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Communication

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Regioselective Double Hydrophosphination of Terminal Arylacetylenes Catalyzed by an Iron Complex

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Ⓢ *Supporting Information*

ABSTRACT: The first catalytic double hydrophosphination of alkynes was achieved by reaction with diarylphosphines in the presence of an iron catalyst. The double hydrophosphination proceeded regioselectively and effectively for various secondary arylphosphines and terminal alkynes to give 1,2-bisphosphinoethane derivatives.

Phosphines have been widely used as versatile and indispensable ligands for various transition metals because the properties of transition metal complexes can be easily tuned by varying the substituents on the phosphorus atoms.[1] Appropriate selections of phosphines have realized the stabilization, isolation, and even structural characterization of reactive complexes, as well as control of the activity and selectivity of transition metal catalysts. Among several methods for the preparation of phosphines, the addition of a P−H bond to an unsaturated C−C bond is one of the most attractive methods because it produces no undesired compounds as byproducts.[2] Additions of P−H bonds in P(V) compounds to alkynes promoted by a transition metal catalyst have been reported.[3,4] These additions have been referred to as hydrophosphinylation and hydrophosphonylation, depending on the substituents on the P(V) atom (Scheme 1). Reduction of the products from P(V) to P(III) affords phosphines.[5] A more straightforward method to obtain phosphines is the addition of a P−H bond of a P(III) compound to an alkyne, which is referred to as hydrophosphination (Scheme 1).[2] However, examples of hydrophosphination catalyzed by a transition metal complex are limited.[6] One of the reasons—presumably the main reason—stems from the coordination of a reactant such as PR_2H and/or a product such as PR_2R' to a transition metal catalyst to form a coordinatively saturated complex, leading to a decrease in or complete loss of catalytic activity. Double hydrophosphination of an alkyne is especially difficult because the product serves as a bidentate ligand, which binds to a transition metal catalyst more strongly than a monodentate ligand because of the chelate effect.[7] If double hydrophosphination of an alkyne could be achieved with a transition metal, it would be a convenient and atom-efficient method to obtain bidentate 1,2-phosphinated ethane derivatives such as bis(diphenylphosphino)ethane (dppe). To our best knowledge, there are only a few *stoichiometric* double hydrophosphinations of alkynes,[8] and no such *catalytic* reaction using a transition metal catalyst has been reported.[9] In this Communication, we describe the first example of catalytic double hydrophosphination of various alkynes promoted by an iron catalyst.

Scheme 1. P−H Bond Addition to Alkyne

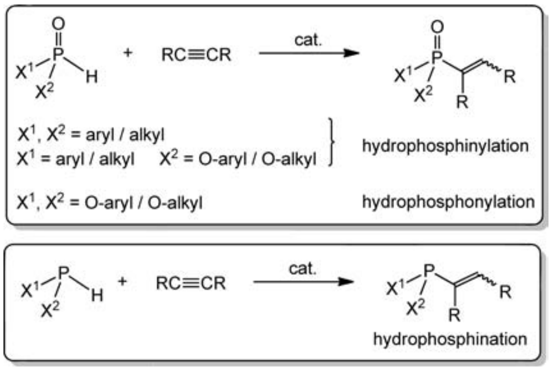
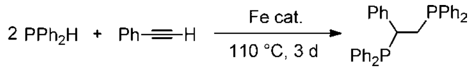


Table 1. Reaction of PPh_2H with PhC≡CH in the Presence of Fe Catalysis[a]



1a

entry	Fe cat.	solvent	cat.[b]/mol%	yield[c]/%
1	$CpFe(CO)_2Me$	neat	5	94
2	$CpFe(CO)_2Me$	hexane	5	NR[d]
3	$CpFe(CO)_2Me$	toluene	5	NR[d]
4	$CpFe(CO)_2Me$	THF	5	NR[d]
5	$CpFe(CO)_2Me$	acetonitrile	5	NR[d]
6	$CpFe(CO)_2Me$	neat	2.5	32[e]
7	$CpFe(CO)_2Me$	neat	1	13[e]
8	$Cp^*Fe(CO)_2Me$	neat	5	92
9	$FeCl_2$	neat	5	NR[d]
10	$FeCl_3$	neat	5	NR[d]
11	$Fe(CO)_5$	neat	5	NR[d]

