095 (m), 1010 (m), 865 (w), 808 (m), 533 (w), 504 (w) cm^{-1}. ^{1}H NMR (200 MHz, CD$_2$Cl$_2$): δ 0.90−2.65 (m, 48H, dcpe), 6.36 (dd, J_{HP} = 10.4, 1.8, =CH), 7.05−7.80 (m, 15H). ^{13}C{^{1}H} NMR (50.3 MHz, CD$_2$Cl$_2$): δ 19.00−25.00 (br m, PCH$_2$), 26.10−30.30 (br m, CH$_2$), 36.33 (d, J_{CP} = 12.5, PCH), 36.58 (d, J_{CP} = 12.5, PCH), 125.30 (br s, CH), 127.33 (CH), 127.80−129.20 (m, CH), 142.60−142.99 (m, C), 147.16−147.46 (m, C). ^{31}P{^{1}H} NMR (81.0 MHz, CD$_2$Cl$_2$): δ −28.7 (dd, $^4J_{PP}$ = 17.9, 6.0), 62.1 (dd, $^2J_{PP}$ = 21.1, $^4J_{PP}$ = 6.0), 66.5 (dd, $^2J_{PP}$ = 21.1, $^4J_{PP}$ = 17.9). EI-MS (C$_{41}$H$_{62}$ClNiP$_3$): *m/z* 766 (1, M − Cl), 515 (17), 339 (100), 286 (11), 257 (19).

Reaction of [Ni(η^2-Ph$_2$PC≡CCO$_2$Me)(dcpe)] (1b) with HCl. As described above, an diethyl ether solution of **1b**, prepared from [Ni(C$_2$H$_4$)(dcpe)] (0.1 mmol) and Ph$_2$PC≡CCO$_2$Me (0.1 mmol), was cooled to 0 °C. A solution of HCl in diethyl ether (0.09 mmol) was added dropwise, forming an orange solution containing a mixture of [NiCl(C(=CHCO$_2$Me)PPh$_2$-κP,C^1)(dcpe)] (**2b**) and [NiCl(η^1-C(CO$_2$Me)=CH(PPh$_2$)(dcpe)] (**3b**) in a 3:2 ratio as shown by ^{31}P NMR spectroscopy (estimated yield 80%). Attempted crystallization did not separate the isomers and no further purification was carried out.

2b. ^{31}P{^{1}H} NMR (81.0 MHz, CD$_2$Cl$_2$): δ −97.1 (br t, $^2J_{PP}$ = 87 ± 1), 68.0 (br), 69.1 (br). ^{31}P{^{1}H} NMR (121.4 MHz, C$_6$D$_6$, 333 K): δ −98.7 (t, $^2J_{PP}$ = 92 ± 1), 66.7 (br), 67.5 (br). ^{31}P{^{1}H} NMR (121.4 MHz, CD$_2$Cl$_2$, 183 K): (a) δ −92.5 (br d, J_{PP} = 185 ± 2), 73.7 (br), 77.5 (br d, J_{PP} = 180 ± 2); (b) δ −105.0 (br d, J_{PP} = 225 ± 2), 65.0 (br d, J_{PP} = 227 ± 2), 70.0 (br).

3b. ^{31}P{^{1}H} NMR (81.0 MHz, CD$_2$Cl$_2$): δ −13.3 (d, $^4J_{PP}$ = 16.5), 67.7 (d, $^2J_{PP}$ = 29.8), 69.4 (dd, $^2J_{PP}$ = 29.8, $^4J_{PP}$ = 16.5).

Reaction of [NiCl(C(=CHMe)PPh$_2$-κP,C^1)(dcpe)] (2a) with CS$_2$. In a NMR tube under nitrogen, a solution of **2a** in CD$_2$Cl$_2$ was treated with an excess of CS$_2$. After 20 h at 25 °C, ^{31}P NMR monitoring showed the reaction to be complete and the formation of **4a** to be quantitative. Attempted crystallizations did not yield crystals suitable for X-ray analysis.

