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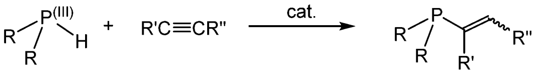
Synthesis of vinylphosphines and unsymmetric diphosphines: iron-catalyzed selective hydrophosphination reaction of alkynes and vinylphosphines with secondary phosphines†‡

Masumi Itazaki,* Shinya Katsube, Masahiro Kamitani§ and Hiroshi Nakazawa*

Iron complex-catalyzed regioselective single hydrophosphination of terminal arylalkynes with secondary phosphines was achieved. Unsymmetric 1,2-bis(phosphino)ethanes with different phosphino groups were obtained by using our catalytic systems. The structures of the obtained vinylphosphine, unsymmetric 1,2-bis(phosphino)ethane, and iron catalyst precursors were confirmed by single crystal X-ray diffraction studies.

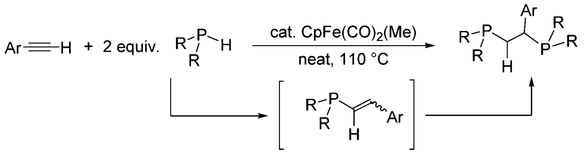
Vinylphosphines have been gaining importance as synthetic intermediates for the preparation of polyphosphines and ligands for transition metal catalysts in organic synthesis.[1] One of the most efficient methods for the synthesis of vinylphosphines is the catalytic addition of a P–H bond in trivalent phosphine to a C≡C triple bond (Scheme 1).



Scheme 1 Hydrophosphination of secondary phosphines with alkynes.

However, hydrophosphination of a P–H bond with alkynes catalyzed by a transition metal complex is generally difficult to be accomplished because the starting phosphine and/or the product (vinyl phosphine) usually coordinate to a catalytically active species to form a coordinatively-saturated complex having less or no catalytic activity. Examples of catalytic addition of a P–H bond of a P(III) compound to a C≡C triple bond are quite limited: one example of Co,[1f] Cu,[2] and Zr[3] and two examples of Ca,[4] Ni,[5] Pd,[5] La,[6] and Yb[4,7] have been reported. Among many kinds of transition metals, iron is a highly abundant, inexpensive, and relatively non-toxic metal. These advantages of iron make it highly attractive as a catalyst. Previously, we found catalytic *trans*-selective hydrogermylation of terminal and internal alkynes by an iron complex.[8] In addition, we reported regioselective double hydrophosphination of terminal arylalkynes catalyzed by an iron complex (Scheme 2).[9] In this case, reactions of terminal arylalkynes with 2 equiv. of secondary arylphosphines (PHR_2) afforded the corresponding diphosphines as a result of double hydrophosphination *via* vinylphosphines being single hydrophosphination products. As vinylphosphines produced in this catalytic system are readily converted into the double hydrophosphination product, we could not isolate the vinylphosphines in high yield. In this communication, we present the first iron complex-catalyzed regioselective synthesis of vinylphosphines and unsymmetric 1,2-bis(phosphino)ethanes with different phosphino groups using our catalytic reactions.

We firstly examined the catalytic activity of $CpFe(CO)_2(Me)$ and $Cp^*Fe(CO)_2(Me)$ (Cp^* stands for η^5-C_5Me_5) for the reaction of equimolar amounts of $PHPh_2$ and phenylacetylene, and found that $CpFe(CO)_2(Me)$ showed low selectivity between single and double hydrophosphination and $Cp^*Fe(CO)_2(Me)$ showed low catalytic activity. After several trials, we found that a methyl(pyridine)iron complex, Cp*Fe(CO)(py)(Me), exhibited good catalytic activity. The reaction of equimolar amounts of $PHPh_2$ with phenylacetylene in a 1 : 1 molar ratio at 110 °C for 48 h in toluene in the presence of 10 mol% of the iron complex produced single and double hydrophosphination compounds in a 4 : 1 molar ratio. Under optimized conditions ($PHPh_2$ (174 μL, 1.0 mmol), 1.5 equiv. of PhC≡CH (164 μL, 1.5 mmol), Cp*Fe(CO)(py)(Me) (32 mg, 0.1 mmol)),



Scheme 2 Regioselective double hydrophosphination of terminal arylalkynes catalyzed by an iron complex.

