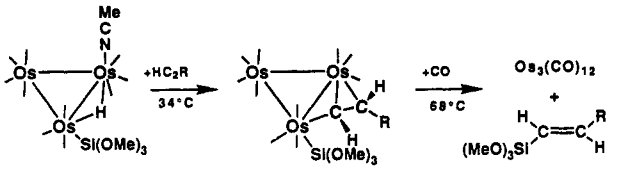
Scheme I



1a **2a**, R = Bu^t

that complex **1a** reacts readily with the terminal alkynes HC_2R (R = Bu^t, *p*-tolyl) to yield intermediate species that upon treatment with CO at 68 °C produce the silylolefins *trans*-R(H)C=C(H)Si(OMe)$_3$ (R = Bu^t, *p*-tolyl).[10] One of these intermediates, $Os_3(CO)_{10}[Si(OR)_3][\mu\text{-}C(H)C(H)Bu^t]$ (**2a**; R = Me) has been isolated and structurally characterized by X-ray diffraction methods.[11,12] An ORTEP diagram of its molecular structure is shown in Figure 1. The molecule consists of a triosmium cluster with a bridging η^2-*tert*-butylvinyl ligand and a terminally coordinated trimethoxysilyl group positioned cis to the bridging carbon atom of the *tert*-butylvinyl group. The Os–Si distance is slightly longer than that in **1b**, 2.427 (4) vs 2.39 (1) Å.[8] The coordination of the bridging η^2-*tert*-butylvinyl ligand is structurally similar to that which has been reported for other osmium cluster complexes.[13] The trans stereochemistry of the hydrogen atoms is similar to that observed for the insertion of alkynes into the metal–hydrogen bonds of triosmium cluster complexes.[13d,14] The salient features of this study are (1) it is the hydrogen atom that is shifted first to the alkyne and (2) the silyl group is positioned adjacent to the bridging carbon atom of the bridging η^2-*tert*-butylvinyl ligand. This latter feature should and does facilitate the reductive-elimination step that is promoted by the CO addition and leads to the formation of the silicon–carbon bond (see Scheme I).

This is to our knowledge the first example of the isolation and structural characterization of an intermediate in an alkyne-hydrosilation reaction. Its isolation was made possible, no doubt, by the stabilization of the complex through the formation of the bridging alkenyl ligand. Efforts to produce a catalytic reaction by the addition of alkynes and silanes to **2** have not yet been successful. Silyl-containing triruthenium complexes have been implicated in the catalytic hydrosilation and silacarbonylation of olefins by $[Ru_3(CO)_{11}(\mu\text{-}H)]^-$.[15]

Acknowledgment. This research was supported by the National Science Foundation.

Registry No. **1a**, 131005-97-5; **2a**, 137540-21-7; **2b**, 137515-98-1; HC_2Bu^t, 917-92-0; HC_2-*p*-tolyl, 766-97-2; *trans*-(MeO)$_3$SiC(H)=C(H)Bu^t, 137515-96-9; *trans*-(MeO)$_3$SiC(H)=C(H)(*p*-tolyl), 137515-97-0.

Supplementary Material Available: Tables of crystal data, positional parameters, bond distances and angles, and anisotropic thermal parameters (10 pages); a table of structure factors (19 pages). Ordering information is given on any current masthead page.

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(9) Compound **1a** was prepared by a procedure analogous to that used for the preparation of **1b**.[8] Analytical data for **1a**: IR (ν_{CO}, cm^{-1}; in hexane) 2104 (m), 2066 (vs), 2042 (vs), 2022 (vs), 2009 (s), 2001 (vs), 1989 (vs), 1977 (m); ^{1}H NMR (δ; in CDCl$_3$) 3.61 (s, O*CH$_3$*, 9 H), 2.59 (s, NC*CH$_3$*, 3 H), −16.57 (s, *OsH*, 1 H).