4a. IR (CH$_2$Cl$_2$): 2933 (m), 2855 (w), 1486 (s, br), 1447 (s), 1438 (s), 1067 (m), 865 (m), 531 (m) cm^{-1}. ^{1}H NMR (500 MHz, CD$_2$Cl$_2$): δ 1.00−2.20 (m, 51H, dcpe + CH$_3$), 6.72 (br d, 1H, J_{HP} = 62.5, =CH), 7.50−7.80 (m, 10H, H^{arom}). ^{13}C{^{1}H} NMR (50.3 MHz, CD$_2$Cl$_2$): δ 20.25−20.70 (m, PCH$_2$), 24.20 (dd, J_{CP} = 16.5, 6.6, CH$_3$), 26.00−32.02 (m, CH$_2$), 35.69 (d, J_{CP} = 21.4, CH), 36.14 (d, J_{CP} = 19.7, CH), 125.74 (d, J_{CP} = 72.6, C^{Ph}), 130.07 (d, J_{CP} = 11.9, CH^{Ph}), 132.88 (d, J_{CP} = 9.6, CH^{Ph}), 134.17 (d, J_{CP} = 2.9, CH^{Ph}), 137.07 (dd, J_{CP} = 19.8, 4.7, Ni−C), 155.82 (dd, J_{CP} = 7.8, 1.5, =CH), 236.45 (dd, J_{CP} = 71.4, 16.5, CS$_2$). ^{31}P{^{1}H} NMR (81.0 MHz, CD$_2$Cl$_2$): δ 30.3 (dd, $^4J_{PP}$ = 5.7, 2.2), 71.0 (dd, $^2J_{PP}$ = 34.5, $^4J_{PP}$ = 5.7), 75.8 (dd, $^2J_{PP}$ = 34.5, $^4J_{PP}$ = 2.2). MALDI/TOF MS (C$_{42}$H$_{62}$ClNiP$_3$S$_2$): *m/z* 788 (100, M$^+$ − C$_2$H$_4$).

Reaction of [NiCl(C(=CHPh)PPh$_2$-κP,C^1)(dcpe)] (2c) with CS$_2$. In a sealed Schlenk tube, a solution of **2c** (50 mg, 0.06 mmol) in CH$_2$Cl$_2$ (10 mL) was treated with an excess of CS$_2$ (0.025 mL). After 5 days at 28 °C, ^{31}P NMR monitoring showed the formation of ca. 40% of **4c**, together with decomposition products and remaining starting material. ^{31}P{^{1}H} NMR (81.0 MHz, CD$_2$Cl$_2$): δ 35.1 (dd, $^4J_{PP}$ = 5.6, 2.5), 63.5 (dd, $^2J_{PP}$ = 28.2, $^4J_{PP}$ = 2.5), 65.3 (dd, $^2J_{PP}$ = 28.2, $^4J_{PP}$ = 5.6).

Reaction of [NiCl(C(=CHMe)PPh$_2$-κP,C^1)(dcpe)] (2a) with CO$_2$. A solution of **2a** in THF was stirred for 70 h at room temperature under 1 atm of technical grade CO$_2$. Monitoring by ^{31}P NMR spectroscopy showed the reaction to be complete. The insertion complex **5a** was the major species,