Department of Chemistry, Graduate School of Science, Osaka City University, 3-3-138 Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan.
E-mail: mitazaki@sci.osaka-cu.ac.jp, nakazawa@sci.osaka-cu.ac.jp

† Dedicated to Professor Kohtaro Osakada on the occasion of his 60th birthday.

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§ Present address: Department of Chemistry, School of Science, Kitasato University, 1-15-1 Kitasato, Minami-ku, Sagamihara, Kanagawa 252-0373, Japan.

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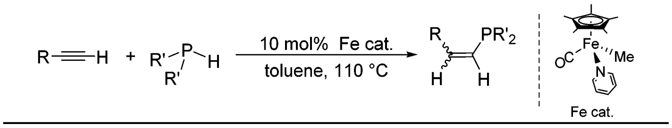
Table 1 Reaction of secondary phosphines with terminal alkynes catalyzed by a methyl(pyridine)iron complex Cp*Fe(CO)(py)(Me)[a]



Entry	R	R′	Time/h	NMR yield^{b,c} % (E/Z)	Isolated yield^{d} %
1	Ph	Ph	48	90 (10/90)	65 **1a**
2	*p*-Me-C_6H_4	Ph	48	79 (20/80)	59 **1b**
3	*p*-MeO-C_6H_4	Ph	48	73 (15/85)	25 **1c**
4	*p*-NH_2-C_6H_4	Ph	48	72 (9/91)	65 **1d**
5	*p*-F-C_6H_4	Ph	48	74 (12/88)	30 **1e**
6	*p*-^{t}Bu-C_6H_4	Ph	48	85 (17/83)	42 **1f**
7	2-Pyridyl	Ph	48	42 (28/72)	22 **1g**
8	3-Thiophenyl	Ph	72	69 (13/87)	32 **1h**
9	Ferrocenyl	Ph	72	72 (28/72)	46 **1i**
10	*p*-NH_2-C_6H_4	*p*-Me-C_6H_4	48	75 (10/90)	65 **1j**
11	*p*-NH_2-C_6H_4	*p*-MeO-C_6H_4	48	72 (9/91)	60 **1k**
12	Alkyl^{e}	Ph	48	NR^{g}	—
13	Ph	Alkyl^{f}	48	NR^{g}	—

[a] Reaction conditions: 110 °C, 10 mL Schlenk tube. $[PHR_2']:[\text{acetylene}]:[Cp^*Fe(CO)(py)(Me)]:[\text{toluene}] = 1:1.5:0.1:10$. [b] Based on ^{31}P NMR using triphenylphosphine oxide P(=O)Ph_3 as an internal standard. [c] Based on ^{31}P NMR. [d] *Z* isomer only. [e] Alkyl = ^{n}Hex, ^{c}Hex, ^{t}Bu. [f] Alkyl = ^{c}Hex, ^{n}Bu. [g] No reaction.

only vinylphosphine was produced in 90% yield as a 10 : 90 *E*/*Z* mixture, according to the ^{31}P NMR measurement. After purification, pure [(1*Z*)-2-phenylethenyl]diphenylphosphine (**1a**) was isolated in 65% yield based on $PHPh_2$ (Table 1, entry 1). This catalytic system to obtain vinylphosphines is applicable for *para*-substituted phenylacetylenes whether the substituent has electron-donation or -withdrawing character (entries 2–6). An alkyne derivative with an aromatic substituent other than a phenyl derivative such as a 2-pyridyl, 3-thiophenyl, or ferrocenyl group could be converted into the corresponding vinylphosphine (entries 7–9). Reaction of 4-ethynyl-benzenamine with PHR_2 (R = *p*-MeC_6H_4, *p*-$MeOC_6H_4$) also afforded the corresponding vinylphosphines (entries 10 and 11). In contrast, the hydrophosphination did not take place when alkylalkynes, RC≡CH (R = ^{n}Hex, ^{c}Hex, and ^{t}Bu), or alkyl phosphines, PHR_2 (R = ^{c}Hex, ^{n}Bu), were used as substrates (entries 12 and 13). In addition, internal alkynes such as diphenyl and methylphenyl acetylene were not converted into hydrophosphination products.

