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Copper-Catalyzed anti-Hydrophosphination Reaction of 1-Alkynylphosphines with Diphenylphosphine Providing (*Z*)-1,2-Diphosphino-1-alkenes

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Abstract: Hydrophosphination of 1-alkynylphosphines with diphenylphosphine proceeds in an anti fashion under copper catalysis, providing an easy and efficient access to a variety of (*Z*)-1,2-diphosphino-1-alkenes and their sulfides. The reaction is highly chemoselective and can be performed even in an aqueous medium. The reaction is reliable enough to realize a gram-scale synthesis of (*Z*)-1,2-diphosphino-1-alkene. Radical reduction of the diphosphine disulfides with tris(trimethylsilyl)silane yields the parent trivalent diphosphines without suffering from the isomerization of the olefinic geometry. Enantioselective hydrogenation of (*Z*)-3,3-dimethyl-1,2-bis(diphenylthiophosphinyl)-1-butene followed by desulfidation leads to a new chiral bidentate phosphine ligand.

Introduction

Organophosphines have been gaining in importance as ligands for transition metal catalysts, as clearly demonstrated in cross-coupling reactions[1] and asymmetric transformations.[2] Creation of new organophosphines and, naturally, of new phosphination reactions can thus have great impact on various fields of chemical science.

Metal-catalyzed hydrophosphination reactions of C−C multiple bonds represent a straightforward method for the synthesis of organophosphines.[3] In particular, catalytic hydrophosphinations of phosphorus-substituted unsaturated C−C bonds seem to be quite useful since the reactions provide bidentate diphosphines. In spite of their potential utility, the hydrophosphinations providing bidentate phosphines are rather limited. Although the hydrophosphinations of vinylphosphines proceed smoothly in the presence of a base to afford useful 1,2-diphosphinoethanes, the hydrophosphinations require the native vinyl group, i.e., $(CH_2{=}CH)_nPR_{3-n}$.[4,5]

In this paper, we focus on 1-alkynylphosphines as the substrates. The precedent hydrophosphinations of 1-alkynylphosphines highlight the difficulty in achieving the transformation. Ethynyldiphenylphosphine and bis(diphenylphosphino)ethyne undergo syn-hydrophosphination in the presence of strong bases such as phenyllithium.[4b,6] Upon complexation with platinum or palladium, 1-alkynylphosphines of some generality participate in anti-hydrophosphination.[7] The use of stoichiometric amounts of expensive transition metals is a definite and significant drawback. Here we report that hydrophosphinations of various 1-alkynylphosphines with diphenylphosphine proceed in an anti fashion under copper catalysis with perfect stereo- and regioselectivity. The diphosphines obtained, (*Z*)-1,2-diphosphino-1-alkenes, are not only structurally intriguing entities but also potentially useful bidentate ligands for transition metals. Furthermore, the carbon−carbon double bonds of the diphosphines can enjoy further functionalizations. Despite their latent rich chemistry, efficient and general methods for the synthesis of (*Z*)-1,2-diphosphino-1-alkenes have scarcely been reported so far.[8,9]

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(5) The only exception: Bookham, J. L.; Smithies, D. M. *J. Organomet. Chem.* **1999**, *577*, 305−315.

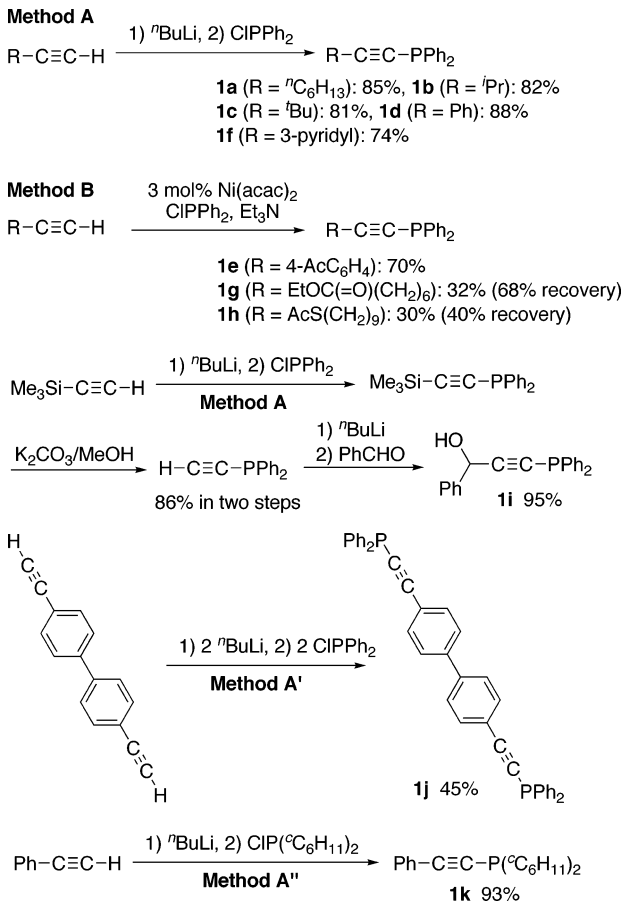
(6) King, R. B.; Kapoor, P. N. *J. Am. Chem. Soc.* **1971**, *93*, 4158−4166.

