Synthesis of μ-Phosphido Diiron Complexes Having a P−H Bond: Hydrophosphination of Phenylacetylene and Methyl Acrylate with the Cationic μ-Phosphido Diiron Complex

Junji Sugiura,[†] Taeko Kakizawa,[†] Hisako Hashimoto,*[,†] Hiromi Tobita,*[,†] and Hiroshi Ogino[§]

Department of Chemistry, Graduate School of Science, Tohoku University, Aoba-ku, Sendai 980-8578, Japan, and Miyagi Study Center, The University of the Air, Sendai 980-8577, Japan

Received December 16, 2004

Thermal reaction of $Cp_2Fe_2(CO)_4$ with PRH_2 (R = Ph, Mes (mesityl)) in refluxing toluene afforded phosphido- and hydrido-bridged diiron complexes $Cp_2Fe_2(CO)_2(\mu\text{-H})(\mu\text{-PHR})$ (**1a**, R = Ph; **1b**, R = Mes). Treatment of **1a** with HOTf under a CO atmosphere produced the phosphido- and carbonyl-bridged cationic complex $[Cp_2Fe_2(CO)_2(\mu\text{-CO})(\mu\text{-PHPh})](OTf)$ (**2**) via hydride abstraction as hydrogen and CO coordination. Complex **2** reacted with phenylacetylene and methyl acrylate at room temperature to give $[Cp_2Fe_2(CO)_2(\mu\text{-CO})(\mu\text{-}(E)\text{-PPh}(CH{=}CHPh))](OTf)$ (**3a**) and $[Cp_2Fe_2(CO)_2(\mu\text{-CO})(\mu\text{-P}(CH_2CH_2CO_2Me)Ph)](OTf)$ (**3b**) in 78% and 65% yield, respectively, in the absence of any additive, as a result of hydrophosphination of the unsaturated carbon−carbon bond of the substrates with the P−H bond of **2**.

Introduction

Functionalization of an E−H group (E = heteroatom such as Si and P) in the organometallic or organoheteroatom ligands coordinated to transition-metal complexes has attracted increasing interest as an important method in synthetic organometallic chemistry.[1−4] Although the majority of the known such reactions need some additives such as radical initiator or base to activate the E−H bond or to abstract the proton from the E−H group, direct functionalization of the E−H group without any additive would be preferable from the viewpoint of atom economy. In relation to this, we previously reported the synthesis and reactivity of silylene- and germylene-bridged diiron complexes having an E−H bond, $Cp_2Fe_2(CO)_2(\mu\text{-CO})(\mu\text{-EHR})$ (E = Si, Ge).[5] The E−H bond in these complexes is highly activated by the attachment of two iron atoms, and the hydrogen is easily replaced with halogen by treatment with organic halides such as CCl_4 at room temperature. With our continuing interest in the reactivity of such dinuclear complexes having an E−H bond, we investigated the isoelectronic phosphorus analogue of them, i.e., cationic phosphido-bridged complexes having a P−H bond, $[Cp_2Fe_2(CO)_2(\mu\text{-CO})(\mu\text{-PHR})]^+$. Although a number of phosphido-bridged dinuclear complexes are already known,[6,7] complexes that have active P−H bonds are relatively less common.[6c,e,7] Nevertheless, this type of

* To whom correspondence should be addressed. Fax: +81-22-217-6543. E-mail: hhashimoto@mail.tains.tohoku.ac.jp; tobita@mail.tains.tohoku.ac.jp.

[†] Tohoku University.

[§] The University of the Air.

(1) For functionalization of a Si−H group, see: (a) Malisch, W.; Kuhn M. *Chem. Ber.* **1974**, *107*, 2835. (b) Malisch, W.; Lankat, R.; Fey, O.; Reising, J.; Schmitzer, S. *J. Chem. Soc., Chem. Commun.* **1995**, 1917. (c) Möller, S.; Fey, O.; Malisch, W.; Seelbach, W. *J. Organomet. Chem.* **1996**, *506*, 239. (d) Nikonov, G. I.; Kuzmina, L. G.; Vyboishchikov, S. F.; Lemenovskii, D. A.; Howard, J. A. K. *Chem. Eur. J.* **1999**, *5*, 2947. (e) Malisch, W.; Hofmann, M.; Kaupp, G.; Käb, H.; Reising, J. *Eur. J. Inorg. Chem.* **2002**, 3235.

(2) For deprotonation of a P−H group, see: (a) Treichel, P. M.; Douglas, W. M.; Dewn, W. K. *Inorg. Chem.* **1972**, *11*, 1615. (b) Seyferth, D.; Wood, T. G.; Henderson, R. S. *J. Organomet. Chem.* **1987**, *336*, 163. (c) Crisp, G. T.; Salem, G.; Wild, S. B. *Organometallics* **1989**, *8*, 2360. (d) Bohle, D. S.; Clark, G. R.; Richard, C. E. F.; Roper, W. R. *J. Organomet. Chem.* **1990**, *393*, 243. (e) Oudet, P.; Bonnet, G.; Moise, C. *Polyhedron* **1995**, *14*, 2173. (f) Edwards, P. G.; Fleming, J. S.; Liyanage, S. S. *J. Chem. Soc., Dalton Trans.* **1997**, *193*.

(3) For insertion of substrates into a P−H bond of metal-coordinated phosphines, see: (a) Huttner, G.; Müller, H.-D.; Friedrich, P.; Kölle, U. *Chem. Ber.* **1977**, *110*, 1254. (b) Treichel, P. M.; Wong, W. K.; Calabrese, J. C. *J. Organomet. Chem.* **1978**, *159*, C20. (c) Nagel, U.; Rieger, B.; Bublewitz, A. *J. Organomet. Chem.* **1989**, *370*, 223. (d) Diel, B. N.; Brandt, P. F.; Haltiwanger, R. C.; Hackeney, M. L. J.; Norman, A. D. *Inorg. Chem.* **1989**, *28*, 2811. (e) Leoni, P.; Pasquali, M.; Sommovigo, M.; Albinati, A.; Lianza, F.; Pregosin, P. S.; Rüegger, H. *Organometallics* **1994**, *13*, 4017. (f) Leoni, P.; Vichi, E.; Lencioni, S.; Pasquali, M.; Chiarentin, E.; Albinati, A. *Organometallics* **2000**, *19*, 3062. (g) Edwards, P. G.; Ingold, F.; Liyanage, S. S.; Newman, P. D.; Wong, W.-K.; Chen, Y. *Eur. J. Inorg. Chem.* **2001**, 2865. (h) Malisch, W.; Klüpfel, B.; Schumacher, D. G.; Nieger, M. *J. Organomet. Chem.* **2002**, *661*, 95. (i) Malisch, W.; Hofmann, M.; Kaupp, G.; Käb, H.; Reising, J. *Eur. J. Inorg. Chem.* **2002**, 3235.