Table 6. Crystal and Structure Refinement Data for Compounds 1a, 2a,c, and 3c

	[Ni(η^2-Ph$_2$PC≡CMe)-(dcpe)] (**1a**)	[NiCl{C(═CHMe)PPh$_2$-*κP*,*C*^{1}}(dcpe)] (**2a**)	[NiCl{C(═CHPh)PPh$_2$-*κP*,*C*^{1}}(dcpe)] (**2c**)	[NiCl{C(Ph)═CHPPh$_2$}(dcpe)] (**3c**)
		(a) Crystal Data		
chem formula	$C_{41}H_{61}NiP_3$	$C_{41}H_{62}ClNiP_3$	$C_{46}H_{64}ClNiP_3 \cdot 1.5C_4H_{10}O \cdot 0.5C_6D_6$	$C_{46}H_{64}ClNiP_3 \cdot 0.53C_6H_5Cl \cdot 3H_2O$
fw	705.55	742.03	954.33	917.79
cryst syst	monoclinic	monoclinic	orthorhombic	monoclinic
unit cell dimens				
a (Å)	11.9211(3)	11.7832(4)	24.6269(2)	16.6280(4)
b (Å)	17.6797(6)	21.0922(6)	16.4198(2)	16.5289(4)
c (Å)	18.1966(5)	16.2440(4)	25.9681(3)	19.8549(5)
α (deg)				
β (deg)	94.922(2)	93.393(2)		102.579(1)
γ (deg)				
V (Å^3)	3821.0(2)	4030.1(2)	10500.7(3)	5326.0(2)
space group	*P*2$_1$/*c* (No. 14)	*P*2$_1$/*c* (No. 14)	*Pbca* (No. 61)	*P*2$_1$/*n* (No. 14)
D_c (g cm^{-3})	1.226	1.22	1.268	1.145
Z	4	4	8	4
F(000)	1520	1624	4112	1963
color, habit	yellow, block	red, block	red, plate	yellow, needle
cryst dimens (mm)	0.30 × 0.12 × 0.10	0.07 × 0.10 × 0.17	0.28 × 0.24 × 0.07	0.40 × 0.22 × 0.12
μ (cm^{-1})	6.61 (Mo Kα)	7.00 (Mo Kα)	5.49 (Mo Kα)	5.67 (Mo Kα)
		(b) Data Collection and Processing		
diffractometer		Nonius KappaCCD		
X-radiation		Mo Kα (graphite monochromator)		
$2\theta_{max}$ (deg)	55.4	47.2	54.94	50.12
data collected (*h*, *k*, *l*)	(−15, −23, −23) to (15, 23, 23)	(−13, −23, −18) to (13, 23, 17)	(−31, −21, −33) to (31, 21, 33)	(−19, −19, −23) to (19, 19, 23)
no. of rflns				
total	41 676	34 024	175 892	76 825
unique ($R_{int/\%}$)	8833 (7.2)	5979 (6.0)	11 959 (6.4)	9390 (11.2)
obsd	6282 ($I > 2\sigma(I)$)	4643 ($I > 3\sigma(I)$)	8861 ($I > 3\sigma(I)$)	4249 ($I > 3\sigma(I)$)
abs cor (transmissn factors)	multiscan (0.939−0.822)	integration (0.906−0.953)	multiscan (0.848−0.967)	multiscan (0.685−0.942)
decay (%)		nil		
		(c) Structure Analysis and Refinement		
structure soln		direct methods (SIR92)		
refinement		full-matrix least squares		
no. of params	406	415	540	520
R(obsd data) (%)	5.1	4.3	4.8	6.1
R_w(obsd data (%)	6.2	4.6	7.3	7.8

but decomposition products, including [NiCl$_2$(dcpe)] (δ_P 81) and Cy$_2$P(O)CH$_2$CH$_2$P(O)Cy$_2$ (δ_P 48), were also present. Attempted crystallization by layering the solution with hexane led only to decomposition.

^{31}P{^{1}H} NMR (81.0 MHz, C$_6$D$_6$): δ 31.8 (dd, $^4J_{PP}$ = 22.4, 6.4), 62.6 (dd, $^2J_{PP}$ = 35.0, $^4J_{PP}$ = 22.4), 69.2 (dd, $^2J_{PP}$ = 35.0, $^4J_{PP}$ = 6.4).

Reaction of [NiCl(C(═CHPh)PPh$_2$-*κP*,*C*^{1})(dcpe)] (2c) with CO$_2$. In a similar reaction, a solution of **2c** in THF was treated with technical grade CO$_2$ to give the unstable complex **5c** as the major species (see text).

^{31}P{^{1}H} NMR (81.0 MHz, CD$_2$Cl$_2$): δ 32.4 (d, $^4J_{PP}$ = 13.5), 64.8 (dd, $^2J_{PP}$ = 34.0, $^4J_{PP}$ = 13.5), 66.0 (d, $^2J_{PP}$ = 34.0).

X-ray Crystallography. Crystal data and details of data collection, data processing, structure analysis, and structure refinement are given in Table 6.

All four crystals were mounted in silicone oil on a glass fiber and measured at −73 °C. The structures were solved by direct methods (SIR92)[50] and expanded with use of Fourier techniques (DIRDIF94).[51] The intensities of the reflections were processed by use of the computer programs Denzo and Scalepak.[52]

The non-hydrogen atoms of **1a** were refined anisotropically by full-matrix least squares. Hydrogen atoms were included at calculated positions (C−H = 0.95 Å) and periodically recalculated but not refined. The maximum and minimum peaks in the final difference Fourier map were 0.38 and −0.41 e/Å^3, respectively.