(7) Carty, A. J.; Johnson, D. K.; Jacobson, S. E. *J. Am. Chem. Soc.* **1979**, *101*, 5612−5619.

(8) Examples of the methods for the synthesis of (*Z*)-1,2-diphosphino-1-alkenes, which lack generality: (a) Banert, K.; Fendel, W.; Schlott, J. *Angew. Chem., Int. Ed.* **1998**, *37*, 3289−3292. (b) Tzschach, V. A.; Baensch, S. *J. Prakt. Chem.* **1971**, *313*, 254−258. (c) Cullen, W. R.; Dawson, D. S. *Can. J. Chem.* **1967**, *45*, 2887−2894. (d) Dodds, D. L.; Haddow, M. F.; Orpen, A. G.; Pringle, P. G.; Woodward, G. *Organometallics* **2006**, *25*, 5937−5945.

10.1021/ja070048d CCC: $37.00

Scheme 1

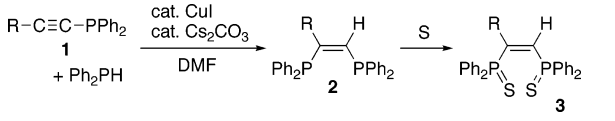


Results and Discussion

Preparation of 1-Alkynylphosphines. Starting alkynes **1** were prepared by nucleophilic substitution reactions of chlorophosphines with 1-lithio-1-alkynes (Scheme 1, method A) or nickel-catalyzed coupling reactions of chlorodiphenyl phosphine and terminal alkynes in the presence of triethylamine (method B).[10] Whereas method A was high-yielding, method B was suitable for the synthesis of **1** having labile functional groups. The nickel-catalyzed reactions of aliphatic alkynes did not go to completion (**1g**, **1h**). Alkynylphosphine **1i**, having a hydroxy group, was available in three steps, i.e., preparation of diphenyl(trimethylsilylethynyl)phosphine by method A, protodesilylation, and nucleophilic addition of diphenylphosphinoethynyllithium to benzaldehyde. Diphosphine **1j** was prepared by the dilithiation of 4,4′-diethynylbiphenyl followed by the reaction with chlorodiphenylphosphine (method A′). Aliphatic phosphine **1k** was prepared in fashions similar to method A by using chlorodicyclohexylphosphine (method A″).

Hydrophosphination Reactions of 1-Alkynylphosphines. Treatment of 1-octynyldiphenylphosphine (**1a**) with diphenylphosphine in the presence of catalytic amounts of copper(I) iodide and cesium carbonate in *N*,*N*-dimethylformamide (DMF) at 20 °C yielded (*Z*)-1,2-bis(diphenylphosphino)-1-octene (**2a**) exclusively (Table 1, entry 1). Handling of **2a** under air for purification led to gradual oxidation. To evaluate the efficiency of the reaction accurately, we isolated the product as phosphine sulfide **3a** after treatment with crystalline sulfur. Isolation of the parent phosphine **2a** and its analogues is discussed in the following section. The yield of **3a** based on ^{31}P NMR was 99%, and the isolated yield was 88%. The formation of the (*Z*) isomer was determined by the coupling constant of $J(^{31}P-^{31}P)$ of **3a** (16 Hz), whereas (*E*)-1,2-bis(diphenylthiophosphinyl)-1-alkenes and 1,1-bis(diphenylthiophosphinyl)-1-alkenes exhibit ca. 50 and 30 Hz of $J(^{31}P-^{31}P)$, respectively.[11]

Table 1. Copper-Catalyzed Hydrophosphination of 1-Alkynylphosphines with Diphenylphosphine[a]



entry	R	CuI /mol %	Cs_2CO_3 /mol %	yield of **3** /%[b]
1	$^{n}C_6H_{13}$ (**a**)	1	10	99 (88)
2[c]	^{i}Pr (**b**)	10	20	98 (84)
3[d]	^{t}Bu (**c**)	2	10	99 (87)
4[c]	^{t}Bu (**c**)	10	20	90 (84)
5	Ph (**d**)	1	10	98 (72)
6	4-Ac-C_6H_4 (**e**)	10	20	98 (87)
7	3-pyridyl (**f**)	2	10	88 (62)
8	EtOC(═O)$(CH_2)_6$ (**g**)	2	10	85 (79)
9[e]	$AcS(CH_2)_9$ (**h**)	20	40	94 (75)
10	PhCH(OH) (**i**)	10	20	87 (84)