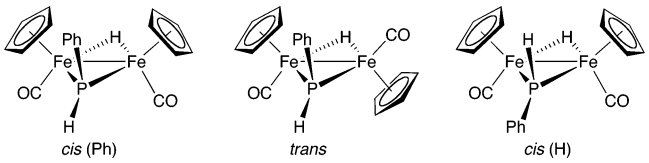
(4) For insertion of substrates into a P−H bond of phosphido-bridged complexes, see: (a) Seyferth, D.; Wood, T. G. *Organometallics* **1987**, *6*, 2563. (b) Seyferth, D.; Wood, T. G. *Organometallics* **1988**, *7*, 717.

(5) (a) Kawano, Y.; Tobita, H.; Ogino, H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 843. (b) Kawano, Y.; Tobita, H.; Ogino, H. *J. Organomet. Chem.* **1992**, *428*, 125. (c) Kawano, Y.; Tobita, H.; Ogino, H. *J. Am. Chem. Soc.* **1994**, *116*, 8575. (d) Fujita, J.; Kawano, Y.; Tobita, H.; Ogino, H. *Chem. Lett.* **1994**, 1353.

(6) See for example: (a) Roberts, D. A.; Geoffroy, G. L. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E., Eds.; Pergmon Press: London, 1982; Chapter 40. (b) Iggo, J. A.; Mays, M. J.; Raithby, P. R. Hendrick, K. *J. Chem. Soc., Dalton Trans.* **1983**, 205. (c) Henrick, K.; McPartlin, M.; Horton, A. D.; Mays, M. J. *J. Chem. Soc., Dalton Trans.* **1988**, 1083. (d) Brunner, H.; Rötzer, M. *J. Organomet. Chem.* **1992**, *425*, 119. (e) Manojlovic-Muir, L.; Muir, K. W.; Jennings, M. C.; Mays, M. J.; Solan, G. A.; Woulfe, K. W. *J. Organomet. Chem.* **1995**, *491*, 255. (f) Mealli, C.; Ienco, A.; Galindo, A.; Perez, E. C. *Inorg. Chem.* **1999**, *38*, 4620. (g) Garcia, M. E.; Riera, V.; Ruiz, M. A.; Reuda, M. T.; Saez, D. *Organometallics* **2002**, *21*, 5515, and references therein.

10.1021/om049000o CCC: $30.25
Publication on Web 02/08/2005

Chart 1

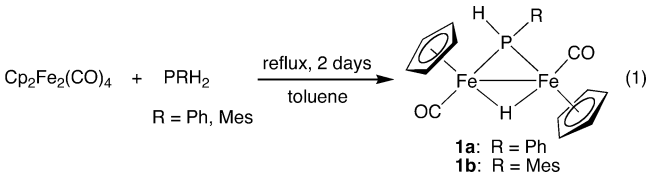


μ-phosphido complexes are potentially useful as reagents for reactions such as hydrophosphination. Indeed, Seyferth et al. have previously reported[4] that the P−H bond of a neutral phosphido-bridged complex $Fe_2(CO)_6(\mu\text{-PPhH})_2$[7b,c] reacted with olefinic and acetylenic α,β-unsaturated carbonyl compounds to afford hydrophosphination products such as $Fe_2(CO)_6(\mu\text{-PPhH})[\mu\text{-PPh}(CH_2CH_2CO_2CH_3)]$ in the presence of base. However, such examples are still limited.

This paper describes the synthesis of new neutral phosphido- and hydrido-bridged complexes having a P−H bond, $Cp_2Fe_2(CO)_2(\mu\text{-H})(\mu\text{-PHR})$ [**1a**, R = Ph; **1b**, R = Mes (2,4,6-trimethylphenyl)], and the conversion of **1a** to the cationic phosphido- and carbonyl-bridged complex $[Cp_2Fe_2(CO)_2(\mu\text{-CO})(\mu\text{-PPhH})](OTf)$ (**2**) by hydride abstraction with acid under a CO atmosphere. The cationic phosphido-bridged complex **2** reacted with phenylacethylene and methyl acrylate at room temperature to produce the hydrophosphination products $[Cp_2Fe_2(CO)_2(\mu\text{-CO})(\mu\text{-PPhR})](OTf)$ (**3a**, R = CH=CHPh; **3b**, R = $CH_2CH_2CO_2Me$), in the absence of any additive. The details of these reactions and the mechanistic studies are also presented.

Results and Discussion

Synthesis of Neutral Phosphido-Bridged Complexes 1a and 1b. Thermal reaction of $Cp_2Fe_2(CO)_4$ with PRH_2 in refluxing toluene produced phosphido- and hydrido-bridged diiron complexes $Cp_2Fe_2(CO)_2(\mu\text{-H})(\mu\text{-PHR})$ (**1a**, R = Ph; **1b**, R = Mes) (eq 1) as red crystals. Similar reactions have been used previously to prepare



related μ-phosphido complexes, e.g., $Cp_2Mo_2(CO)_4(\mu\text{-H})(\mu\text{-PPhH})$.[6c,7f] Among the possible three geometrical isomers (Chart 1), *trans*-isomers of **1a** and **1b** were isolated in 46% and 45% yields, respectively, and were fully characterized. A mixture of two complexes that were assignable to *cis*-isomers were also obtained in 5% yield in the case of **1a** but were not in the case of **1b** (eq 1, Chart 1). The ^{31}P NMR spectra of *trans*-isomers of **1a** and **1b** show the μ-phosphido signals at moderately low field (131.3 ppm for **1a**; 103.6 ppm for **1b**). Their μ-hydrido signals appear at very high field (−19.00 ppm for **1a**; −18.80 ppm for **1b**) as a doublet of doublets coupled with a phosphorus atom and a proton on the phosphorus. Their *trans*-structure is supported by the appearance of only one CO band (1903 cm^{-1} for **1a**; 1905 cm^{-1} for **1b**) in each IR spectrum and two inequivalent Cp signals in each ^1H NMR spectrum (4.25 and 4.27 ppm for **1a**; 4.18 and 4.25 ppm for **1b**). The structure of *trans*-**1b** was further confirmed by X-ray crystallography as shown in Figure 1. Two Cp rings are positioned *trans* to each other with respect to the Fe(1)−Fe(2)−P three-membered ring. The aromatic ring of the mesityl group is oriented nearly parallel to the Cp rings to minimize the steric hindrance among them. The Fe−Fe and Fe−P bond lengths are within normal single-bond lengths.