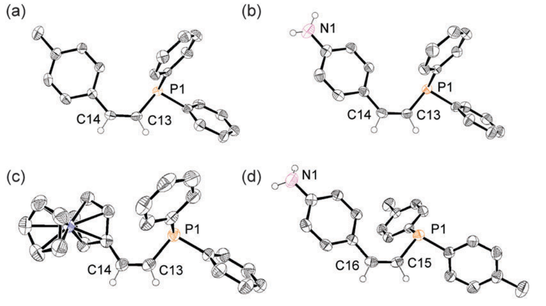
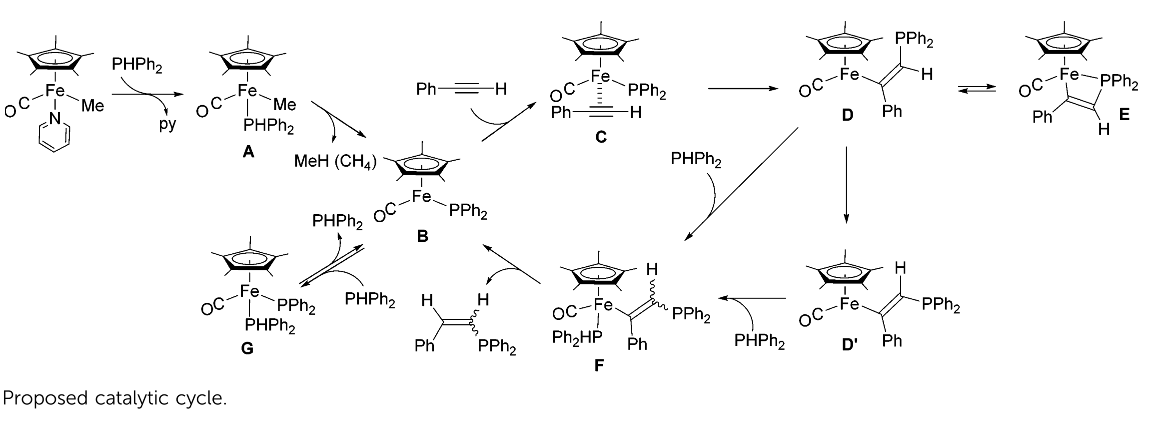


Fig. 1 ORTEP drawings of (a) **1b**, (b) **1d**, (c) **1i** and (d) **1j** with 50% thermal ellipsoidal plots. Hydrogen atoms except vinyl protons and amine protons are omitted for simplicity.

The molecular structures of **1b**, **1d**, **1i**, and **1j** were determined using single crystal X-ray diffraction (Fig. 1). The C=C bond portion apparently possesses the *Z* configuration in these compounds. The C=C bond distance (1.342(4) Å for **1b**, 1.341(2) Å for **1e**, 1.346(6) Å for **1i**, 1.345(3) Å for **1j**) is similar to that for *Z*-diphenylstyrylphosphine (1.339(2) Å) reported previously,[10] but is longer than a typical vinylic C(sp^2)=C(sp^2) bond distance (1.299 Å)[11] and the C=C bond distance found in C_2H_4 (1.3142(3) Å).[12]

The proposed catalytic cycle for hydrophosphination of terminal alkynes is shown in Scheme 3. We reported a similar catalytic cycle for double hydrophosphination[8] and it was supported by DFT calculations.[13] In Scheme 3, Cp*Fe(CO)(py)(Me) reacts with $PHPh_2$ to give Cp*Fe(CO)($PHPh_2$)(Me) (**A**). Conversion of **A** into Cp*Fe(CO)(PPh_2) (**B**) occurs either *via* P–H oxidative addition and MeH (CH_4) elimination or *via* concerted MeH elimination from the coordinated $PHPh_2$ and the Me ligand. The alkyne coordinates to the iron center of **B** in an η^2-fashion (**B** → **C**). This species **C** undergoes an insertion of the coordinated alkyne into the Fe–P bond (**C** → **D**). The corresponding alkyne insertion into an M–P bond was proposed by DFT calculation for Ni, Pd, Pt, and Rh complexes.[14] The phosphorus atom in **D** may coordinate to the iron center to give a four-membered metallacycle complex **E**, and they may be in equilibrium.[15,16] Complex **D** is converted into **D′** when vinyl isomerization (**D** → **D′**) takes place. Similar isomerization has been reported for hydrometalation of alkynes.[8,17] The coordination of $PHPh_2$ to the Fe center of **D′** affords **F** and then the C–H bond formation from **F** yields



Scheme 3 Proposed catalytic cycle.