(10) A 51.5-mg (0.051-mmol) amount of **1a** was allowed to react with 0.10 mL of *tert*-butylacetylene in 50 mL of CH_2Cl_2 at 34 °C for 4.5 h. The product was separated from unreacted **1a** by TLC using a 2/1 (v/v) hexane/methylene chloride mixture as the eluent. This yielded red $Os_3(CO)_{10}[Si(OMe)_3][\mu\text{-}C(H)C(H)Bu^t]$ (**2a**; 13.0 mg, 0.012 mmol, 43% yield based on amount of **1a** consumed) and 23.0 mg of unreacted **1a**. Longer reaction times led to decomposition of the product and a decrease in the overall yield. Analytical data for **2a**: IR (ν_{CO}, cm^{-1}; in hexane) 2116 (s), 2066 (s), 2049 (vs), 2030 (vs), 2016 (s), 1996 (m), 1992 (m), 1977 (m), 1965 (s); ^{1}H NMR (δ; in CDCl$_3$) 9.33 (d, *CH*, $^3J_{HH}$ = 12.7 Hz, 1 H), 4.29 (d, *CH*, $^3J_{HH}$ = 12.7 Hz, 1 H), 3.60 (s, O*CH$_3$*, 9 H), 1.07 (s, *CH$_3$*, 9 H). Anal. Calcd for **2a**·C_5H_{12}: C, 25.6; H, 2.86. Found: C, 25.5; H, 2.54. $Os_3(CO)_{10}[Si(OR)_3][\mu\text{-}C(H)C(H)(p\text{-tolyl})]$ (**2b**) was obtained from **1a** by a similar treatment using HC_2-*p*-tolyl. Analytical data for **2b**: IR (ν_{CO}, cm^{-1}; in hexane) 2116 (s), 2067 (s), 2049 (vs), 2031 (vs), 2021 (s), 1999 (m), 1992 (m), 1978 (m), 1971 (s); ^{1}H NMR (δ; in CDCl$_3$) 9.76 (d, *CH*, $^3J_{HH}$ = 12.6 Hz, 1 H), 7.18 (d, *C$_6$H$_4$*, 2 H), 7.10 (d, *C$_6$H$_4$*, 2 H), 5.16 (d, *CH*, $^3J_{HH}$ = 12.6 Hz, 1 H), 3.55 (s, O*CH$_3$*, 9 H), 2.33 (s, *CH$_3$*, 3 H). A 50-mL solution of hexane containing 13.9 mg (0.013 mmol) of **2a** was refluxed for 5 h under a CO atmosphere. An aliquot of this solution was then removed and distilled at 50 °C and 0.5 mmHg pressure. A GC/MS analysis of this sample showed the peaks expected for (MeO)$_3$SiC(H)=C(H)Bu^t (*m/e* (%)): [M$^+$] 204 (3.2), 172 (2.8), 157 (5.2), 147 (0.4), 121 (100.0), 91 (34.8), 82 (28.0). ^{1}H NMR (δ; in CDCl$_3$): 6.44 (d, *CH*, $^3J_{HH}$ = 19.3 Hz, 1 H), 5.26 (d, *CH*, $^3J_{HH}$ = 19.3 Hz, 1 H), 3.55 (s, O*CH$_3$*, 9 H), 1.01 (s, *CH$_3$* 9 H). The $^3J_{HH}$ coupling constants of the olefinic hydrogen atoms are indicative of the trans stereochemistry. Due to the small amount of material involved, an accurate amount of the olefin that was formed could not be determined; however, 8.2 mg of $Os_3(CO)_{12}$ (69% yield) coproduct was obtained. *trans*-(MeO)$_3$SiC(H)=C(H)(*p*-tolyl) was obtained similarly. ^{1}H NMR (δ; in CDCl$_3$): 7.36 (d, *C$_6$H$_4$*, 2 H), 7.16 (d, *CH*, $^3J_{HH}$ = 19.2 Hz, 1 H), 7.14 (d, *C$_6$H$_4$*, 2 H), 6.06 (d, *CH*, $^3J_{HH}$ = 19.3 Hz, 1 H), 3.60 (s, O*CH$_3$*, 9 H), 2.33 (s, *CH$_3$*, 3 H). Mass spectral analysis (*m/e* (%)): [M$^+$] 238 (42.2), 223 (31.4), 208 (23.0), 176 (53.9), 146 (12.3), 118 (100.0), 107 (24.9), 91 (72.0).

