conditions. The sample for spectra in Figure 2 was prepared in dark, but the sample for the published one was prepared under room light.

We made a matrix using the data of 150 spectra. The data of each spectrum are arrayed in a column in the matrix. Consequently, the data of 150 spectra make 150 columns. In this case, the rows in matrix correspond to the time evolution of each channel.

Time evolution of the SERS intensity of the band at 1427 cm^{-1} with different power levels of Ar ion laser beam is shown in Figure 3. The jagged lines are experimental data and the smooth lines are calculated ones according to the equation described previously. Best fits were obtained with $k=1200\ \text{sec}^{-1}$.

In the previous model, we did not consider the effect of diffusion. The volume of the sample irradiated by laser beam is very small and the local temperature is much higher than that of surroundings due to the absorption of laser beam. Therefore, the effect of diffusion will become important when the flow becomes slow. Indeed, we could get a slightly better fitting by including a diffusion term.[7] Particularly, the fitting of the tail part of the graphs was slightly improved.

The intensities of most bands in Figure 2 decreased monotonically with increasing the exposure time of laser beam. No band growth near 1400 cm^{-1} attributable to graphite carbon was observed.[4,7] Therefore, we conclude that the ODIB on surfaces may simply leave the surface after absorption of a photon.

In conclusion, we have shown that flow method is very useful to study the photochemistry of molecules adsorbed on Ag colloid surfaces. Particularly, the flow method can give us more advantage to use a multichannel detection system.

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Reactions of Polyhedral Boron Hydrides with Transition-Metal Acetylide: Synthesis Characterization of the New Metallaborane Clusters *nido*-5-Me_2S-6-$Cp(CO)_2FeHC=CPh$-$B_{10}H_{11}$ and *nido*-9-$Cp(CO)_2FeHC=CPh$-6-SB_9H_{10}.

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The reaction of decaborane(14) $B_{10}H_{14}$ with an alkyne in the presence of dimethyl sulfide is a well-established route to *ortho*-carborane 1,2-$C_2B_{10}H_{12}$ and its derivatives.[1] Previous studies[2] have suggested that this reaction involves the initial formation of bis(dimethylsulfide) decaborane(12) $B_{10}H_{12}(SMe_2)_2$, which can then dissociate a dimethylsulfide unit, yielding a reactive $B_{10}H_{12}SMe_2$ species. Further reaction of this $B_{10}H_{12}SMe_2$ intermediate with an alkyne then leads to the direct insertion of a two-carbon acetylenic unit into the cage along with dissociation of the remaining SMe_2 and H_2 loss to yield the final product.

$$B_{10}H_{12}(SMe_2)_2 \rightarrow B_{10}H_{12}SMe_2 + SMe_2 \qquad (1)$$

$$B_{10}H_{12}SMe_2 + RC{\equiv}CR \rightarrow B_{10}H_{12}SMe_2R_2C_2 \qquad (2)$$

$$B_{10}H_{12}SMe_2R_2C_2 \rightarrow 1,2\text{-}R_2C_2B_{10}H_{10} + H_2 + SMe_2 \qquad (3)$$

Also, reactions of $B_{10}H_{12}(SMe_2)_2$ with the silylated acetylenes, bis(trimethylsilyl) acetylene and (trimethylsilyl) propyne,[3] have been studied and did not yield the expected *ortho*-carborane derivatives but instead gave either alkenyldecaborane or monocarbon carborane products.

$$\begin{aligned} &B_{10}H_{12}(SMe_2)_2 + Me_3SiC{\equiv}CSiMe_3 \rightarrow \\ &\qquad 9\text{-}Me_2S\text{-}7\text{-}(Me_3Si)_2CH\text{-}CB_{10}H_{11} \\ &\qquad + 5\text{-}Me_2S\text{-}6\text{-}(Me_3Si)_2C{=}CH\text{-}B_{10}H_{11} \qquad (4) \end{aligned}$$

$$\begin{aligned} &B_{10}H_{12}(SMe_2)_2 + Me_3SiC{\equiv}CMe \rightarrow \\ &\qquad 5\text{-}Me_2S\text{-}6\text{-}(Me_3Si)MeC{=}CH\text{-}B_{10}H_{11} \qquad (5) \end{aligned}$$