[a] Hydrophosphination conditions: **1** (0.50 mmol), Ph_2PH (0.60 mmol), DMF (3 mL), 25 °C, 4 h. Sulfidation conditions: sulfur (2 mmol), 25 °C, 1 h. [b] Based on ^{31}P NMR with a sufficient first decay period. Isolated yields are in parentheses. [c] The reaction was performed for 6 h. [d] The reaction was performed at 90 °C. [e] The reaction was performed for 20 h.

Aprotic polar solvents are the choice of solvents. The reactions in dimethyl sulfoxide, THF, and ether afforded **3a** in 94%, 62%, and 0% NMR yields, respectively, under the otherwise same reaction conditions. Surprisingly, the reaction in aqueous DMF (1:1) also provided **3a** in 82% yield.

Copper(I) iodide is the best among transition metal catalysts we tested. Copper(I) chloride was as effective as CuI (98% yield). Other copper salts such as CuCN, CuBr, CuBr·Me_2S, and $CuCl_2$ also effected the hydrophosphination albeit the yields were lower (10%, 57%, 87%, and 84%, respectively). Neither metallic copper, CuO, nor Cu_2O are inactive. Silver(I) iodide (5 mol % in DMSO) also served to afford **3a** in 88% yield. None of gold(I) chloride, nickel(II) chloride, or cobalt(II) chloride exhibited any catalytic activity. The use of 5 mol % of palladium(II) chloride or platinum(II) chloride yielded **3a** in 5% yield, which invokes the formation of a stable and catalytically inactive palladium or platinum complex in the reaction mixture.[7] It is worth noting that a diphenylphosphide anion has been regarded as an untransferable dummy ligand in cuprate chemistry.[12]

(9) A number of hydrophosphonylations, the additions of pentavalent hydrophosphorous compounds, aiming at the synthesis of bidentate ligands, were reported: (a) Stockland, R. A., Jr.; Taylor, R. I.; Thompson, L. E.; Patel, P. B. *Org. Lett.* **2005**, *7*, 851−853 and references therein. (b) Allen, A., Jr.; Ma, L.; Lin, W. *Tetrahedron Lett.* **2002**, *43*, 3707−3710. (c) Ref 4f.

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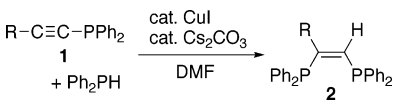
(12) (a) Bertz, S. H.; Dabbagh, G.; Villacorta, G. M. *J. Am. Chem. Soc.* **1982**, *104*, 5824−5826. (b) Martin, S. F.; Fishpaugh, J. R.; Power, J. M.; Giolando, D. M.; Jones, R. A.; Nunn, C. M.; Cowley, A. H. *J. Am. Chem. Soc.* **1988**, *110*, 7226−7228. We have observed a copper-mediated phosphination reaction of trialkyl(dibromomethyl)silanes: (c) Kondo, J.; Someya, H.; Kinoshita, H.; Shinokubo, H.; Yorimitsu, H.; Oshima, K. *Org. Lett.* **2005**, *7*, 5713−5715.

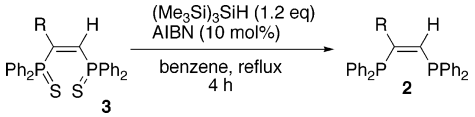
Table 2. Isolation of 1,2-Bis(diphenylphosphino)-1-alkenes[a]



entry	R	CuI /mol %	Cs_2CO_3 /mol %	yield of **2** /%[b]
1[c]	^{t}Bu (**c**)	2	10	69 (99)
2	^{n}C$_6$H$_{13}$ (**a**)	1	10	71
3	Ph (**d**)	1	10	70
4	4-Ac-C$_6$H$_4$ (**e**)	10	20	60
5	3-pyridyl (**f**)	2	10	65
6	PhCH(OH) (**i**)	10	20	51
7[c,d]	^{t}Bu (**c**)	10	20	87

[a] Hydrophosphination conditions: **1** (0.50 mmol), Ph_2PH (0.52 mmol), DMF (3.0 mL), 25 °C, 4 h. [b] Isolated yields. NMR yield is in parenthesis. [c] The reaction was performed at 90 °C. [d] The reaction was performed with 1.0 g of **1c** (3.8 mmol) and 0.71 g of diphenylphosphine (3.8 mmol).