In the crystal structure of **2a**, the molecular species was clearly defined, but a very marginal disorder was observed in one cyclohexyl ring; hence, the carbon atoms C(18), C(19), and C(20) were best modeled by displacement ellipsoids. All non-hydrogen atoms were refined anisotropically by full-matrix least squares. Hydrogen atoms were included at calculated positions (C−H = 0.96 Å) and left riding with their carbon of attachment. The maximum and minimum peaks in the final difference Fourier map were 0.44 and −0.40 e/Å^3, respectively.

In the crystal structure of **2c**·1.5C$_4$H$_{10}$O·0.5C$_6$D$_6$, the molecular species (**2c**) and one diethyl ether solvent molecule were clearly defined, but other disordered solvent molecules were also present. They were assigned to a disordered 1:1 mixture of benzene, arising from the reference solvent used for the ^{31}P NMR monitoring, and diethyl ether. Restraints were imposed upon these solvent molecules, all the atom sites were given a common isotropic displacement factor, and the relative occupancies of the two units were refined. Hydrogen atoms were placed at calculated positions for **2c** and for the ordered diethyl ether molecule but were not included in the disordered region. The maximum and minimum peaks in the final difference Fourier map were 0.587 and −0.568 e/Å^3, respectively, located in the disordered solvent area.

---

(50) Altomare, A.; Cascarano, M.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. *J. Appl. Crystallogr.* **1994**, *27*, 435.

(51) Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Israel, R.; Smits, J. M. M. The DIRDIF-94 Program System; Technical Report of the Crystallographic Laboratory; University of Nijmegen, Nijmegen, The Netherlands, 1994.

(52) Otwinowski, Z.; Minor, W. In *Methods in Enzymology*; Carter, C. W., Jr., Sweet, R. M., Eds.; Academic Press: New York, 1997; Vol. 276, p 307.

The crystal of **3c**·$0.53C_6H_5Cl·3H_2O$ was of poor quality and diffracted weakly, but the molecular species (**3c**) was clearly defined. Molecules of chlorobenzene were also present, but the occupancy was clearly less than 1. Restraints were imposed upon these solvent molecules, and they were refined. Another region of solvation was attributed to molecules of water. They were solved with constraints on occupancy, and their hydrogen atoms were not located.

All the calculations were performed with use of the crystallographic software packages maXus,[53] teXsan,[54] and Xtal.[55]

The neutral atom scattering factors were taken from ref 56 for structure **1a**, from ref 57 for structure **2a**, and from ref 58 for structure **2c**. $\Delta f'$ and $\Delta f''$ values and mass attenuation coefficients were taken from ref 58 for all structures.

Note Added in Proof. Other examples of monomeric tungsten complexes that contain a η^2-diphenylphosphinovinyl fragment have recently been reported.[59]

Acknowledgment. J.C. gratefully acknowledges the receipt of a Summer Research Scholarship from the Research School of Chemistry, Australian National University. M.R.K. thanks the Alexander von Humboldt Foundation for a Feodor von Lynen Fellowship, and E.W. is grateful to the Australian Research Council for the award of a QEII Research Fellowship.

Supporting Information Available: Tables giving X-ray data for **1a**, **2a**, **2c**·$1.5C_4H_{10}O·0.5C_6D_6$, and **3c**·$0.53C_6H_5Cl·3H_2O$. This material is available free of charge via the Internet at http://pubs.acs.org.

OM000895O

---

(53) Mackay, S.; Gilmore, C. J.; Edwards, C.; Stewart, N.; Shankland, K. maXus Computer Program for the Solution and Refinement of Crystal Structures; Nonius, MacScience, and The University of Glasgow, 1999.

(54) TEXSAN: Single-Crystal Structure Analysis Software, version 1.8; Molecular Structure Corp., 3200 Research Forest Drive, The Woodlands, TX 77381, 1997.

(55) XTAL3.0 Reference Manual, Universities of Lamb and Perth, 1990.

(56) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV.

(57) Waasmaier, D.; Kirfel, A. *Acta Crystallogr., Sect. A* **1995**, *A51*, 416.

(58) *International Tables for Crystallography*; Wilson, A. J. C., Ed.; Kluwer Academic: Dordrecht, The Netherlands, 1992; Vol. C.

(59) Ipaktschi, J.; Klotzbach, T.; Dülmer, A. *Organometallics* **2000**, *19*, 5281.