We have investigated the reactions of decaborane(14) $B_{10}H_{14}$ and thiaborane(11) SB_9H_{11} with the transition-metal acetylide $Cp(CO)_2Fe(CCPh)$, and observed that, in contrast to the results discussed above, these reactions do not result in the formation of *ortho*-carborane derivatives. Instead, hydroboration of the acetylene accompanied by dimethyl sulfide group migration is observed to yield 5-(dimethylsulfide)-6-alkenyldecaborane(14) as the major product. Another single product, apparently resulting from the hydroboration of a single carbon of the acetylenic unit into the thiaborane cage, was also isolated in good yields in the reaction of transition-metal acety-

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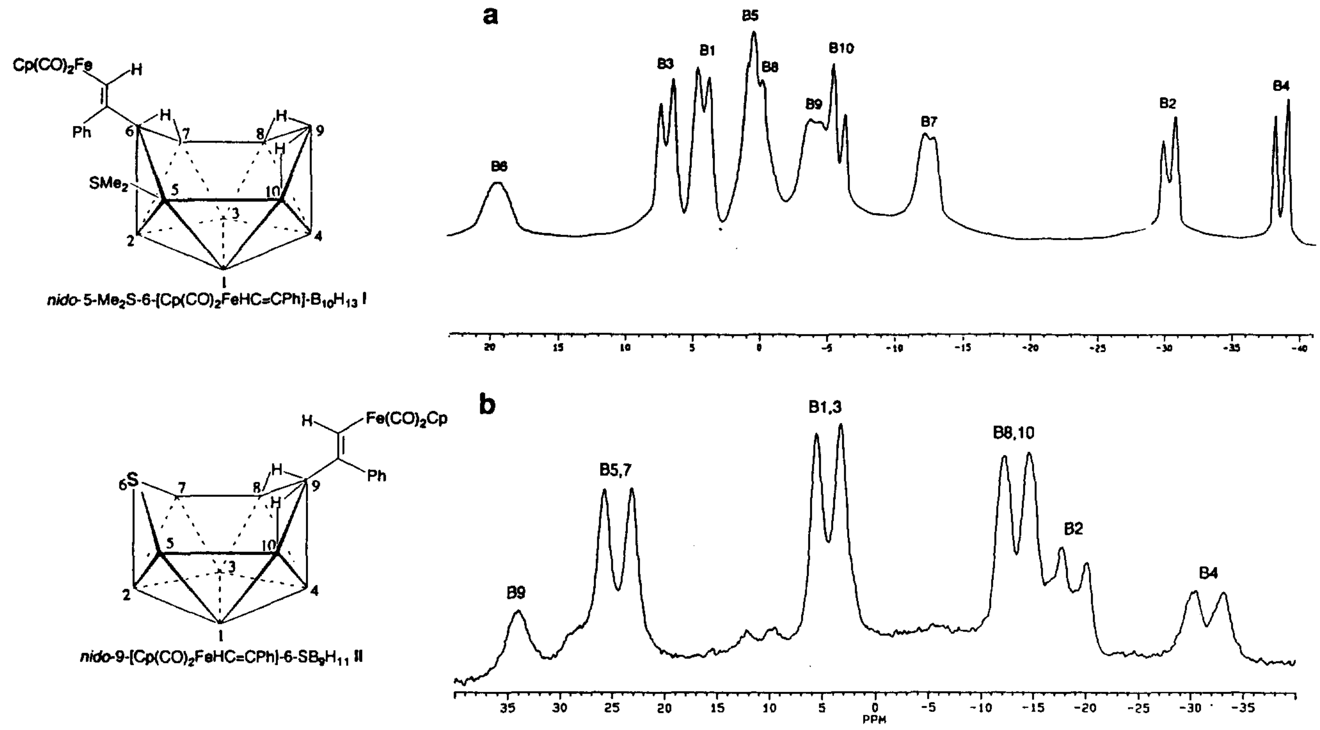