Table 3. Radical Reduction of **3** to **2** by TTMSS[a]



entry	R	isolated yield of **2** /%
1	^{t}Bu (**c**)	89
2	^{n}C$_6$H$_{13}$ (**a**)	87 (97)[b]
3	Ph (**d**)	78 (94)[b]
4	4-Ac-C$_6$H$_4$ (**e**)	63
5	3-pyridyl (**f**)	44
6[c]	3-pyridyl (**f**)	58

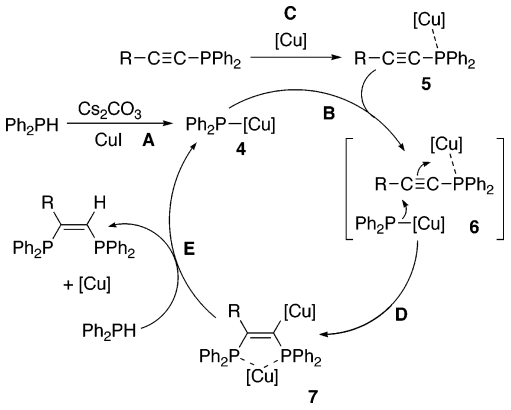
[a] Conditions: **3** (0.25 mmol), TTMSS (0.30 mmol), AIBN (0.025 mmol), benzene (3.0 mL), reflux, 4 h. [b] NMR yields are in parentheses. [c] The reaction was performed with TTMSS (0.60 mmol) for 12 h.

The use of Cs_2CO_3 is crucial. Potassium carbonate, sodium carbonate, and triethylamine promoted the hydrophosphination reaction much less effectively (18%, 3%, and 2% yields, respectively). Neutral CsCl did not induce the reaction. Instead of the CuI/Cs_2CO_3/DMF system, a CuI (10 mol %)/^{n}BuLi (20 mol %)/THF system was effective yet led to slower conversion (4 h, 49%; 8 h, 76%; 20 h, 86%). Without copper salts, Cs_2CO_3 by itself could not promote the reaction. Although butyllithium alone could effect the hydrophosphination in THF at ambient temperature, the reaction afforded a mixture of the (*Z*) and (*E*) isomers in 27% and 70% yields, respectively.

A wide range of 1-alkynylphosphines **1** were subjected to the phosphination reaction (Table 1). Sterically demanding 1-alkynylphosphines including **1b** and **1c** underwent the hydrophosphination smoothly, although higher catalyst loadings were required to complete the reaction (Table 1, entries 2 and 4). An elevated temperature also facilitated the reaction of **1c** (Table 1, entry 3). A variety of functional groups such as keto and hydroxy groups were compatible under the reaction conditions (Table 1, entries 6−10), whereas known hydrophosphination reactions of alkynes were generally unsatisfactory with regard to the functional group compatibility.[13] Pyridine-containing **2f** or **3f** (Table 1, entry 7) and sulfur-containing **2h** or **3h**

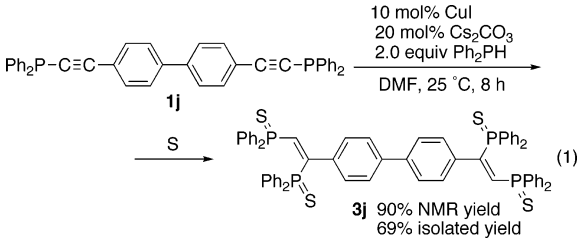
(13) (a) Douglass, M. R.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **2001**, *123*, 10221−10238. (b) Takaki, K.; Koshoji, G.; Komeyama, K.; Takeda, M.; Shishido, T.; Kitani, A.; Takehira, K. *J. Org. Chem.* **2003**, *68*, 6554−6565. (c) Kazankova, M. A.; Efimova, I. V.; Kochetkov, A. N.; Afanas'ev, V. V.; Beletskaya, I. P.; Dixneuf, P. H. *Synlett* **2001**, 497−500.

Scheme 2. Plausible Reaction Mechanism



(Table 1, entry 9) can be useful for constructing supramolecular architectures.

The reaction was efficient enough to provide tetraphosphine sulfide **3j** in excellent yield (eq 1). Although hydrophosphination



across **1k** having a dicyclohexylphosphino group at 25 °C led to complete recovery of **1k**, the anticipated **3k** could be prepared at 90 °C (eq 2). Attempts to perform the addition of dicyclo-

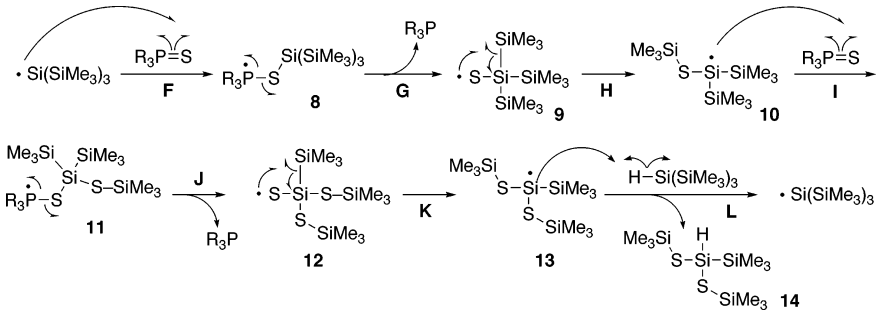
hexylphosphine to **1a** or **1d** resulted in failure.