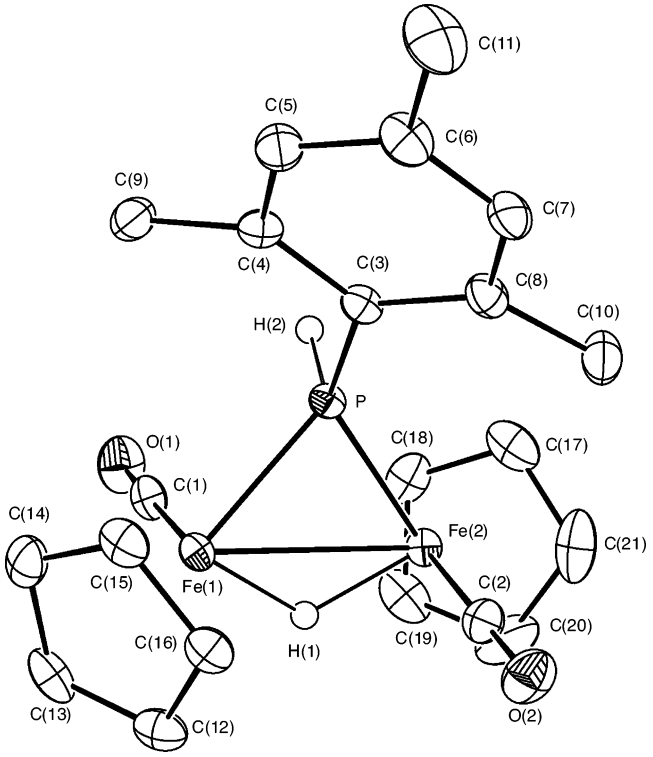
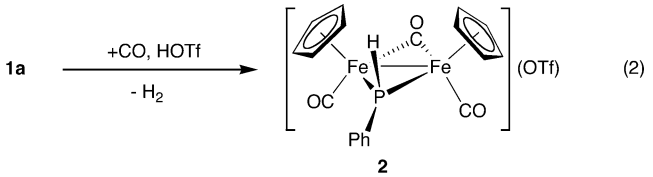


Figure 1. ORTEP diagram of *trans*-**1b** with thermal ellipsoids drawn at the 50% probability level. Selected bond distances (Å) and angles (deg): Fe(1)−Fe(2) 2.6969(6), Fe(1)−P 2.1897(9), Fe(2)−P 2.1829(3), Fe(1)−H(1) 1.58(5), Fe(2)−H(1) 1.66(5), P−H(2) 1.38(5); Fe(1)−P−Fe(2) 76.16(3).

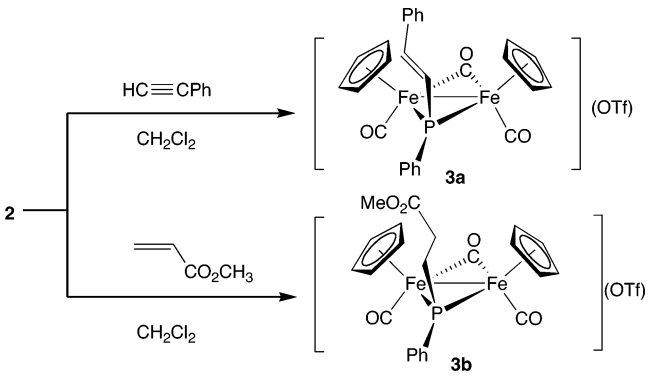
Synthesis of Cationic Phosphido-Bridged Complex 2. Treatment of *trans*-**1a** with HOTf under a CO atmosphere gave a cationic complex, $[Cp_2Fe_2(CO)_2(\mu\text{-CO})(\mu\text{-PHPh})](OTf)$ (**2**), as dark red microcrystals in 75% yield (eq 2). In this reaction, the bridging hydrido ligand



of **1** was selectively attacked by an acidic proton and

(7) (a) Treichel, P. M.; Dean, W. K.; Douglas, W. M. *J. Organomet. Chem*. **1972**, *42*, 145. (b) Treichel, P. M.; Dean, W. K.; Douglas, W. M. *Inorg. Chem*. **1972**, *12*, 1609. (c) Bartsch, R.; Hietkamp, S.; Morton, S.; Stelzer, O. *J. Organomet. Chem*. **1981**, *222*, 263. (d) Müller, M.; Vahrenkamp, H. *Chem. Ber*. **1983**, *116*, 2311. (e) Arif, A. M.; Cowley, A. H.; Pakulski, M.; Hursthouse, M. B.; Karauloz, A. *Organometallics* **1985**, *4*, 2227. (f) Woodward, S.; Curtis, M. D. *J. Organomet. Chem*. **1992**, *439*, 319. (g) Haupt, H.-J.; Schwefer, M.; Flörke, U. *Inorg. Chem*. **1995**, *34*, 292. (h) Manojlobvic-Muir, L.; Muir, K. W.; Jennings, M. C.; Mays, M. J.; Solan, G. A.; Woulfe, K. W. *J. Organomet. Chem*. **1995**, *491*, 255. (i) Oudet, P.; Bonnet, G.; Moise, C. *Polyhedron* **1995**, *14*, 2173. (j) Davis, J. E.; Mays, M. J.; Raithby, P. R.; Shields, G. P.; Tompkin, P. K. *Chem. Commun*. **1997**, 361. (k) Davies, J. E.; Feeder, N.; Gray, C. A.; Mays M. J.; Woods, A. D. *J. Chem. Soc., Dalton Trans*. **2000**, 1695.