nido-5-Me_2S-6-[$Cp(CO)_2FeHC{=}CPh$]-$B_{10}H_{13}$ **I**

nido-9-[$Cp(CO)_2FeHC{=}CPh$]-6-SB_9H_{11} **II**

Figure 1. 160.5-MHz ^{11}B NMR spectrum of **I** (a) and 64.2-MHz ^{11}B NMR spectrum of **II** (b) in C_6D_6.

lide with thiaborane(11).

$$B_{10}H_{12}(SMe_2)_2 + Cp(CO)_2Fe\text{-}C{\equiv}CPh \rightarrow 5\text{-}Me_2S\text{-}6\text{-}Cp(CO)_2FeHC{=}CPh-B_{10}H_{11}\ \mathbf{I} \qquad (6)$$

$$SB_9H_{11} + Cp(CO)_2Fe\text{-}C{\equiv}CPh \rightarrow 9\text{-}Cp(CO)_2FeHC{=}CPh-6\text{-}SB_9H_{10}\ \mathbf{II} \qquad (7)$$

The reaction of $B_{10}H_{12}(SMe_2)_2$[4] with transition-metal acetylide $Cp(CO)_2Fe(CCPh)$ at benzene reflux for 1 h resulted in the isolation of compound **I**. Compound **I** is a red solid which was separated by column chromatography. Further recrystallization from benzene and hexane gave the pure form of compound **I**. Similar reaction of thiaborane SB_9H_{11}[5] with transition-metal acetylide $Cp(CO)_2Fe(CCPh)$ also gave only one product **II**, a red colored solid, which was shown to be structurally related to the previously characterized compound 9-$R_1HC{=}CR_2$-6-SB_9H_{10},[6] as discussed below.

Chemical analysis and/ or exact mass determination established that both **I** and **II** have the proposed molecular formulas corresponding to $C_{17}B_{10}FeH_{28}O_2S$ and $C_{15}B_9FeH_{21}O_2S$, respectively. Both compounds show parent ions consistent with the proposed formulas.

Both the ^{11}B and ^{1}H NMR spectra of **I** indicate that the compound lacks a plane of symmetry. The ^{11}B NMR spectrum at 160.5 MHz contains ten resonances, two being of intensity one, with the singlets at 18.9 and 0.5 ppm assigned to the $PhC{=}CH\text{-}CpFe(CO)_2$ substituted boron and the dimethyl sulfide substituted boron, respectively. The assignment for **I** given in Figure 1 is in agreement with 2D ^{11}B-^{11}B COSY NMR experiments, which show cross-peaks arising from all adjacent borons, except those borons bridged by hydrogen atoms. As seen in the figure, the compound **I** has a decaborane(14) cage geometry with a dimethyl sulfide bound to the 5-boron position and a-$PhC{=}CH\text{-}CpFe(CO)_2$ group bound at the 6-boron position. Thus, the boron spin-decoupled ^{1}H NMR spectrum shows two resonances of intensity 2 and 1 (at shifts -1.40 and -3.65 ppm, respectively) characteristic of boron-bridging protons. The ^{1}H NMR spectrum also shows a singlet resonance of intensity five for cyclopentadienyl protons, multiplets of intensity five for phenyl protons, and an intensity one resonance at 6.39 ppm which is assigned to the olefinic proton of the -$PhC{=}CH$- moiety. The absence of a plane of symmetry in the cage is reflected in the fact that separate resonances are observed for each of the dimethyl sulfide methyl groups. The spectral data obtained for **I** are also consistent with those of the previously characterized acetylene hydroboration product: 5-Me_2S-6-$(Me_3Si)_2C{=}CH\text{-}B_{10}H_{11}$.[3]