(11) Red crystals of **2a** were grown from a pentane solution by slow evaporation of solvent at 10 °C. Crystal data: space group $P2_1/a$, a = 13.309 (4) Å, b = 12.307 (4) Å, c = 17.499 (4) Å, β = 103.93 (2)°, Z = 4, 2711 reflections, R = 0.032.

(12) Diffraction measurements at 20 °C were made on a Rigaku AFC6S four-circle diffractometer using Mo Kα radiation. The structure solution and refinement was made by using the TEXSAN structure-solving program library (version 5.0) of the Molecular Structure Corp., The Woodlands, TX. An absorption correction was applied to the data.

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Unusual Selective α-Fission of Indium–*sec*-Alkyl Bonds in Solution

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Summary: Indium trialkyls possessing an α-branch such as In(Bu-*s*)$_3$ and In(Pr-*i*)$_3$ decompose through α-fission to give the corresponding alkyl radical selectively during solution pyrolysis.

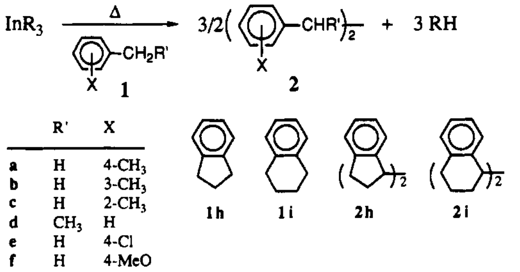
Increasing attention has been paid to organometallic sources, as an innovative materials in the process for VLSI and the preparation of alloy semiconductors. Since it is important to lower the deposition temperature and to increase the purity of the layer for the production of high-performance and high-reliability devices, understanding the thermal decomposition path of the organo-

Table I. Pyrolysis of Indium Tributyl in Decalin[a]

InR_3[b]	hydrocarbon products (yield, %)[c]
$InBu_3$	1-butene (60), butene (tr)
$In(Bu\text{-}i)_3$	isobutene (96), isobutane (tr)
$In(Bu\text{-}s)_3$	butane (40), 2-butene (30), 3,4-dimethylhexane (10)

[a] Indium tributyl (1.6 mmol) and decalin (10 mL) were employed. Pyrolysis was carried out at 140 °C for 24 h under dry and deoxygenated N_2. After termination of the pyrolysis gray indium metal was obtained in quantitative yield. [b] These indium trialkyls were prepared by the usual Grignard method.[12] [c] GLC yields, based on the amounts of butyl groups, are presented; e.g., in the reaction described in the top line, 2.9 mmol of 1-butene was obtained.

Scheme I



metallic sources in detail is of primary importance.[1] Recently, we reported new single-source processes for preparing thin layers of indium oxide[2] and sulfide[3] and ternary compounds[4] by starting from indium butyl derivatives in both the vapor phase and solution. During these studies, the selection of alkyl moieties attached to the indium center influenced the properties of the resulting semiconductor layers significantly. Very limited information is, however, available on the thermal behavior of group 13 metal alkyls,[5-7] especially butyl derivatives.[8] Thus, we attempted the thermal decomposition of indium tributyls in solution.