Scheme 1



removed as a hydrogen molecule. The resulting vacant site was saturated by CO coordination to produce **2**. The addition of acid is a common method to prepare cationic complexes, but the addition of acid that is followed by hydrogen release is rare. For example, the addition of HBF_4 to $M_2(CO)_4(\mu\text{-H})(\mu\text{-P}^t\text{Bu}_2)(\mu\text{-dppm})$ (M = Fe, Ru) affords a μ-dihydride complex $[M_2(CO)_4(\mu\text{-H})_2(\mu\text{-P}^t\text{Bu}_2)(\mu\text{-dppm})](BF_4)$.[8] Further, although some related complexes formulated as $[Cp_2Fe_2(CO)_2(\mu\text{-CO})(\mu\text{-PPhR})](X)$ (R = Me, Ph, CH_2SiMe_3, etc.; X = Cl, I, and BPh_4) have been prepared by photoirradiation of $[Cp_2Fe_2(CO)_4(\mu\text{-PPhR})](X)$,[9] the ones that have active P−H bonds have not been prepared by this method. Our thermal method is useful to prepare cationic phosphido-bridged complexes having P−H bonds.

Complex **2** exclusively takes a *cis*-geometry, as evidenced by spectroscopic data. Thus, the ^{1}H NMR spectrum of **2** shows a single Cp signal at 5.68 ppm (10H intensity), which indicates a symmetrical *cis*-structure. The IR spectrum exhibits two terminal CO bands (2013 and 1986 cm^{-1}) and a bridging CO band (1821 cm^{-1}). The intensity of the νCO_{sym} band (2013 cm^{-1}) is distinctly higher than that of the νCO_{asym} band (1986 cm^{-1}). On consideration of the steric repulsion among two Cp rings and a phenyl group on the μ-phosphido ligand, the *cis* (H) type geometry in Chart 1 is preferred to the *cis* (Ph) type one. A similar *cis*-configuration is also found in a closely related cationic complex $[Cp_2Fe_2(CO)_2(\mu\text{-CO})(\mu\text{-PH}^t\text{Bu})][FeCl_3(THF)]$, reported by Fenske et al.[10] Apparently, by replacing the bridging hydrido ligand in **1a** with a bridging carbonyl ligand to form **2**, the geometry changed drastically from *trans* to *cis*. This may be attributable to the much larger steric requirement of the μ-CO in **2** compared to that of the μ-H in **1a**. The ^{31}P NMR spectrum of **2** shows a signal at 191.0 ppm in a lower field compared to that of neutral complex *trans*-**1a** (131.3 ppm). The ^{1}H NMR signal of a PH group also appears at 9.19 ppm (d, $^1J_{PH}$ = 406.6 Hz) that is greatly downfield shifted compared to that of *trans*-**1a** (5.95 ppm). These large downfield shifts can be attributable to the cationic nature of **2**. In addition, the same treatment of *trans*-**1b** with HOTf afforded only an unidentified product mixture.

Reaction of 2 with Phenylacetylene. The P−H bond of the bridging ligand of cationic complex **2** was highly activated and smoothly underwent hydrophosphination under mild conditions. Thus, reaction of **2** with an excess of phenylacetylene at room temperature afforded $[Cp_2Fe_2(CO)_2(\mu\text{-CO})(\mu\text{-}(E)\text{-PPh(CH=CHPh)})](OTf)$ (**3a**) in 78% yield (Scheme 1). Complex **3a** was structurally characterized by X-ray crystallography. The ORTEP view of the cationic part is shown in Figure 2. The iron centers are bridged by a CO ligand and a modified phosphido ligand, P(*E*-CH=CHPh)Ph. The *trans* addition of the P−H bond took place exclusively to generate an *E*-styryl group on the phosphorus atom. No *Z*-styryl isomer was observed. The *cis*-configuration of two Cp ligands is retained, and they are also on the same side of the styryl group with respect to the Fe_2P three-membered ring. The four-membered ring composed of Fe(1), P, Fe(2), and C(1) is folded at the Fe−Fe bond, and the dihedral angle between the two three-membered rings, Fe(1)−Fe(2)−P and Fe(1)−Fe(2)−C(1), is 164°. Similar folding of the dinuclear framework has also been observed in a number of carbene-, silylene-, and germylene-bridged diiron μ-carbonyl complexes with *cis*-configurations.[5]

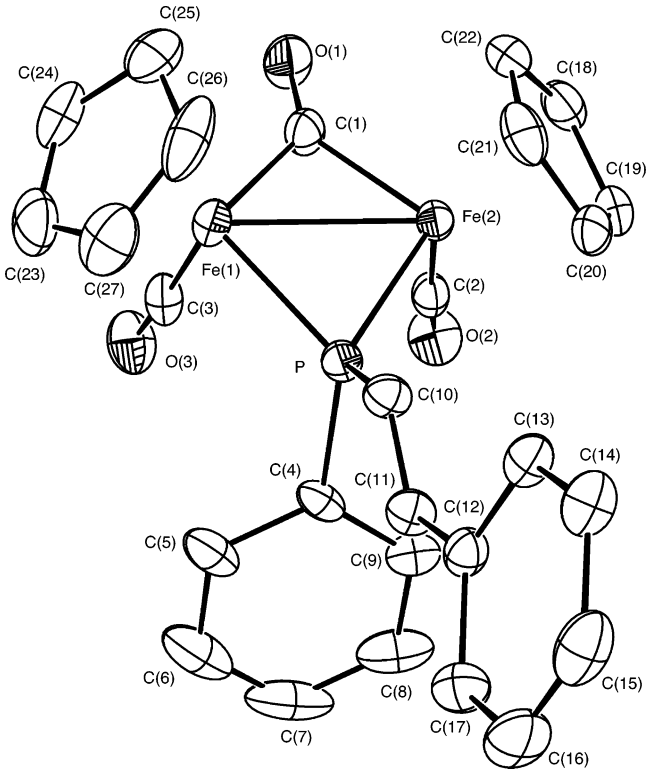


Figure 2. ORTEP diagram of the cationic part of **3a** with thermal ellipsoids drawn at the 30% probability level. Selected bond distances (Å) and angles (deg): Fe(1)−Fe(2) 2.6175(10), Fe(1)−P 2.1947(14), Fe(2)−P 2.1891(14), P−C(4) 1.805(5), P−C(10) 1.788(5); Fe(1)−P−Fe(2) 73.32(5), Fe(1)−C(1)−Fe(2) 84.4(2), P−C(10)−C(11) 125.8(4).