The spectral data obtained for **II** are consistent with its formulation as the acetylene hydroboration product: 9-$Cp(CO)_2FeHC{=}CPh$-6-SB_9H_{10}. The ^{11}B NMR spetrum of **II** contains six resonances with relative intensities of 1 : 2 : 2 : 2 : 1 : 1. The singlet resonance at $+35$ ppm is consistent with an assignment of the boron (B9) which is bonded to the alkenyl substituent in the cage. This spectrum is reminiscent of that for SB_9H_{11} except for the marked down field shift of the 9-position boron and its collapse from a doublet to a broad singlet due to replacement of a B-H by a B-C bond.[7] Thus, the boron spin-decoupled ^{1}H NMR spectrum shows one resonance at -2.17 ppm characteristic of boron-bridging protons. The ^{1}H NMR spectrum also shows a singlet resonance of intensity five for cyclopentadienyl protons, multiplets of intensity five for phenyl protons, and an intensity one resonance at 5.83 ppm which is assigned to the vinyl proton moiety. The IR spectrum also has a characteristic C=C stretch at 1590-1615 cm^{-1}.

The results presented above demonstrate that reactions of $B_{10}H_{12}(SMe_2)_2$ and SB_9H_{11} with the transition-metal acetylide $Cp(CO)_2Fe(CCPh)$ do not result in alkyne insertion but rather yield alkenylborane products. The initial reaction sequence leading to the formation of these compounds is undoubtedly related to the reaction mechanism involved in the formation of *ortho*-carborane. For example, in the synthesis $1,2\text{-}C_2B_{10}H_{12}$, the first step most likely involves the dissociation of one dimethyl sulfide ligand from $B_{10}H_{12}(SMe_2)_2$ as shown in reaction **1**. The acetylene adduct may then undergo hydroboration by the 6-position B-H group to yield an alkenyldecaborane product. A rearrangement in this compound involves the migration of the Me_2S group form the 9-position to the 5-position. Tolpin[8] previously observed that $B_{10}H_{12}(SMe_2)_2$ also hydroborated olefins to yield compounds analogous to **I**. For example, the reaction product of $B_{10}H_{12}(SMe_2)_2$ with cyclohexene was crystallographically determined[9] to be $9\text{-}C_6H_{11}\text{-}5\text{-}Me_2S\text{-}B_{10}H_{12}$. The cage structures observed for both $9\text{-}C_6H_{11}\text{-}5\text{-}Me_2S\text{-}B_{10}H_{12}$ and **I** are similar to that found for the isoelectronic $B_{10}H_{13}$- anion.[10] The formation of both products involves a Me_2S migration to the 5-position boron atom, but the difference in the preference for hydroboration at the 6-or 9-position is not readily apparent.

Also a facile and clean hydroboration reaction for *nido*-6-SB_9H_{11} with transition-metal acetylide $Cp(CO)_2Fe(CCPh)$ is demonstrated. Hydroboration of transition-metal acetylide by *nido*-6-SB_9H_{11} clearly occurs by the addition of *exo*-BH at the 9-position across the unsaturated C-C bond.

Since *nido*-6-SB_9H_{11} is isoelecronic with *nido*-$B_{10}H_{12}(SMe_2)$, the hydroboration product from the reaction of acetylenes with *nido*-6-SB_9H_{11} suggests an intermediate for the insertion of C_2H_2 into *nido*-$B_{10}H_{12}(SMe_2)$ to ultimately give $C_2B_{10}H_{12}$. Based on the examples of hydroboration by *nido*-6-SB_9H_{11} and *nido*-$B_{10}H_{12}(SMe_2)$, it would appear that a low-coordinate BH vertex attached to the polyhedron through only three nearest-neighbor borons and two bridge hydrogens is a prerequisite for facile hydroboration. We are continuing to study the scope of these reactions with other transition-metal acetylides.