Reaction Mechanism. The mechanism of the phosphination reaction is not clear. Radical inhibitors such as 2,2,6,6-tetramethylpiperidine-*N*-oxyl had little influence on the reaction, which is suggestive of an ionic reaction process. With several experiments, we are tempted to propose the mechanism outlined in Scheme 2. Deprotonation by Cs_2CO_3 with the aid of copper iodide would provide copper phosphide[14] (step A). As mentioned above, highly basic Cs_2CO_3 is thus essential to abstract the hydrogen of the CuI·$HPPh_2$ complex.[15] The phosphide would then attack 1-alkynylphosphine to form **7** (steps B and D). The alkynylphosphine probably coordinates to copper to be activated

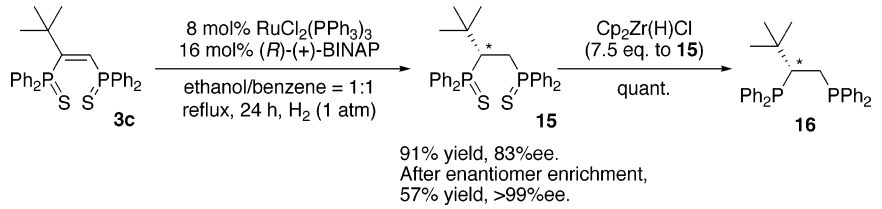
(14) (a) Eichhöfer, A.; Fenske, D.; Holstein, W. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 242−245. (b) Cowley, A. H.; Giolando, D. M.; Jones, R. A.; Nunn, C. M.; Power, J. M. *J. Chem. Soc., Chem. Commun.* **1988**, 208−209.

(15) One singlet signal appeared at $\delta = -41.6$ ppm in the ^{31}P NMR spectrum of diphenylphosphine in DMF. The addition of a stoichiometric amount of CuI to the DMF solution resulted in the formation of a clear solution and in broadening the signal with unambiguous splitting. Upon further addition of a stoichiometric amount of cesium carbonate, the signal disappeared and no new discrete signals were observed. These facts indicate that the copper−phosphorus bond of the complex [CuI·$HPPh_2$] would be labile and that many sorts of copper−phosphide species might be formed upon the addition of cesium carbonate.

Scheme 3. Mechanism for Desulfidation of **3** with a Substoichiometric Amount of TTMSS



Scheme 4. Synthesis of a New Bidentate Chiral Diphosphine



in the form of **5**[16] (step C).[17] The activation by copper is indispensable, due to the experimental fact that both 1-octynyldiphenylphosphine sulfide and oxide resisted the hydrophosphination reaction under the otherwise same reaction conditions. Unlike the insertion of an alkyne to a transition metal−phosphorus bond which proceeds in a syn manner, nucleophilic addition to alkyne usually proceeds in an anti manner. The latter is the case for the present reaction (step D). Immediate formation of chelating diphosphine skeleton **7** controls the complete stereoselectivity. During the reaction, no (*E*) isomer was detected, which suggests that it is improbable that initially formed (*E*)-diphosphine isomerizes into its (*Z*) form in the reaction flask. Protonation of the vinylcopper **7** by $HPPh_2$ affords the product and regenerates the copper phosphide (step E).

Isolation of Trivalent Phosphines 2. The diphosphines **2** could be handled under air, although gradual oxidation occurred. The isolations of trivalent phosphines **2** are summarized in Table 2. The oxidation led to lower yields of **2**, compared to the yields of sulfides **3** (Table 2 vs Table 1). When the hydrophosphination reaction of **1c** was conducted on a 0.5 mmol scale, **2c** was obtained in 99% NMR yield and 69% isolated yield (Table 2, entry 1). Without special care to avoid oxidation, other phosphines, **2a**, **2d**−**2f**, and **2i**, were isolated in good yields (Table 2, entries 2−6).

The catalytic hydrophosphination reaction was reliable enough to permit a gram-scale synthesis (Table 2, entry 7). The reaction of 1.0 g of **1c** (3.8 mmol) and 0.71 g of diphenylphosphine (3.8 mmol) provided 1.5 g of **2c** (3.3 mmol) in 87% isolated yield after purification on silica gel under ambient atmosphere. The lower isolated yield in the smaller-scale synthesis (Table 2, entry 1) would originate from the formation of a larger proportion of phosphine oxide of **2c**.