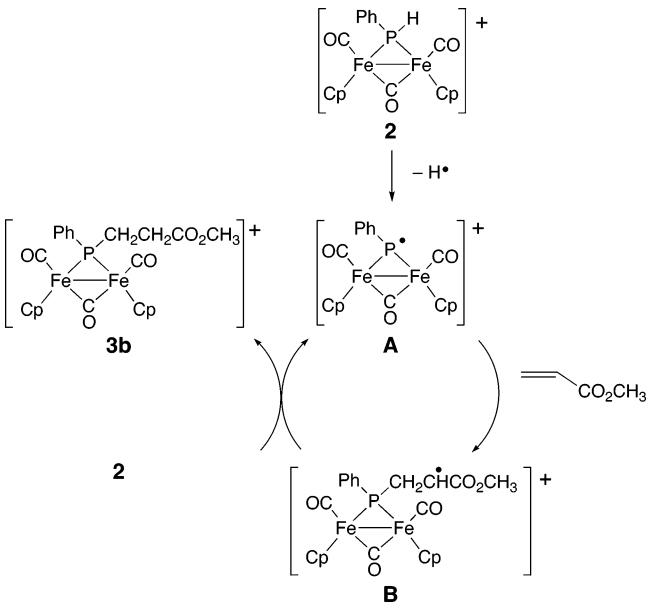
As mentioned in the Introduction, Seyferth et al. reported[4] the related hydrophosphination of olefinic and acetylenic α,β-unsaturated carbonyl compounds with neutral complex $Fe_2(CO)_6(\mu\text{-PPhH})_2$. Although these reactions need the addition of a secondary amine such as piperidine, our hydrophosphination system does not need any additive. It should also be mentioned that some insertion reactions of alkynes and alkenes into the P−H bonds of metal-coordinated secondary phosphines[3]

(8) Bottcher, H.-C.; Graf, M.; Merzweiler, K.; Wagner, C. *J. Organomet. Chem*. **2001**, *628*, 144.

(9) (a) Klasen, C.; Effinger, G.; Schmid, S.; Lorenz, I.-P. *Naturforsh. Z*. **1993**, *48b*, 705. (b) Lorenz, I.-P.; Pohl, W.; Nöth, H.; Schmidt, M. *J. Organomet. Chem*. **1994**, *475*, 211

(10) Fenske, D.; Schottmuller, H. *Z. Anorg. Allg. Chem*. **1998**, *624*, 443.

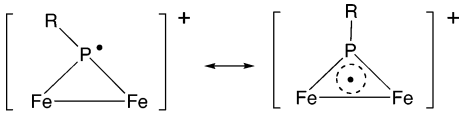
Scheme 2



and a cluster having μ_3-P−H ligands[11] are reported. Most of such reactions are assisted by base, and only a few cases proceed without base. For example, Huttner et al. reported that phenylacetylene inserted into the P−H bond of $CpMn(CO)_2(PPhH_2)$ without base, but it took 10 days at 80 °C to be completed.[3a] Albinati et al. also reported the insertion of ethylene into the P−H bond of cationic complex $[Pd_2(\mu\text{-}PCy_2)(PCy_2H)_4](OTf)$.[3e] Interestingly, this reaction proceeds at room temperature, but the mechanistic studies have not been reported.

Reaction of 2 with Methyl Acrylate and the Reaction Mechanism. Complex **2** also reacted with methyl acrylate at room temperature to produce $[Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}P(CH_2CH_2CO_2Me)Ph)](OTf)$ (**3b**) in 65% isolated yield. Complex **3b** was also fully characterized. The spectroscopic data supports its *cis*-configuration based on their similarity with those of **3a**. Importantly, this reaction was completed within a day at room temperature, but took 5 days in the presence of 1 molar equiv of duroquinone, a typical radical scavenger. These observations suggest a radical chain mechanism for the hydrophosphination with **2**.[12] A possible radical chain mechanism is illustrated in Scheme 2. The key steps of the mechanism consist of (1) homolytic cleavage of the P−H bond to produce radical intermediate **A**, (2) addition of **A** to the double bond of alkene to produce radical intermediate **B**, and (3) abstraction of a hydrogen radical from **2** with **B** to produce **A** and **3b**. It is likely that the reaction of **2** with phenylacetylene also proceeds via a similar mechanism. The easy occurrence of this radical reaction for **2** is in contrast to that for organic hydrophosphines, which requires photoirradiation or radical initiators to be induced.[13] Generation of the intermediate phosphorus-centered radical from the cationic complex **2** would be facilitated by delocalization of the unpaired electron over two iron atoms in this dinuclear system (Chart 2).

Chart 2



Conclusions. We synthesized new neutral phosphido- and hydrido-bridged complexes having a P−H bond, $Cp_2Fe_2(CO)_2(\mu\text{-}H)(\mu\text{-}PHR)$ (**1a**, R = Ph; **1b**, R = Mes) by the reaction of $Cp_2Fe_2(CO)_4$ with primary phosphine PRH_2 (R = Ph, Mes). Complex **1a** was converted to the cationic phosphido-bridged complex $[Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}PHPh)](OTf)$ (**2**) by hydride abstraction with HOTf under a CO atmosphere. The P−H bond of cationic phosphido-bridged complex **2** is highly activated and smoothly reacted with phenylacethylene and methyl acrylate at room temperature to afford the hydrophosphination products in good yields without any base or other additive. The hydrophosphination reactions in this system are suggested to proceed through a radical chain mechanism. Further investigations on the reactivity of the cationic phosphido-bridged complexes are in progress.

Experimental Section

General Procedures. All manipulations were carried out under high vacuum or a dry nitrogen atmosphere. Toluene, hexane, and ether were freshly distilled from sodium-benzophenone ketyl. Dichloromethane was dried over calcium hydride and distilled just before use. Benzene-d_6, acetone-d_6, and dichloromethane-d_2 were dried over molecular sieves 4 A. Duroquinone[14] and mesitylphosphine[15] were prepared according to the literature methods. All other compounds were used as received. NMR spectra were recorded on a Bruker ARX-300 Fourier transform spectrometer at room temperature. IR spectra were measured on a HORIBA FT-200 or FT-730 spectorometer. Mass analyses were performed on a Hitachi M-2500 or JMS-HX 110 or a Shimadzu QP5050 spectorometer at the Instrumental Analysis Center for Chemistry, Tohoku University. Elemental analyses were performed at the Instrumental Analysis Center for Chemistry, Tohoku University.