Experimental Section

All manipulations were carried out using standard high-vacuum or inert-atmosphere techniques.

^{11}B NMR spectra at 160.5 and 64.2 MHz and ^1H NMR spectra at 200 MHz were obtained on Bruker AM-500 and Bruker AF-200 spectrometers equipped with appropriate decoupling accessories. All ^{11}B chemical shifts are referenced to $BF_3 \cdot O(C_2H_5)_2$ (0.01 ppm) with a negative sign indicating an upfield shift. All proton chemical shifts were measured relative to internal residual benzene from the lock solvent (99.5%, C_6D_6) and then referenced to Me_4Si (0.0 ppm).

Tow-dimensional COSY $^{11}B\text{-}^{11}B$ NMR experiments were conducted with s-type selection parameters at 160.5 MHz for **I**. The sweep widths in the F_2 direction was 25000 Hz and in the F_1 direction 12500 Hz and a total of 256 increments (increment size 0.04 ms) was collected, with each slice having 1 K F_2 data points. The data were zero-filled once in the F_1 directions and subjected to 2D Fourier transformation with sine-bell apodization in both domains. A total of 256 scans was taken for each increment with a recycling time of 100 ms.

High-and low-resolution mass spectra were obtained on a VG Micromass 7070H mass spectrometer. Infrared spectra were obtained on a Perkin-Elmer 1430 spectrophotometer.

Reaction of $B_{10}H_{12}(SMe_2)_2$ with $Cp(CO)_2Fe(CCPh)$. In a typical experiment, to a solution of 0.73 g (3 mmol) of $B_{10}H_{12}(SMe_2)_2$ in benzene (~25 ml) at ~ −20 ℃ was added 0.83 g (3 mmol) of $Cp(CO_2)Fe_{(CCPh)}$. The solution was allowed to warm slowly to room temperature and refluxed for 1 h. ^{11}B NMR spectra taken at this point confirmed the exclusive formation of complex **I**. The solvent was removed in vacuo and subsequent separation was performed by flash chromatography with hexane and benzene (50 : 50) to give 0.92 g (2.0 mmol) of $5\text{-}Me_2S\text{-}6\text{-}Cp(CO)_2FeHC{=}CPh\text{-}B_{10}H_{11}$ **I**. This corresponds to a 66.7% yield based on the consumed $B_{10}H_{12}(SMe_2)_2$. ^{11}B NMR (160.5 MHz, ppm, C_6D_6) 18.9 (s, B_6), 9.0 (d, B_3, $J_{BH}=140$ Hz), 4.5(d, B_1, $J_{BH}=130$ Hz), 0.7 (s, B_5), 0.5 (d, B_8, $J_{BH}=160$ Hz), −3.7 (d, B_9, $J_{BH}=135$ Hz), −4.9 (d, B_{10}, $J_{BH}=130$ Hz), −13.0 (d, B_7, $J_{BH}=110$ Hz), −30.1 (d, B_2, $J_{BH}=140$ Hz), −38.5 (d, B_4, $J_{BH}=145$ Hz); 2D $^{11}B\text{-}^{11}B$ COSY NMR (160.5 MHz, ppm, C_6D_6, ^{11}B spindecoupled) $B_6\text{-}B_5$, $B_6\text{-}B_2$, $B_3\text{-}B_1$, $B_3\text{-}B_8$, $B_3\text{-}B_7$, $B_3\text{-}B_2$, $B_3\text{-}B_4$, $B_1\text{-}B_5$, $B_1\text{-}B_{10}$, $B_1\text{-}B_2$, $B_1\text{-}B_4$, $B_5\text{-}B_{10}$, $B_5\text{-}B_2$, $B_8\text{-}B_7$, $B_8\text{-}B_4$, $B_9\text{-}B_4$, $B_{10}\text{-}B_4$, $B_7\text{-}B_2$; ^1H NMR (200.13 MHz, ppm, C_6D_6, ^{11}B spin-decoupled) 7.2 (m, 6, C_6H_5), 6.4 (s, 1, HC=C), 4.9 (s, 5, C_5H_5), 2.67 (s, 3, CH_3S), 2.65 (s, 3, CH_3S), −1.45 (s, 2, BHB), −3.7 (s, 1, BHB); exact mass measurement calcd for $^{12}C_{17}{}^{11}B_{10}{}^{56}Fe{}^1H_{28}{}^{16}O_2{}^{32}S$ 462.2081, found 462.2111; Anal. Calcd: C, 44.35; H, 6.13. Found: C, 43.18; H, 5.72. $R_f=0.65$ in Benzene; Mp=127-129 ℃ (dec); IR spectrum (KBr pellet, cm^{-1}) 3025 w, 2580 s, 2000 s, sh, 1997 s, 1955 s, 1770 s, 1595 m, 1430 m, 1270 w, 1080 w, 1020 w, 840 w, 700 w, 640 w, 594 w, 546 w.