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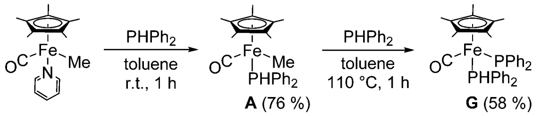
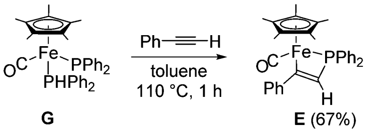


Scheme 4 Synthesis of the phosphine complex **A** and the phosphine(phosphide) complex **G**.

the *Z*-vinylphosphine and reinstates an intermediate **B** to complete the catalytic cycle. On the other hand, *E*-vinylphosphine is obtained by the reaction of **D** with $PHPh_2$. Although iron complex **B** is a very important intermediate in the catalytic cycle, the complex is too reactive to be isolated due to a 16e species. A 16e phosphide complex **B** has a possibility of reacting with $PHPh_2$ present in solution to give a phosphine(phosphide)iron complex, Cp*Fe(CO)($PHPh_2$)(PPh_2). Therefore, we attempted the isolation of the phosphine(phosphide)iron complex. Reaction of the methyl(pyridine)iron complex Cp*Fe(CO)(py)(Me) with $PHPh_2$ led to the isolation of Cp*Fe(CO)($PHPh_2$)(Me) (**A**). Reaction of the isolated **A** with $PHPh_2$ (1 : 1 molar ratio) in toluene at 110 °C for 1 h led to the isolation of the phosphine(phosphide)iron complex, Cp*Fe(CO)($PHPh_2$)(PPh_2) (**G**) (Scheme 4).

The ORTEP drawings of Cp*Fe(CO)(py)(Me), **A** and **G** are shown in Fig. 2. Structural disorder in Cp*Fe(CO)(py)(Me) was observed between CO and Me ligands. Complexes **A** and **G** have η^5-Cp*, CO, and $PHPh_2$ ligands on the central iron and a methyl ligand for **A** and a diphenylphosphide ligand for **B**, and adopt a typical three-legged piano-stool structure. The Fe–P1(phosphine) bond distance (2.1575(6) Å for **A**, 2.1808(4) Å for **G**) is shorter than the Fe–P2(phosphide) bond distance (2.3081(4) Å).

As **G** corresponds to a resting state of the catalytic cycle in Scheme 3, we expected that **G** would react with phenylacetylene. The reaction of **G** with phenylacetylene in the 1 : 1 molar ratio at 110 °C for 1 h in toluene afforded a metallaphosphacyclobutene complex **E** as a result of a regioselective insertion of phenylacetylene into the Fe–PPh_2 bond (see Scheme 3) (eqn (1)).



(1)

Fig. 3 shows the molecular structure of **E** by X-ray diffraction studies. Complex **E** contains a planar four-membered ring with a P–Fe–C angle (68.34(10)°) that is larger than that of a corresponding Ru complex, [Ru(η^5-indenyl)(κ^2-PhC=CHPPh$_2$)] (65.63(6)°).[16]

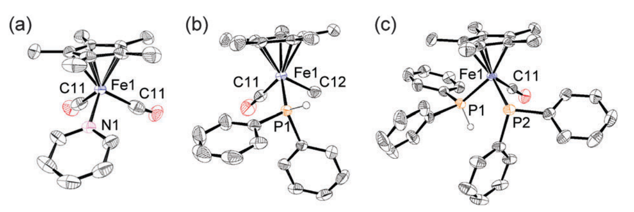


Fig. 2 ORTEP drawings of (a) Cp*Fe(CO)(py)(Me), (b) **A**, and (c) **G** with 50% thermal ellipsoidal plots. Hydrogen atoms except the hydrogen atom on the P atom are omitted for simplicity.

