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

Masumi Itazaki, Shinya Katsube, Masahiro Kamitania
and Hiroshi Nakazawa

ITAZAKI, M., KATSUBE, S., KAMITANI, M., & NAKAZAWA, H. (2016). Synthesis of vinylphosphines and unsymmetric diphosphines: iron-catalyzed selective hydrophosphination reaction of alkynes and vinylphosphines with secondary phosphines. *CHEMICAL COMMUNICATIONS*. 52, 3163-3166. http://doi.org/10.1039/C5CC10185A

ChemComm

COMMUNICATION

Synthesis of Vinylphosphine and Unsymmetric Diphosphine: Iron-catalyzed Selective Hydrophosphination Reaction of Alkynes and Vinylphosphines with Secondary Phosphines†,‡

Masumi Itazaki,*[a] Shinya Katsube,[a] Masahiro Kamitani[a,b] and Hiroshi Nakazawa*[a]

Iron complex-catalyzed regioselective single hydrophosphination of terminal arylalkyne with secondary phosphine was achieved. Unsymmetric 1,2-bis(phosphino)ethanes with different phosphino groups were obtained by using our catalytic systems. The structures of 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 in importance as the 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 vinylphosphine is the catalytic addition of a P–H bond in trivalent phosphine to a C≡C triple bond (Scheme 1).
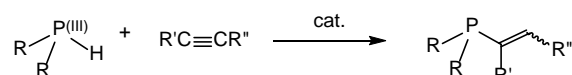
Scheme 1 Hydrophosphination of secondary phosphine with alkyne.

However, hydrophosphination of a P–H bond with alkyne 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 for Co,[1f] Cu,[2] Zr[3] and two examples of Ca,[4] Ni,[5] Pd,[6] La,[7] 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
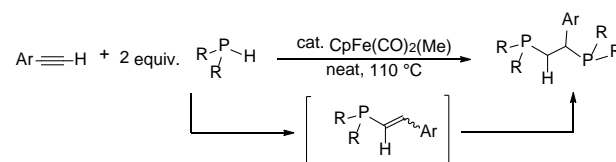
Scheme 2 Regioselective double hydrophosphination of terminal arylalkynes catalyzed by an iron complex.

with 2 equiv. of secondary arylphosphines (PHR₂) 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 vinylphosphine in high yield. In this communication, we present the first iron complex-catalyzed regioselective synthesis of vinylphosphine and unsymmetric 1,2-bis(phosphino)ethane with different phosphino groups using our catalytic reactions.

We firstly examined catalytic activity of CpFe(CO)$_2$(Me) and Cp*Fe(CO)$_2$(Me) (Cp* stands for η^5-C$_5$Me$_5$) 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 amount of PHPh$_2$ with phenylacetylene in 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)), only the vinylphosphine was produced in 90% yield as a 10:90 E/Z mixture, according to the ^{31}P NMR measurement. After purification, pure [(1Z)-2-phenylethenyl]diphenylphosphine (**1a**) was isolated in

[a.] Department of Chemistry, Graduate School of Science, Osaka City University, 3-3-138 Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan
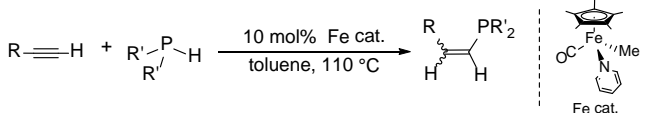E-mail: mitazaki@sci.osaka-cu.ac.jp, nakazawa@sci.osaka-cu.ac.jp
[b.] Present address: Department of Chemistry, School of Science, Kitasato University, 1-15-1 Kitasato, Minami-ku, Sagamihara, Kanagawa 252-0373, Japan

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] (E/Z)[c]	Isolated yield %[d]
1	Ph	Ph	48	90 (10/90)	65 **1a**
2	p-Me-C$_6$H$_4$	Ph	48	79 (20/80)	59 **1b**
3	p-MeO-C$_6$H$_4$	Ph	48	73 (15/85)	25 **1c**
4	p-NH$_2$-C$_6$H$_4$	Ph	48	72 (9/91)	65 **1d**
5	p-F-C$_6$H$_4$	Ph	48	74 (12/88)	30 **1e**
6	p-^{t}Bu-C$_6$H$_4$	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$_6$H$_4$	p-Me-C$_6$H$_4$	48	75 (10/90)	65 **1j**
11	p-NH$_2$-C$_6$H$_4$	p-MeO-C$_6$H$_4$	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'$_2$] : [Acetylene] : [Cp*Fe(CO)(py)(Me)] : [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.