Synthesis of $Cp_2Fe_2(CO)_2(\mu\text{-}H)(\mu\text{-}PHR)$ (1a, R = Ph; 1b, R = Mes). A solution of $Cp_2Fe_2(CO)_4$ (0.75 g, 2.1 mmol) and $PPhH_2$ (0.24 g, 2.1 mmol) in dry toluene (30 mL) was refluxed for 2 days. The resultant mixture was evaporated and chromatographed on a silica gel flash column. Elution with hexane/ether (20:1) first gave a red solution. Removal of the solvent afforded the *trans*-isomer of $Cp_2Fe_2(CO)_2(\mu\text{-}H)(\mu\text{-}PHPh)$ (**1a**) as a dark red solid (0.40 g, 0.95 mmol, 46%). Further elution gave the second red fraction, which contained a mixture of *cis*- and *trans*-isomers of the known complex $Cp_2Fe_2(CO)_2(\mu\text{-}PHPh)_2$[7a] in 19% yield (0.21 g, 0.41 mmol). Finally, the fraction with yellow-brown color was collected and the solvent was removed to give an isomeric mixture of two *cis*-**1a** (see Chart 1) in 5% total yield (42 mg, 0.10 mmol). The ratio of the major isomer and the minor isomer of *cis*-**1a** is approximately 2:1 by the ^{1}H NMR spectrum. *trans*-**1a**. ^{1}H NMR (300 MHz, C_6D_6): δ −19.00 (dd, $^2J_{PH}$ = 42.9 Hz, $^3J_{HH}$ = 1.4 Hz, 1H, μ-H), 4.25 (d, $^3J_{PH}$ = 1.1 Hz, 5H, Cp), 4.27 (d, $^3J_{PH}$ = 1.6 Hz, 5H, Cp), 5.95 (dd, $^1J_{PH}$ = 340.3 Hz, $^3J_{HH}$ = 1.4 Hz, 1H, PH), 7.06−7.11,

(11) Caryn, C. B.-B.; Bautista, M. T.; Aschauer, C. K.; White, P. S. *J. Am. Chem. Soc*. **2000**, *122*, 3952.

(12) (a) Schroeder, N. C.; Angelici, R. J. *J. Am. Chem. Soc*. **1986**, *108*, 3688. (b) Gracey, B. P.; Knox, S. A. R.; Macpherson, K. A.; Orpen, A. G.; Stobart, S. R. *J. Chem. Soc., Dalton Trans*. **1985**, 1935.

(13) Smith, D. J. H. In *Comprehensive Organic Chemistry*; Sutherland, I. O., Ed.; Pergamon Press: Oxford, 1979; Vol. 2, p 1121.

(14) Smith, L. I. *Organic Syntheses*; Wiley: New York, 1943; Collect. Vol. II, p 254.

(15) Oshikawa, T.; Yamashita, M. *Chem. Ind*. (*London*) **1985**, 126.

7.72−7.80 (m, 5H, Ph). ^{31}P NMR (36.3 MHz, C_6D_6): δ 131.3. ^{13}C NMR (75.5 MHz, C_6D_6): δ 80.5, 81.1 (s, Cp), 128.5 (d, J_{PC} = 10.4 Hz, *o*-C_6H_5), 129.0 (d, J_{PC} = 3.4 Hz, *p*-C_6H_5), 132.6 (d, J_{PC} = 9.0 Hz, *m*-C_6H_5), 141.9 (d, J_{PC} = 30.6 Hz, *ipso*-C_6H_5), 216.5 (d, $^2J_{PC}$ = 20.8 Hz), 217.7 (d, $^2J_{PC}$ = 19.7 Hz, CO). IR (KBr, cm^{-1}): 1903 (vs, *ν*CO), 1420 (w, PPh). EI-MS (70 eV): *m/z* 408 (26, M$^+$), 380 (78, M$^+$ − CO), 350 (100, M$^+$ − CO − 2H). Anal. Calcd for $C_{18}H_{17}Fe_2O_2P$: C, 52.99; H, 4.20. Found: C, 53.18; H, 4.11. Data for a mixture of two *cis*-**1a**: ^{1}H NMR (300 MHz, C_6D_6): major isomer, δ −19.97 (d, $^2J_{PH}$ = 45.3 Hz, 1H, *μ*-H), 4.07 (d, $^3J_{PH}$ = 1.3 Hz, 10H, Cp), 6.59 (d, $^1J_{PH}$ = 321.1 Hz, 1H, PH), 7.01−7.88 (m, 5H, Ph), minor isomer, −19.38 (dd, $^2J_{PH}$ = 43.4 Hz, $^3J_{PH}$ = 1.7 Hz, 1H, *μ*-H), 4.13 (s, 10H, Cp), 5.39 (dd, $^1J_{PH}$ = 358.2 Hz, $^3J_{PH}$ = 1.7 Hz, 1H, *μ*-H), 7.01−7.88 (m, 5H, Ph). ^{31}P NMR (121.5 MHz, C_6D_6): δ 134.0, 138.2. IR (C_6H_6, cm^{-1}): 2023 (w, *ν*PH), 1954 (vs, *ν*CO), 1915 (s, *ν*CO), 1435 (w, *ν*PPh).

Complex **1b** was prepared by a similar procedure with use of $PMesH_2$ in 45% yield. No *cis*-isomers were detected in this case. *trans*-**1b**: ^{1}H NMR (300 MHz, C_6D_6): δ −18.80 (dd, $^2J_{HP}$ = 40.1 Hz, $^3J_{HH}$ = 1.4 Hz, 1H, *μ*-H), 2.13 (s, 3H, *p*-CH_3), 2.86 (s, 6H, *o*-CH_3), 4.18 (d, $^2J_{HP}$ = 1.2 Hz, 5H, Cp), 4.25 (d, $^2J_{HP}$ = 1.8 Hz, 5H, Cp), 5.70 (d, $^1J_{HP}$ = 334.2 Hz, 1H, PH), 6.83 (s, 2H, ArH). ^{31}P NMR (121.5 MHz, C_6D_6): δ 103.6. ^{13}C NMR (75.5 MHz, C_6D_6): δ 21.2 (s, *p*-CH_3), 24.2 (d, J_{pc} = 7.6 Hz, *o*-CH_3), 81.0, 82.0 (s, Cp), 129.9 (d, J_{pc} = 8.3 Hz, *o*-$C_6H_3Me_3$), 132.2 (d, J_{pc} = 27.9 Hz, *ipso*-$C_6H_3Me_3$), 138.7 (d, J_{pc} = 3.8 Hz, *p*-C_6H_3-Me_3), 142.2 (d, J_{pc} = 6.0 Hz, *m*-$C_6H_3Me_3$), 217.4 (d, $^2J_{pc}$ = 20.4 Hz), 218.3 (d, $^2J_{pc}$ = 19.6 Hz, CO). IR (KBr, cm^{-1}): 1905 (vs, *ν*CO), 1450 (w, PMes). EI-MS (70 eV): *m/z* 450 (16, M$^+$), 422 (54, M$^+$ − CO), 394 (3.9, M$^+$ − 2CO), 390 (100, M$^+$ − 2CO − 4H). Anal. Calcd for $C_{21}H_{23}Fe_2O_2P$: C, 56.04; H, 5.15. Found: C, 56.15; H, 5.59