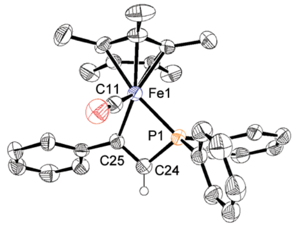
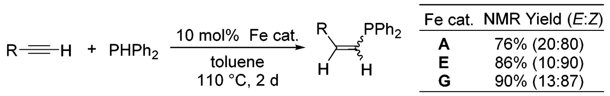


Fig. 3 ORTEP drawing of **E** with 50% thermal ellipsoidal plots. Hydrogen atoms except methylene protons are omitted for simplicity.



Scheme 5 Catalytic activity for hydrophosphination of complexes **A**, **E**, and **G**.

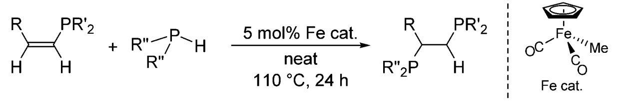
The Fe–PPh_2 bond distance of **E** (2.2067(11) Å) is shorter than that of **G** (2.3081(4) Å) because of ring strain for small internal bond angle. The C(24)–C(25) bond distance (1.351(5) Å) is a typical C=C double bond distance and the metallated carbon ($\sum$ C(25)∠ = 359.9°) is planar.

We checked the catalytic activity for hydrophosphination of complexes **A**, **E**, and **G**. Reaction of $PHPh_2$ with phenylacetylene in the presence of 10 mol% of **A**, **E**, or **G** at 110 °C yielded the desired vinylphosphine in high yield (Scheme 5).

It is considered that complexes **A** and **G** can readily form the active species Cp*Fe(CO)(PPh_2) **B** and the dissociation of coordinated P atoms from iron center in **E** forms **D**. These results show that complexes **A**, **E**, and **G** are the catalyst precursors in our reaction.

In the reaction of $PHAr_2$ with Ar′C≡CH, $CpFe(CO)_2(Me)$ was reported to serve as a precatalyst for double hydrophosphination[9] and this work revealed that Cp*Fe(CO)(py)(Me) served as an effective precatalyst for single hydrophosphination. Thus, we examined the reaction of *Z*-vinylphosphine (**1a** or **1j**) obtained in this work with secondary diarylphosphines catalyzed by $CpFe(CO)_2(Me)$ at 110 °C for 24 h with the hope of formation of unsymmetric 1,2-bis(phosphino)ethanes with different phosphine substituents. The results are shown in Table 2. Unsymmetric diphosphines **2a–2e** were obtained in high yields (entries 1–5). The molecular structure of **2e** was confirmed by X-ray diffraction (Fig. 4).

Table 2 Synthesis of unsymmetric diphosphines catalyzed by $CpFe(CO)_2(Me)$[a]



Entry	Vinylphosphine	R″	Isolated yield %
1	**1a**	Ph	84 **2a**
2	**1a**	*p*-Me-C_6H_4	85 **2b**
3	**1a**	*p*-MeO-C_6H_4	83 **2c**
4	**1a**	*p*-F-C_6H_4	69 **2d**
5	**1j**	Ph	88 **2e**

[a] Reaction conditions: 110 °C, 10 mL Schlenk tube, [PHR_2] : [vinylphosphine] : [Fe cat.] = 1 : 1 : 0.05.

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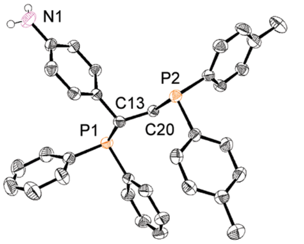

Fig. 4 ORTEP drawing of **2e** with 50% thermal ellipsoidal plots. Hydrogen atoms except amine protons are omitted for simplicity.

In summary, we found that Cp*Fe(CO)(py)(Me) was an effective precatalyst for single hydrophosphination in the reaction of terminal arylalkynes with secondary phosphines. The main products were *Z*-vinylphosphines. We proposed a catalytic cycle, and Cp*Fe(CO)(PHPh$_2$)(PPh$_2$) (**G**) and a metallaphosphacyclobutene (**E**) corresponding to the resting states in the cycle were isolated and fully characterized. The combination of the knowledge of double and single hydrophosphination realized the catalytic formation of unsymmetric 1,2-bis(phosphino)ethanes with different phosphine moieties.

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