65% yield based on PHPh$_2$ (Table 1, Entry 1). This catalytic system to obtain vinyl phosphines 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 phenyl derivative such as 2-pyridyl, 3-thiophenyl, or ferrocenyl group could be converted into the corresponding vinyl phosphine (Entries 7-9). Reaction of 4-ethynyl-benzenamine with PHR$_2$ (R = p-MeC$_6$H$_4$, p-MeOC$_6$H$_4$) also afforded the corresponding vinylphosphines (Entries 10-11). 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 12-13). In addition, internal alkynes such as diphenyl and methylphenyl acetylene were not converted into hydrophosphination products.

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 Z configuration in these compounds. The C=C
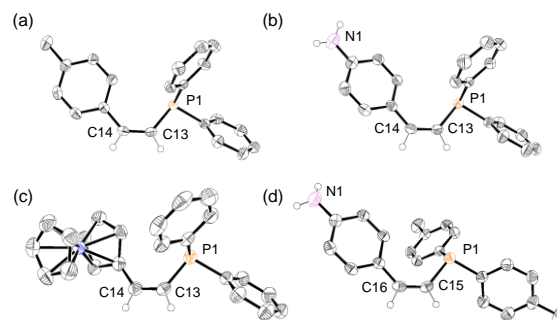

Fig. 1 ORTEP drawings of (a) **1b**, (b) **1d**, (c) **1i** and (d) **1j** with 50% thermal ellipsoidal plots. Hydrogen atoms except vinyl protons and amine protons were omitted for simplicity.

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 of Z-diphenylstyrylphosphine (1.339(2) Å) reported previously,[10] but is longer than those for a typical vinyllic C(sp^2)=C(sp^2) bond (1.299 Å)[11] and the C=C bond distance found in C$_2$H$_4$ (1.3142(3) Å).[12]

The proposed catalytic cycle for hydrophosphination of terminal alkyne 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**). 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 alkyne.[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 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 the 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 to react with PHPh$_2$ present in solution to give a phosphine(phosphide)iron
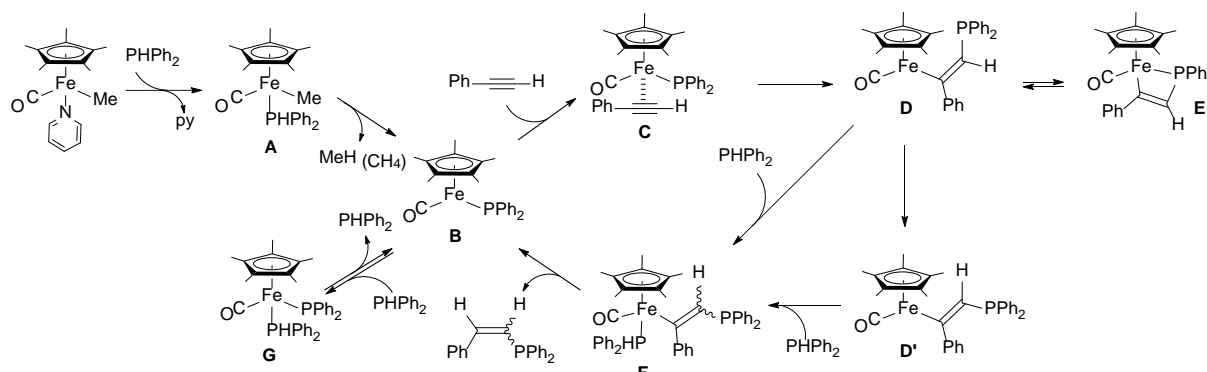
Scheme 3 Proposed catalytic cycle.

complex, Cp*Fe(CO)(PHPh$_2$)(PPh$_2$). Therefore, we attempted the isolaton of the phosphine(phosphide)iron complex. Reaction of the methyl(pyridine)iron complex Cp*Fe(CO)(py)(Me) with PHPh$_2$ led 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 the isolation of the phosphine(phosphide)iron complex, Cp*Fe(CO)(PHPh$_2$)(PPh$_2$) (**G**) (Scheme 4).
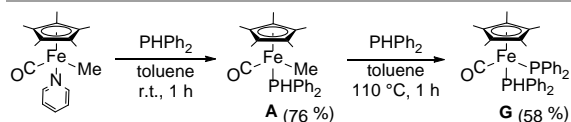
Scheme 4 Synthesis of the phosphine complex **A** and the phosphine(phosphide) complex **G**.