[a] Reaction conditions: 110 °C, $[PPh_2H]/[phenylacetylene] = 2{:}1$. [b] Based on $[Ph_2PH]$. [c] Isolated yield. [d] No reaction. [e] Phenylacetylene was completely consumed, but the single hydrophosphination compound was also formed.

PPh_2H (465 mg, 2.50 mmol), PhC≡CH (137 μL, 1.25 mmol), and $CpFe(CO)_2Me$ (12.0 mg, 0.125 mmol, corresponding to 5 mol% based on PPh_2H) (Cp stands for η^5-C_5H_5) were charged in a Schlenk tube under a nitrogen atmosphere. After the reaction mixture was heated at 110 °C for 3 days, the

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volatile materials were removed under reduced pressure. The residue was washed with hexane and dried under vacuum to give 1,2-bis(diphenylphosphino)-1-phenylethane (**1a**) in 94% yield (Table 1, entry 1). In this reaction, PPh_2H and PhC≡CH served as both reagents and solvents. Interestingly and importantly, when the reaction was performed in an organic solvent such as hexane, toluene, THF, or acetonitrile, the double hydrophosphination product was not obtained; rather, $CpFe(CO)(PPh_2H)\{C(O)Me\}$ was formed (entries 2−5), as determined by comparison from the NMR data of the reaction mixture to those from the authentic complex.[10] Even when the amount of $CpFe(CO)_2Me$ was reduced from 5 mol% to 2.5 mol% or 1 mol%, the PhC≡CH was completely consumed. However, both the single and double hydrophosphination compounds were produced (entries 6 and 7). Some other iron complexes were also examined as catalyst precursors. $Cp^*Fe(CO)_2Me$ (Cp^* stands for η^5-C_5Me_5) showed similar catalytic activity (entry 8). In contrast, $FeCl_2$, $FeCl_3$, and $Fe(CO)_5$ showed no catalytic activity, even for the single hydrophosphination reaction (entries 9−11).[11]

In the reactions shown in entries 2−5 of Table 1, $CpFe(CO)(PPh_2H)\{C(O)Me\}$ was produced, indicating that this iron complex could be a catalyst precursor. The reaction of PhC≡CH with 2 equiv of PPh_2H in the presence of 5 mol% of $CpFe(CO)(PPh_2H)\{C(O)Me\}$ was examined, and it was revealed that the iron complex is catalytically active for the double hydrophosphination reaction (Scheme 2).

Scheme 2. Double Hydrophosphination Promoted by $CpFe(CO)(PPh_2H)\{C(O)Me\}$ Complex

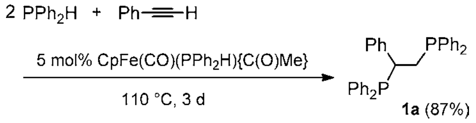
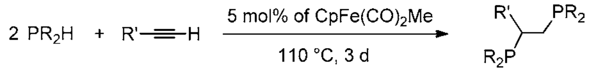


Table 2. Double Hydrophosphination of PR_2H with Alkynes Promoted by $CpFe(CO)_2Me$[a]



entry	R	R′	compd	yield[b]/%
1	Ph	*p*-Me-C_6H_4	**1b**	95
2	Ph	*p*-^{t}Bu-C_6H_4	**1c**	73
3	Ph	*p*-MeO-C_6H_4	**1d**	82
4	Ph	*p*-NH_2-C_6H_4	**1e**	72
5	Ph	*p*-F-C_6H_4	**1f**	91
6	Ph	3-pyridyl	**1g**	91
7	Ph	3-thiophenyl	**1h**	77
8	Ph	2-pyridinyl	**1i**	27
9	Ph	alkyl[c]	–	0
10	*p*-Me-C_6H_4	Ph	**1j**	92
11	*p*-MeO-C_6H_4	Ph	**1k**	73
12	alkyl[d]	Ph	–	0