Radical Reduction of 3 to 2. We surveyed an efficient method for the reduction of phosphine sulfides **3** to the parent phosphines **2**. Radical desulfidation with tris(trimethylsilyl)silane (TTMSS) proved to be a reliable procedure (Table 3). Although the original report employed 1−3 equimolar amounts of TTMSS,[18] we found that a substoichiometric amount of TTMSS to P═S bond is sufficient. A plausible radical chain mechanism is depicted in Scheme 3. The first equimolar amount of **3** would undergo desulfidation in the reported manner[18] (steps F and G). The silicon-centered radical **10**, which is to be generated by a 1,2-Si shift[19] (step H), would be reactive enough to reduce a P═S moiety. [Bis(trimethylsilylthio)trimethylsilyl]silyl radical (**13**), formed through the second 1,2-Si shift (step K), seemed unreactive, based on the fact that a smaller amount of TTMSS for the reduction of **3** led to unsatisfactory conversion of **3**. The radical **13** would abstract the hydrogen of TTMSS (step L) to form tris(trimethylsilyl)silyl radical, which completes the radical chain. Purification on silica gel was quite easy, simply removing less polar silicon residues through a short-path column.

Complexation of $NiCl_2$ with 2c. The *Z* stereochemistry of **2** was also confirmed by X-ray crystallographic analysis of [$NiCl_2$(**2c**)] (Figure 1). Due to the bulky *tert*-butyl group, the atoms, P1, P2, Cl1, and Cl2, coordinating to the nickel are not in one plane (Figure 1b).

Enantioselective Hydrogenation Leading to Chiral Bidentate Phosphine Ligand. Compounds **2** and **3** have carbon−carbon double bonds, which can enjoy further transformations. In light of the importance of chiral bidentate ligands in transition metal-catalyzed asymmetric synthesis, we examined enantioselective hydrogenation of **3c** to obtain a new chiral ligand. Enantioselective hydrogenation of **3c** under the catalysis of [$RuCl_2(PPh_3)_3$]/(*R*)-(+)-BINAP provided a *tert*-butyl-substituted chiral diphosphine disulfide **15** in 91% isolated yield with 83% ee (Scheme 4).[20] Recrystallization of the product yielded an enantiomerically pure form of **15** in the supernatant, whereas the crystals were a mixture of the enantiomers. The desulfidation

(16) There can be an interaction between the copper and the acetylenic part of **5**.

(17) One singlet signal appeared at $\delta = -34.7$ ppm in the ^{31}P NMR spectrum of **1a** in DMF. The addition of a stoichiometric amount of CuI to the DMF solution furnished a clear homogeneous solution, which exhibited a broad and highly splitting signal at the same chemical shift. The dissolution of CuI indicates the formation of the complex [CuI·**1a**]. The NMR experiments suggest that the complex would not be robust.

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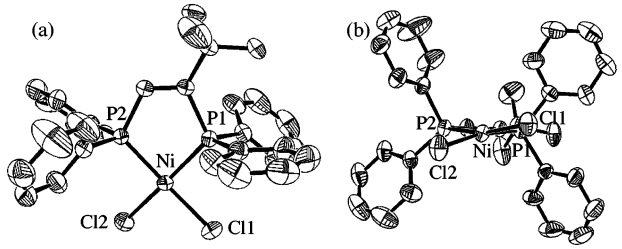

Figure 1. ORTEP drawing of [$NiCl_2$(**2c**)]. (a) Top view. (b) Side view.

of **15** with a large excess of $Cp_2Zr(H)Cl$[21,22] afforded enantiomerically pure bidentate phosphine **16**. The typical S_N2 phosphination reactions of the ditosylates of chiral diols[23] may suffer in the synthesis of phosphines with a sterically congested chiral center. The sequential phosphination/hydrogenation protocol offers an alternative to the conventional approach.

Conclusion

We have devised a highly efficient method for the synthesis of (*Z*)-1,2-diphosphino-1-alkenes. The method will create a variety of functionalized bidentate phosphines, which can be applicable to various fields of chemical science. As exemplified by the synthesis of a new chiral bidentate ligand **16**, the (*Z*)-1,2-diphosphino-1-alkene derivatives can be precursors of new phosphorus compounds.