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 diphenlylphosphide 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 that for the Fe–P2(phosphide) bond distance (2.3081(4) Å).
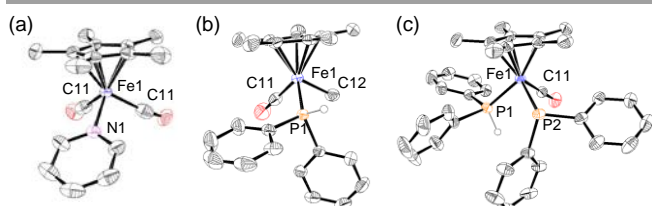

Fig. 2 ORTEP drawings of (a) Cp*Fe(CO)(py)Me, (b) **A**, and (c) **G** with 50% thermal ellipsoidal plots. Hydrogen atoms except the hydrogen on P atom are omitted for simplicity.

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) (eq. 1).
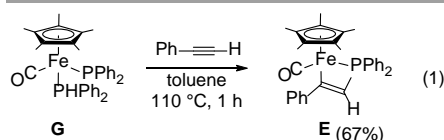

Fig. 3 shows the molecular structure of **E** by X-ray diffraction study. Complex **E** contains a planar four-membered ring with a P–Fe–C angle (68.34(10)°) that is larger than that of a corresponding Ru complex, [Ru(η^5-indenyl)(κ^2-PhC=CHPPh$_2$)] (65.63(6)°).[16] The Fe–PPh$_2$ bond distance of **E** (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 (Σ C(25)$\angle$ = 359.9°) is planar.
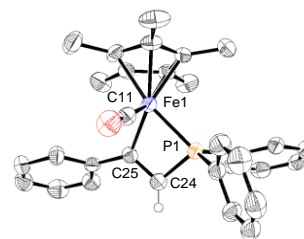

Fig. 3 ORTEP drawing of **E** with 50% thermal ellipsoidal plots. Hydrogen atoms except methylene proton are omitted for simplicity.

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).

Fe cat.	NMR Yield (*E:Z*)
A	76% (20:80)
E	86% (10:90)
G	90% (13:87)
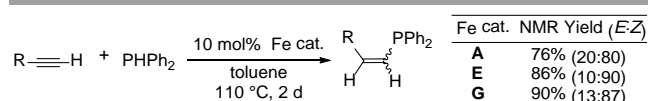
Scheme 5 Catalytic activity for hydrophosphination of complexes **A**, **E**, and **G**.

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 atom from iron center in **E** forms **D**. These results show that the complexes **A**, **E**, and **G** are the catalyst precursor 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 diaryphosphines catalyzed by CpFe(CO)$_2$(Me) at 110 °C for 24 h with the hope of formation of unsymmetric 1,2-bis(phosphino)ethane with different phosphine substituents. The results were 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 diphosphine catalyzed by CpFe(CO)$_2$Me.[a]

Entry	vinylphosphine	R''	Isolated yield %
1	**1a**	Ph	84 **2a**
2	**1a**	*p*-Me-C$_6$H$_4$	85 **2b**
3	**1a**	*p*-MeO-C$_6$H$_4$	83 **2c**
4	**1a**	*p*-F-C$_6$H$_4$	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.
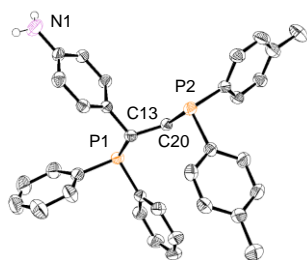
Fig. 4 ORTEP drawing of **2e** with 50% thermal ellipsoidal plots. Hydrogen atoms except amine protons were omitted for simplicity.

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 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.