Reaction of SB_9B_{11} with $Cp(CO_2)Fe(CCPh)$. In a similar manner as described above, 0.43 g (3 mmol) of SB_9H_{11} was reacted with 0.83 g (3 mmol) of $Cp(CO)_2Fe(CCPh)$ in benzene for 1 h. Following the reaction, the solution was quickly filtered through celite and concentrated. Separation by flash chromatography using a 1 : 9 benzene/hexane solution as the eluent solvent to give 0.56 g (1.3 mmol) of $9\text{-}Cp(CO)_2FeHC{=}CPh\text{-}6\text{-}SB_9H_{10}$ **II**. This corresponds to a 44.6 % yield based on the consumed SB_9H_{11}. ^{11}B NMR (64.2 MHz, ppm, C_6D_6) 33.9 (s, B_9), 24.4 (d, $B_{5,7}$, $J_{BH}=170$ Hz), 4.3 (d, $B_{1,3}$ $J_{BH}=150$ Hz), −13.5 (d, $B_{8,10}$ $J_{BH}=150$ Hz), −18.9 (d, B_2, $J_{BH}=150$ Hz), −31.8 (d, B_4, $J_{BH}=170$ Hz); ^1H NMR (200.13 MHz, ppm, C_6D_6, ^{11}B spin decoupled 7.18 (m, 6, C_6H_5), 5.83 (s, 1, HC=C), 4.80 (s, 5, C_5H_5), −2.17 (s, 2, BHB); Exact mass measurement calcd for $^{12}C_{15}{}^{11}B_9{}^{56}Fe{}^1H_{21}{}^{16}O_2{}^{32}S$ 420.1449, found 420.1697; Anal. Calcd: C, 43.04; H, 5.06. Found: C, 41.98; H, 4.82. $R_f=0.57$ in Hexane; Mp=97-98 ℃ (dec); IR spectrum (KBr Pellet, cm^{-1}) 3020 w, 2960 w, 2930 w, 2580 s, 2060 m, 2000 s, sh, 1950, 1810 m, 1772 s, 1595 m, 1490 w, 1479 w, 1446 w, 1428 w, 1374 m, br, 1024 w, 809 m, 797 m, 732 m, 680 m, 662 w, 629 m, 581 m, 567 m, 536 m.