Experimental Section

Preparation of 1-Alkynylphosphines 1a−1d, 1f, 1j, and 1k (Method A). Preparation of **1a** is representative. Under an atmosphere of argon, a solution of 1-octyne (1.2 g, 11 mmol) in THF (15 mL) was placed in a 50-mL reaction flask. Butyllithium (6.6 mL, 1.6 M in hexane, 11 mmol) was added to the flask at 0 °C. The resulting mixture was stirred for 30 min at the same temperature. Chlorodiphenylphosphine (2.2 g, 10 mmol) was then added at 0 °C. After the addition, the reaction mixture was stirred for 1 h at ambient temperature. After water (20 mL) was added, the product was extracted with a hexane/ethyl acetate mixture. Concentration followed by silica gel column purification provided 2.5 g of **1a** (8.5 mmol, 85%) as a yellow oil. It is worth noting that 1-alkynylphosphines are so stable under air that no observable oxidation occurred during the conventional handling. The alkynylphosphines could be stored at least for 6 months in a capped vial.

Preparation of 1-Alkynylphosphines 1e, 1g, and 1h (Method B). Preparation of **1e** is representative. Nickel acetylacetonate (39 mg, 0.15 mmol) was placed in a 50-mL reaction flask under argon. Toluene (10 mL), *p*-ethynylacetophenone (0.79 g, 5.5 mmol), chlorodiphenylphosphine (1.1 g, 5.0 mmol), and triethylamine (1.5 g, 15 mmol) were sequentially added. The mixture was heated at 80 °C for 4 h. After being cooled to room temperature, the mixture was filtered and the filtrate was concentrated. The crude oil obtained was chromatographed on silica gel to yield **1e** in 70% yield (1.1 g, 3.5 mmol).

Preparation of 1i. Crude diphenyl(trimethylsilylethynyl)phosphine was prepared from trimethylsilylacetylene (0.99 mL, 7.0 mmol) by method A. The crude product was dissolved in methanol (10 mL). Potassium carbonate (2.0 g, 14 mmol) was then added. The whole mixture was stirred for 1 h. The product was extracted with a hexane/ethyl acetate mixture. Concentration followed by purification on silica gel provided 1.3 g of ethynyldiphenylphosphine (6.0 mmol, 86%). A part of the ethynylphosphine (0.44 g, 2.1 mmol) was dissolved in 4 mL of THF under argon. At 0 °C, butyllithium (1.3 mL, 1.6 M in hexane, 2.0 mmol) was added dropwise. The mixture was stirred for 30 min. After benzaldehyde (0.20 g, 1.9 mmol) was charged, the mixture was stirred for an additional 1 h at 25 °C. The reaction was quenched with 10 mL of water. Extraction, concentration, and purification furnished **1i** in 95% yield (0.57 g, 1.8 mmol).

Typical Procedure for Copper-Catalyzed anti-Hydrophosphination of 1-Alkynylphosphines with Diphenylphosphine to Obtain 1,2-Bis(diphenylthiophosphinyl)-1-alkene 3 (Table 1). Copper(I) iodide (1 mg, 0.005 mmol) and cesium carbonate (16 mg, 0.050 mmol) were placed in a 20-mL reaction flask under argon. DMF (3.0 mL), **1a** (0.15 g, 0.50 mmol), and diphenylphosphine (0.11 g, 0.60 mmol) were sequentially added. The resulting mixture was stirred for 4 h at 25 °C. Elemental sulfur (64 mg, 2.0 mmol) was then added, and the mixture was stirred for 1 h. Water (10 mL) was added, and the product was extracted with ethyl acetate (10 mL × 3). The combined organic layer was dried over sodium sulfate and concentrated under reduced pressure. Chromatographic purification on silica gel yielded (*Z*)-1,2-bis(diphenylthiophosphinyl)-1-octene (**3a**, 0.24 g, 0.44 mmol, 88%) as a white solid.

Hydrophosphination to Isolate 1,2-Bis(diphenylphosphino)-1-alkene (Table 2, Entries 1−6). Isolation of **2c** is representative. Copper(I) iodide (1.9 mg, 0.010 mmol) and cesium carbonate (0.016 g, 0.050 mmol) were placed in a 20-mL reaction flask under an atmosphere of argon. DMF (3.0 mL), **1c** (0.13 g, 0.50 mmol), and diphenylphosphine (0.097 g, 0.52 mmol) were sequentially added. The mixture was heated at 90 °C for 4 h. After being cooled to room temperature, the mixture was passed through a pad of florisil. The filtrate obtained was evaporated to leave solid. Purification on silica gel provided **2c** (0.16 g, 0.35 mmol) in 69% yield as a white solid. During the process, no deaerated solvents were employed.