Notes and references

1   See, for instance: (*a*) R. B. King and P. N. Kapoor, *J. Am*. *Chem*. *Soc*. 1969, **91**, 5191; (*b*) R. B. King and P. N. Kapoor, *J. Am. Chem. Soc.*, 1971, **93**, 4158; (*c*) L. Solujić, E. B. Milosavljević, J. H. Nelson, N. W. Alcock and J. Fischer, *Inorg. Chem.*, 1989, **28**, 3453; (*d*) L. Weber, O. Kaminski, R. Boese and D. Blaser, *Organometallics*, 1995, **14**, 820; (*e*) D. Soulivong, C. Wieser, M. Marcellin, D. Matt, A. Harriman and L. Toupet, *J. Chem. Soc., Dalton Trans.,* 1997, 2257; (*f*) H. Ohmiya, H. Yorimitsu and K. Oshima, *Angew. Chem. Int. Ed.*, 2005, **44**, 2368.
2   A. Kondoh, H. Yorimitsu and K. Oshima, *J. Am. Chem. Soc.*, 2007, **129,** 4099.
3   A. J. Roering, S. E. Leshinski, S. M. Chan, T. Shalumova, S. N. MacMillan, J. M. Tanski, and R. Waterman, *Organometallics,* 2010, **29**, 2557.
4   (*a*) M. R. Crimmin, A. G. M. Barrett, M. S. Hill, P. B. Hitchcock, and P. A. Procopiou, *Organometallics,* 2007, **26**, 2953; (*b*) H. Hu, C. Cui, *Organometallics*, 2012, **31**, 1208.
5   (*a*) M. A. Kazankova, I. V. Efimova, A. N. Kochetkov, V. V. Afanas'ev, I. P. Beletskaya and P. H. Dixneuf, *Synlett,* 2001, 497; (*b*) M. A. Kazankova, I. V. Efimova, A. N. Kochetkov, V. V. Afanas'ev and I. P. Beletskaya, *Russ. J. Org. Chem.,* 2002, **38**, 1465.
6   (*a*) M. R. Douglass and T. J. Marks, *J. Am. Chem. Soc.*, 2000, **122**, 1824; (*b*) M. R. Douglass, C. L. Stern and T. J. Marks, *J. Am. Chem. Soc.,* 2001, **123**, 10221.
7   K. Takaki, M. Takeda, G. Koshoji, T. Shishido and K. Takehira, *Tetrahedron Lett.,* 2001, **42**, 6357.
8   M. Itazaki, M. Kamitani and H. Nakazawa, *Chem. Comm.* 2011, **47**, 7854.
9   M. Kamitani, M. Itazaki, C. Tamiya and H. Nakazawa, *J. Am. Chem. Soc.,* 2012, **134**, 11932.
10   M. Taillefer, H. J. Cristau, A. Fruchier and V. Vicente, *J. Organomet. Chem.*, 2001, **624**, 307.
11   R. Lide, *Handbook of Chemistry and Physics*, 76th ed.; CRC Press: New York, 1995.
12   G. J. H. Van Nes and A. Vos, *Acta Crystallogr.,* 1979, **B35**, 2593.
13   M. Liu, C. Sun, F. Hang, N. Sun and D. Chen, *Dalton Trans.*, 2014, **43**, 4813.
14   V. P. Ananikov and I. P. Beletskaya, *Chem. Asian. J.* 2011, **6**, 1423.
15   W. Malisch, U. Hirth, A. Fried and H. Pfister, *Phosphorus, Sulfur and Silicon,* 1993, **77**, 17.
16   E. J. Derrah, R. McDonald and L. Rosenberg, *Chem. Commun.*, 2010, **46**, 4592.
17   (*a*) R. S. Tanke and R. H. Crabtree, *J. Am. Chem. Soc.,* 1990, **112**, 7984; (b) I. Ojima, N. Clos, R. J. Donovan and P. Ingallina, *Organometallics,* 1990, **9**, 3127; (*c*) C. H. Jun and R. H. Crabtree, *J. Organomet. Chem.,* 1993, **447**, 177; (*d*) L. W. Chung, Y.-D. Wu, B. M. Trost and Z. T. Ball, *J. Am. Chem. Soc.,* 2003, **125**, 11578; (*e*) B. M. Trost and Z. T. Ball, *J. Am. Chem. Soc.,* 2005, **127**, 17644.