[a] Reaction conditions: 110 °C, 3 days, 10 mL Schlenk tube, $[PR_2H]$/[phenylacetylene]/$[CpFe(CO)_2Me]$ = 20:10:1. [b] Isolated yield. [c] Alkyl = *n*-hexyl, cyclohexyl, benzyl. [d] Alkyl = ^{c}Hex, ^{t}Bu.

Because the double hydrophosphination of a C≡C triple bond is unprecedented, we examined further instances of this reaction by utilizing different combinations of secondary phosphines and alkynes. The results are summarized in Table 2, where the reaction conditions employed were the same as those shown in entry 1 of Table 1. Various *para*-substituted phenylacetylenes were effectively converted into double hydrophosphination products (entries 1−6), whether the substituent was an electron-donating or electron-withdrawing group. It should be noted that the NH_2 group remains intact during the reaction (entry 4), indicating that the reactive and coordinative amino group did not disturb this catalytic system. 3-Pyridyl and 3-thiophenyl derivatives were also converted into the corresponding diphosphines (entries 6 and 7). Although the 2-pyridyl derivative showed a low isolated yield due to its high solubility in hexane that was used for purification of the product, the phosphine was converted into the corresponding diphosphine in 78% yield, according to the ^{31}P NMR measurement (entry 8). In contrast, *n*-hexyl-, cyclohexyl-, and benzylacetylene did not undergo hydrophosphination (entry 9). In addition, internal alkynes such as diphenylacetylene and dimethylacetylene dicarboxylate (DMAD) did not undergo hydrophosphination. These results suggest that this catalytic system is effective for terminal arylacetylenes but not for alkylacetylenes and internal alkynes. $P(p\text{-}MeC_6H_4)_2H$ and $P(p\text{-}MeOC_6H_4)_2H$ also reacted with PhC≡CH to give double hydrophosphination products in the present catalytic system (entries 10 and 11). However, alkylphosphines, PR_2H (R = ^{c}Hex ^{t}Bu), did not afford any hydrophosphination product (entry 12).

All hydrophosphination compounds were characterized by ^1H, ^{13}C, and ^{31}P NMR. The molecular structures of **1b** and **1d** were confirmed by X-ray diffraction (Figure 1). In both cases, the two sp carbons in the starting alkyne were changed to sp^3 carbons, and each of them has one PPh_2 group. The carbon−carbon bond lengths are 1.538 and 1.545 Å, showing that they are single bonds. The two phosphorus atoms were not oxidized.

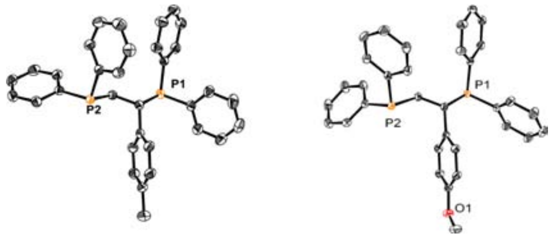


Figure 1. ORTEP drawings of **1b** and **1d** with 50% thermal ellipsoidal plots. Hydrogen atoms are omitted for simplicity.

The reaction of 1 equiv of PhC≡CH, 2 equiv of PPh_2H, and 0.1 equiv of $CpFe(CO)_2Me$ was monitored by ^{31}P NMR (without H decoupling). A plot of the amounts of phosphorus-containing compounds as functions of time is shown in Figure 2. The amount of PPh_2H decreased constantly. The single hydrophosphination product with *Z* configuration (**2-*Z***)[12] increased for 12 h after the reaction started and then decreased gradually. In contrast, very little (*E*)-vinylphosphine (**2-*E***)[13] was formed. The double hydrophosphination product (**1a**) constantly increased with time. This time-dependence curve lets us envision the following catalytic profile: PPh_2H reacts with PhC≡CH to give **2-*Z*** selectively, which then reacts with PPh_2H to afford **1a**; a very small degree of isomerization of **2-*Z*** to **2-*E*** takes place. The molar ratio of **1a**:**2-*Z***:**2-*E***:PPh_2H after 48 h was 84:7:4:5.