Reaction of *trans*-1a with HOTf: Synthesis of *cis*-[$Cp_2Fe_2(CO)_2$(*μ*-CO)(*μ*-PHPh)](OTf) (2). Under a CO atmosphere (1 atm), HOTf (0.20 g, 1.3 mmol) was added to a CH_2Cl_2 (50 mL) solution of *trans*-**1a** (0.50 g, 1.2 mmol) at −48 °C. After stirring for 4 h at room temperature, the solution was filtered and evaporated under high vacuum. Recrystallization of the resulting solid from dichloromethane layered with ether provided *cis*-[$Cp_2Fe_2(CO)_2$(*μ*-CO)(*μ*-PPhH)](OTf) (**2**) as a dark red microcrystalline solid (0.53 g, 0.90 mmol, 75%). Data for **2**: ^{1}H NMR (300 MHz, acetone-d_6): δ 5.68 (d, $^3J_{PH}$ = 1.4 Hz, 10H, Cp), 7.54−7.67, 7.85−7.91 (m, 5H, Ph), 9.19 (d, $^1J_{PH}$ = 406.6 Hz, 1H, PH). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 191.0. ^{13}C NMR (75.5 MHz, acetone-d_6): δ 88.7 (s, Cp), 129.6 (d, J_{PC} = 12.8 Hz, *o*-C_6H_5), 132.7 (d, J_{PC} = 4.8 Hz, *p*-C_6H_5), 132.7 (d, J_{PC} = 10.3 Hz, *m*-C_6H_5), 135.0 (d, J_{PC} = 47.8 Hz, *ipso*-C_6H_5), 207.8 (d, $^2J_{PC}$ = 18.1 Hz, CO), 253.7 (d, $^2J_{PC}$ = 3.8 Hz, *μ*-CO). IR (KBr, cm^{-1}): 2013 (vs), 1986 (s) (*ν*CO_{term}), 1821 (vs, *ν*CO_{brid}), 1423 (m, PPh), 1273 (vs, *ν*SO). FAB-MS (Xe, *m*-nitrobenzyl alcohol): *m/z* 435 (100, M$^+$), 407 (14, M$^+$ − CO), 379 (2, M$^+$ − 2CO), 351 (27, M$^+$ − 3CO). Anal. Calcd for $C_{20}H_{16}F_3Fe_2O_6PS$: C, 41.18; H, 2.93. Found: C, 41.13; H, 2.76.

Reaction of *trans*-1b with HOTf. Complex *trans*-**1b** was treated with HOTf in a method similar to that described for the reaction of *trans*-**1a** with HOTf. After workup, a red oil was obtained. The ^{31}P NMR spectrum of the oil shows several signals around −50 ppm, but the signal assignable for the analogous complex of **2** was not observed.

Synthesis of [$Cp_2Fe_2(CO)_2$(*μ*-CO)(*μ*-PPhR)](OTf) (3a, R = CH=CHPh; 3b, R = $CH_2CH_2CO_2Me$). A Pyrex glass tube (10 mm o.d.) was charged with **2** (50 mg, 0.086 mg). Dichloromethane (5 mL) and phenylacetylene (47 *μ*L, 0.43 mmol) were transferred to the tube by trap-to-trap distillation and flame-sealed under high vacuum. The sample was allowed to stand at room temperature. After 10 days, the reaction mixture was filtered and evaporated under reduced pressure. The residue was washed with 8 mL of dichloromethane/hexane (3:5) and then recrystallized from a mixture of dichloromethane, hexane, and ether (4:5:5, 7 mL) to afford **3a** as a dark red microcrystalline solid (46 mg, 0.067 mmol, 78%). **3a**: ^{1}H NMR (300 MHz, acetone-d_6): δ 5.74 (d, $^3J_{PH}$ = 0.7 Hz, 10H, Cp), 6.64 (dd, $^3J_{HH}$ = 16.5 Hz, $^3J_{PH}$ = 22.4 Hz, 1H, PCH=C*H*Ph), 7.79 (dd, $^3J_{HH}$ = 16.5 Hz, $^2J_{PH}$ = 30.7 Hz, 1H, PC*H*=CHPh), 7.40−7.43, 7.61−7.68, 8.03−8.10 (m, 10H, Ph). ^{31}P NMR (121.5 MHz, acetone-d_6): δ 237.6. ^{13}C NMR (75.5 MHz, acetone-d_6): δ 90.5 (s, Cp), 129.3 (d, J_{PC} = 1.4 Hz, *o*-C_6H_5CH=CH), 129.6 (d, J_{PC} = 11.0 Hz, *o*-PC_6H_5), 129.8 (s, *m*-C_6H_5CH=CH), 131.1 (s, *p*-C_6H_5CH=CH), 132.6 (d, J_{PC} = 2.6 Hz, *p*-PC_6H_5), 134.6 (d, J_{PC} = 49.5 Hz, *ipso*-PC_6H_5), 135.2 (d, $^1J_{PC}$ = 40.9 Hz, *C*H=CHPh), 135.6 (d, J_{PC} = 49.5 Hz, *ipso*-C_6H_5CH=CH), 136.0 (d, J_{PC} = 8.8 Hz, *p*-PC_6H_5), 146.1 (d, $^2J_{PC}$ = 3.4 Hz, CH=*C*HPh), 208.7 (d, $^2J_{PC}$ = 17.9 Hz, CO), 256.0 (d, $^2J_{PC}$ = 3.3 Hz, *μ*-CO). IR (THF, cm^{-1}): 2013 (vs), 1986 (s) (*ν*CO_{term}), 1821 (vs, *ν*CO_{brid}), 1423 (m, PPh), 1273 (vs, *ν*SO). FAB-MS (Xe, *m*-nitrobenzyl alcohol): *m/z* 435 (100, M$^+$), 407 (14, M$^+$ − CO), 379 (2, M$^+$ − 2CO), 351 (27, M$^+$ − 3CO). Anal. Calcd for $C_{28}H_{22}F_3Fe_2O_6PS$: C, 49.00; H, 3.23. Found: C, 48.65; H, 3.56.