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7. The B(9) resonance for $6\text{-}SB_9H_{11}$ is at +17.3 with J_{BH}= 170 Hz. The B(9) resonance for the alkenyl thiaborane investigated here is found at +35 ppm. The remainder of the spectrum differs little from that of $6\text{-}SB_9H_{11}$.
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Synthesis of Prostaglandins IV. Facile Synthesis of Luteolytic Prostaglandin Fenprostalene

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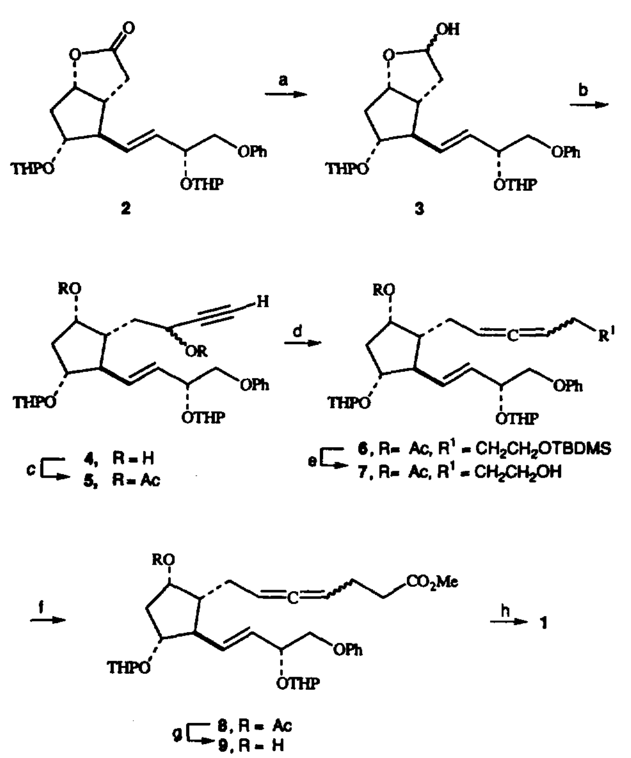
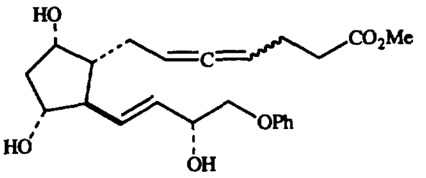
Prostaglandins (PGs) are a family of extremely potent natural hormones with a remarkable range of biological and pharmaceutical properties. The unavailability of a suitable natural source coupled with their potential drug utility has led to the clinical development of a number of synthetic PG analogs. Among them, fenprostalene (1), a 4,5,6-allenic 16-phenoxy PGF analog, has been found to possess a luteolytic activity in various animal species.[1] Luteolytic PGs have an important place in veterinary medicine. Thus, the PGs can be used to control the bovine estrus cycle; stemming from this are the benifits of artificial insemination.



Scheme 1. *Reagents and conditions*: a, DIBAH, toluene, −78 ℃, 2 h; b, see Table 1, 82-93%; c, Ac_2O, cat. DMAP, NEt_3, CH_2Cl_2, rt., 3 h, 91%; d, $TBDMSOCH_2CH_2CH_2MgBr$, CuI·$P(OEt)_3$, THF, −40 ℃, 10 min, 76%; e, TBAF, THF, rt, 3 h, 99%; f, i. PDC/CH_2Cl_2, rt, 20 h, ii. PDC/DMF, MeOH, rt, 20 h, 84%; g, K_2CO_3, MeOH, rt, 14 h; then 1 N HCl, 0 ℃ (89%); h, AcOH-H_2O-THF, 40 ℃, 20 h, 65%.



1, fenprostalene

The introduction of allenic side chain attracted substantial synthetic efforts of many organic chemists. Since its development[2], a number of synthetic methods for the preparation of allenic prostaglandins have been reported[3].

The introduction of allenyl group in prostaglandins was done by the reaction of propargylic ester with lithium dimethylcuprate[2] or by using an orthoester Claisen rearrangement of propargylic alcohol intermediate.[3c] The specificity for the formation of protonated allene from propargylic ester depends on the various factors like the kind of propargylic derivatives, cuprate reagents, reaction temperature, work-up conditions, etc.[4] Therefore, the possibilities for the formation of alkylated allene and alkylated acetylene was a main drawback for the synthesis of allenic prostaglandin derivatives.[3a,5]