The proposed mechanism for the catalytic reaction of Ph_2PH with phenylacetylene is shown in Scheme 3. CO insertion into the Fe−Me bond in $CpFe(CO)_2Me$ and PPh_2H coordination

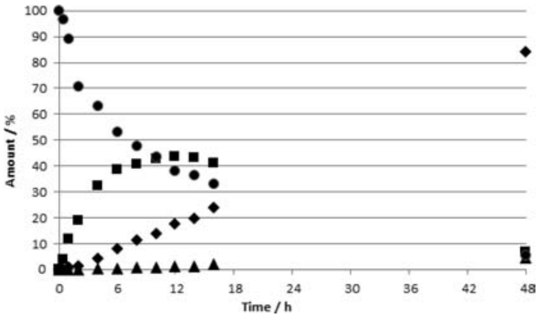


Figure 2. Plot of the amounts of phosphorus-containing compounds as functions of time in the reaction of $CpFe(CO)_2Me$, phenylacetylene, and diphenylphosphine in 1:10:20 ratio at 110 °C. ◆, ■, ▲, and ● stand for **1a**, **2-*Z***, **2-*E***, and diphenylphosphine.

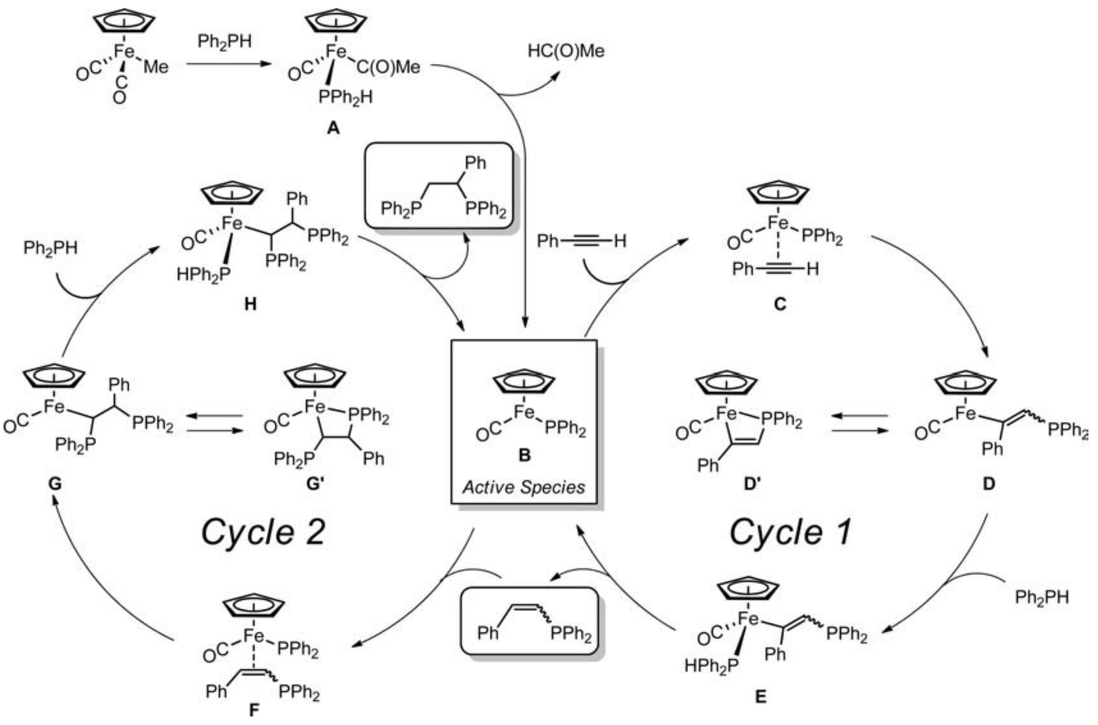
take place to give **A**. As mentioned above, **A** can be isolated when the reaction is performed in an organic solvent. Conversion of **A** into **B** with a PPh_2 ligand occurs either via P−H oxidative addition and HC(O)Me elimination[14] or via concerted HC(O)Me elimination from the coordinated PPh_2H and the C(O)Me ligand. $PhC\equiv CH$ coordinates to **B** through the $C\equiv C$ triple bond to give **C**. The phosphide iron complex, $CpFe(CO)(PMes_2)$, which is similar to **B**, has been reported previously to be reactive with an unsaturated bond in isothiocyanate.[15] The $PhC\equiv CH$ in **C** inserts into the Fe−P bond to form **D**. The phosphorus atom in **D** may coordinate to the iron center to give **D′**, and they may be in equilibrium.[15,16] Relevant alkyne insertion into the M−P bond (M = Ni, Pd, Pt, Rh) was suggested by DFT calculation.[17] The second PPh_2H coordinates to **D** to form **E**, which is converted into **B** with $PhHC{=}CH(PPh_2)$ generation. Complex **B** goes into Cycle 1 when it reacts with $PhC\equiv CH$. Alternatively, **B** may react with the $PhHC{=}CH(PPh_2)$ produced in Cycle 1 to go into Cycle 2, which consists of **B**→**F** (olefin coordination), **F**→**G** (olefin insertion into the Fe−P bond), **G**→**H** (PPh_2H coordination), and **H**→**B** (reproduction of **B** with formation of $(Ph_2P)C(Ph)HCH_2(PPh_2)$). In this catalytic cycle, species **D** and **G** are in equilibrium with catalytically inactive **D′** and **G′**, respectively. These equilibria may be responsible for the relatively slow reaction: it takes about 3 days to finish the catalytic reaction.