Complex **3b** was prepared by a similar method with use of methyl acrylate (65%). **3b** (dark red crystals): ^{1}H NMR (300 MHz, acetone-d_6): δ 2.89 (td, $^3J_{HH}$ = 8.2 Hz, $^2J_{PH}$ = 10.8 Hz, 2H, PC$H_2$$CH_2$), 3.57 (s, 3H, CO_2*Me*), 3.59 (td, $^3J_{HH}$ = 8.2 Hz, $^3J_{PH}$ = 8.2 Hz, 2H, PCH_2CH_2), 5.76 (d, $^3J_{PH}$ = 0.9 Hz, 10H, Cp), 7.50−7.53, 7.95−8.02 (m, 5H, Ph). ^{31}P NMR (121.5 MHz, acetone-d_6): δ 258.5. ^{13}C NMR (75.5 MHz, acetone-d_6): δ 32.6 (d, $^2J_{PC}$ = 5.2 Hz, PCH_2*C*H_2), 37.6 (d, $^1J_{PC}$ = 19.3 Hz, P*C*H_2-CH_2), 52.2 (s, CO_2*Me*), 90.4 (s, Cp), 129.3 (d, J_{PC} = 10.5 Hz, *o*-PC_6H_5), 132.2 (d, J_{PC} = 2.6 Hz, *p*-PC_6H_5), 135.0 (d, J_{PC} = 8.2 Hz, *m*-PC_6H_5), 137.3 (d, J_{PC} = 42.2 Hz, *ipso*-PC_6H_5), 172.2 (s, *C*O_2Me), 208.7 (d, $^2J_{PC}$ = 17.9 Hz, CO). IR (THF, cm^{-1}): 2019 (vs), 1992 (s) (*ν*CO_{term}), 1828 (vs, *ν*CO_{brid}), 1741 (m, *ν*CO), 1432 (m, PPh), 1255 (vs, *ν*SO). FAB-MS (Xe, *m*-nitrobenzyl alcohol): *m/z* 521 (91, M$^+$), 493 (100, M$^+$ − CO), 465 (6, M$^+$ − 2CO), 437 (35, M$^+$ − 3CO). Anal. Calcd for $C_{24}H_{22}F_3Fe_2O_8PS$: C, 43.01; H, 3.31. Found: C, 42.63; H, 3.39.

NMR Monitoring of the Reaction of 2 with Methyl Acrylate. A Pyrex NMR tube equipped with a high-vacuum stopcock was loaded with **2** (8.0 mg, 0.014 mmol), methyl acrylate (0.014 mL, 0.15 mmol), and CD_2Cl_2 (0.4 mL). The sample was flame-sealed under high vacuum. The reaction was allowed to proceed at room temperature and was monitored by ^{1}H NMR spectroscopy. After 24 h, **2** was completely consumed and the ^{1}H NMR spectrum revealed the formation of **3b**.

NMR Monitoring of the Reaction of 2 with Methyl Acrylate in the Presence of Duroquinone. A solution of **2** (8.0 mg, 0.014 mmol), methyl acrylate (0.010 mL, 0.11 mmol), and duroquinone (0.2 mg, 0.014 mmol) in CD_2Cl_2 (0.4 mL) in a sealed NMR tube was kept at room temperature and monitored by ^{1}H NMR spectroscopy. After 5 days, **2** was completely consumed to produce **3b**.

X-ray Crystal Structure Determination of *trans*-1b and 3b. The crystals of *trans*-**1b** and **3a** suitable for X-ray crystal structure determination were mounted on a glass fiber. The intensity data for *trans*-**1b** were collected on a RIGAKU RAXIS-RAPID imaging plate diffractometer with graphite-monochromated Mo Kα radiation to a maximum 2*θ* value of 55.0 at 150 K. A total of 44 images, corresponding to 220.0° oscillation angles, were collected with two different goniometer settings. Exposure time was 1.30 min/deg. Readout was performed in the 0.100 mm pixel mode. Numerical absorption collections were applied on the crystal shape. The intensity data for **3a** were collected by a Rigaku AFC-6A four-circle diffractometer with graphite-monochromated Mo Kα radiation at 18 °C. Diffraction data were collected in the *ω*−2*θ* scan mode. The structure of *trans*-**1b** was solved by Patterson and Fourier transform methods. All non-hydrogen atoms were refined by full-matrix least-squares techniques with anisotropic displacement parameters based on F^2 with all reflections. The positions of two hydrogen atoms directly attached to phosphorus and iron atoms were found on the difference

Fourier synthesis and refined with isotropic thermal parameters. All other hydrogen atoms were placed at their geometrically calculated positions and added to the structure factor calculations without refinement. The final residue R and the weighted R_w for total reflections (4341) were $R = 0.073$ and $R_w = 0.153$ and the R1 for reflections (3634) with $I > 2\sigma(I)$ was R1 = 0.046. All calculations were performed using the teXsan crystal structure analysis package.[16]The structure of **3a** was solved by the heavy-atom method and refined by the block-diagonal least-squares method with individual anisotropic thermal parameters for non-hydrogen atoms. The positions of all hydrogen atoms were found by difference Fourier syntheses and refined with isotropic thermal parameters. The final residue $R1$ and the weighted $wR2$ for reflections (3417) with $I > 2\sigma(I)$ was $R1 = 0.0545$ and $wR2 = 0.1168$. All calculations were performed using the SHELEX 86 program for crystal structure analysis package.[17] Crystallographic information has been deposited with the Cambridge Crystallographic Data Centre (CCDC Nos. 232043 (*trans*-**1b**), 232044 (**3a**)).

Acknowledgment. This work was supported by the Ministry of Education, Culture, Sports, Science and Technology of Japan [Grants-in-Aid for Scientific Research Nos. 14204065, 14078202, and 14044010].

Supporting Information Available: Crystallographic data for *trans*-**1b** and **3a**, including tables of atomic coordinates, anisotropic thermal parameters, bond distances and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

OM049000O

(16) *teXsan*: Crystal Structure Analysis Package; Molecular Structure Corporation, 1985 & 1999.

(17) Sheldrich, G. M. *SHELX 86*, Program for Crystal Structure Determination; University of Göettingen: Germany, 1986.