Gram-Scale Hydrophosphination to Isolate 2c (Table 2, Entry 7). The procedure is similar to the smaller-scale reaction. Copper(I) iodide (0.014 g, 0.075 mmol), cesium carbonate (0.12 g, 0.38 mmol), **1c** (1.0 g, 3.8 mmol), and diphenylphosphine (0.71 g, 3.8 mmol) were mixed in DMF (7.5 mL). The whole mixture was heated at 90 °C for 4 h. Filtration through a pad of florisil, concentration, and purification afforded 1.5 g of **2c** (3.3 mmol) in 87% yield.

Representative Procedure for TTMSS-Mediated Radical Reduction of 3 to 2 (Table 3). In a 20-mL reaction flask, **3c** (0.13 g, 0.25 mmol) and AIBN (4.1 mg, 0.025 mmol) were placed under argon. Benzene (3.0 mL) and TTMSS (0.075 g, 0.30 mmol) were added, and the resulting mixture was boiled for 4 h. After cooling, evaporation followed by purification on silica gel furnished 0.10 g of **2c** (0.22 mmol) in 89% yield.

Preparation of [$NiCl_2$(2c)] for X-ray Crystallographic Analysis. Nickel(II) chloride (52 mg, 0.40 mmol) was placed in a 20-mL reaction flask under argon. Ethanol (2.0 mL) was charged to dissolve the nickel salt. Diphosphine **2c** (0.20 g, 0.44 mmol) in ethanol (20 mL) was added. Immediately, orange precipitate appeared. The precipitate was washed with ether and dried in vacuo. The complex weighed 0.093 g (0.16 mmol, 40%, unoptimized). X-ray quality crystals were grown from acetonitrile. Crystallographic data for the structure has been deposited with the Cambridge Crystallographic Data Center (CCDC 601317).

Ruthenium-Catalyzed Enantioselective Hydrogenation of (*Z*)-3,3-Dimethyl-1,2-bis(diphenylthiophosphinyl)-1-butene. Tris(triphen-

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(22) The radical desulfidation of **15** with TTMSS (1.2 equiv to **15**) was also successful. However, after several attempts, separation of **15** and silicon-containing residue proved to be problematic in our hands. Small amounts of the corresponding monooxides of **15** were generated during careful chromatographic purification on silica gel for isolation of **15**. Purification using a solid phase technique (see the Supporting Information) resulted in unsatisfactory separation of **15** and the silicon-containing residue. We expect that, if the TTMSS-mediated reduction and purification of **15** were performed in a glovebox filled with inert gas, one could isolate **15** in excellent yield.

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ylphosphine)ruthenium(II) dichloride (9.6 mg, 0.010 mmol) and (*R*)-(+)-2,2′-bis(diphenylphosphino)-1,1′-biphenyl ((*R*)-BINAP, 12 mg, 0.020 mmol) were placed in a 20-mL reaction flask under hydrogen. Ethanol (0.50 mL) and benzene (0.50 mL) were added at 25 °C. After the mixture was stirred for 10 min, (*Z*)-3,3-dimethyl-1,2-bis(diphenylthiophosphinyl)-1-butene (**3c**, 65 mg, 0.13 mmol) was added. The resulting mixture was heated at reflux for 24 h. After the mixture was cooled to room temperature, water (10 mL) was added and the product was extracted with ethyl acetate (10 mL × 3). The organic layer was dried over sodium sulfate and evaporated in vacuo. Purification of the crude solid by gel permeation chromatography provided 3,3-dimethyl-1,2-bis(diphenylthiophosphinyl)butane (**15**, 59 mg, 0.11 mmol) in 91% yield and with 83% ee. Recrystallization from ethanol/benzene yielded crystals. The crystals were a mixture of the enantiomers. Concentration of the supernatant provided an optically pure form of **15** (37 mg, 0.071 mmol, 57%, > 99% ee). HPLC conditions: CHIRALCEL AD-H, hexane/2-propanol = 90:10, 1.3 mL/min, retention time = 4.0 min for the major enantiomer; retention time = 5.7 min for the minor enantiomer.

Desulfidation of 15 for Synthesis of New Bidentate Ligand 16. Zirconocene chloride hydride (0.19 g, 0.75 mmol) and **15** (0.052 g, 0.10 mmol) were placed in a 20-mL reaction flask under argon. After 1,4-dioxane (3.0 mL) was added, the mixture was stirred for 12 h at reflux. The reaction mixture was directly subjected to evaporation. A mixture of hexane and ethyl acetate (5:1, 10 mL, degassed) was added to dissolve **16**. The supernatant was passed through a silica, long-body Sep-Pak cartridge. The filtrate was concentrated to afford 0.045 g of pure **16** (0.10 mmol, 100%). The absolute configuration of **16** was assigned as *R* by comparing the specific rotations of **16** and of analogous chiral diphosphines.[23c,d]

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Supporting Information Available: Experimental details and characterization data for new compounds, and crystallographic data of [$NiCl_2$(**2c**)] (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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