We conducted some additional experiments to check whether the radical pathway can be ruled out. When more than 1 equiv of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) or galvanoxyl was used as a radical inhibitor, diphenylphosphine was converted into the corresponding phosphine oxide even without an iron catalyst.[18] When 5 mol% (vs phosphine) of the radical inhibitor was added under standard conditions (Table 1, entry 1), a large amount of double hydrophosphination compound and a small amount of phosphine oxide were formed. We also conducted several reactions under light-shielding conditions and under an argon atmosphere, but no significant difference was observed. It has been reported that a radical reaction of PPh_2H with alkyne promoted by AIBN or photoirradiation yielded only the single hydrophosphination product, but never yielded the double hydrophosphination product in one pot.[12] These results indicate that our catalytic reaction does not occur via a radical pathway, although a radical pathway cannot be ruled out completely.

Hydrophosphination involving cationic species has been proposed.[19] A cationic iron complex bearing PRH_2, $[CpFe(CO)_2(PRH_2)]^+$, was reported to undergo hydrophosphination to alkynes and alkenes.[19b] This cationic complex reacted with DMAD to give a double hydrophosphination product, whereas DMAD did not undergo hydrophosphination in our reaction system. Therefore, it is highly likely that a cationic iron complex bearing phosphine as a ligand is not involved in our catalytic cycle.

In summary, an unprecedented catalytic double hydrophosphination was achieved in the reaction of a terminal

Scheme 3. Proposed Catalytic Cycle



arylalkyne with a secondary arylphosphine using an iron complex. The key point is that no organic solvent is used; the arylalkyne and arylphosphine are used as both solvents and reagents. It should be noted that the iron catalyst, presumably $CpFe(CO)(PPh_2)$, does not suffer considerable (if any) loss of activity from coordination by PPh_2H and the diphosphine formed.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Detailed experimental procedures and characterization of products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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