Table II. Dimerization of *p*-Xylene by Various Metal Alkyls[a]

MR_n	yield,[b] %	MR_n	yield,[b] %
$In(Bu\text{-}s)_3$	85	$Al(Bu\text{-}s)_3$	nr[e]
$InBu_3$	*c*	$Sb(Bu\text{-}s)_3$	6
$In(Bu\text{-}i)_3$	*d*	*s*-BuMgCl[f]	2
$In(Pr\text{-}i)_3$	67		

[a] Metal alkyls (1.6 mmol) and 10 mL (ca. 96 mmol) of *p*-xylene were heated with stirring by a magnet at 140 °C for 9 h under dry and deoxygenated N_2. *p*-Xylene dimer (**2a**) was isolated by preparative TLC (silica gel, eluted by hexane). [b] GLC yields, based on the amounts of butyl group (see Scheme I). [c] Polybutene was obtained: yield 58%; $\bar{M}_n$ 2100. [d] Polybutene was obtained: yield 95%; $\bar{M}_n$ 1700. [e] No pyrolysis product was detected. [f] Bu_2O solution (0.5 mol/L).

Table III. Selective Coupling of Methylarene by *s*-Bu_3In[a]

methylarene	product	yield,[b] %
p-xylene	**2a**	21
m-xylene	**2b**	83
o-xylene	**2c**	72
toluene		trace
ethylbenzene	**2d**	51 (25/26)[c]
p-chlorotoluene	**2e**	60
p-methoxytoluene	**2f**	35
indane	**2h**	62 (31/31)[c]
tetralin	**2i**	60 (28/32)[c]

[a] Pyrolysis was carried out under conditions similar to those described in Table II. [b] GLC yields. [c] A *dl*/*meso* mixture was obtained, and the ratio of the isomers is displayed in parentheses (determined by ^1H NMR spectroscopy).

In general, it is believed that the thermal decomposition of aluminum tributyls and other group 13 analogues predominately goes through a β-elimination pathway to give the corresponding olefins together with metal hydrides.[8] As expected, pyrolysis of InR_3 (R = *n*-Bu, *i*-Bu) in decalin gave butene and isobutene in good yields, respectively, as shown in Table I. In contrast, InR_3 (R = *s*-Bu) mainly gave saturated hydrocarbons such as butane and octane (3,4-dimethylhexane) along with 2-butene as a minor product, although *s*-Bu possesses greater numbers of β-hydrogens than *n*-Bu. These results surprisingly suggest that the thermal decomposition of $In(Bu\text{-}s)_3$ predominately proceeds via an α-fission pathway.

Next we attempted to trap the intermediate *sec*-butyl radical. Thus, pyrolysis of several metal alkyls including $In(Bu\text{-}s)_3$ in *p*-xylene was investigated, and the results obtained are presented in Table II. The pyrolysis of $In(Bu\text{-}s)_3$ resulted in the quantitative evolution of *n*-butane with formation of *p*-xylene dimer (**2a**), which is derived from an abstraction of benzylic hydrogen by cage-escaped *s*-Bu radical[9] followed by a coupling of the resulting *p*-xylyl radicals. In contrast, $Al(Bu\text{-}s)_3$ isomerized to $AlBu_3$ under these conditions and no pyrolysis occurred, because aluminum trialkyls that have α-substituents generally experience a reversible β-elimination–hydroalumination to be converted to more stable straight-chain derivatives.[10] On the other hand, the pyrolysis of *s*-BuMgCl gave a complex pyrolysate mixture consisting of butene and Wultz type products etc., while $Sb(Bu\text{-}s)_3$ was so stable as to be recovered in almost 90% yield but gave **2a** in 6% yield. Similar selective formation of **2a** was also observed in the pyrolysis of $In(Pr\text{-}i)_3$. Thus, it can be said that the strong

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preference of α-fission is characteristic of indium trialkyls possessing α-substituents.

Generally, the possibility of β-elimination should lower the decomposition temperature of metal alkyls[11] and some branching at the β-position weakens their M–C bonds extensively.[10] It is well-known that ethyl derivatives decompose at significantly lower temperatures than methyl derivatives and the isobutyl derivatives decompose faster than ethyl derivatives.[11] As indicated in Tables I and II, yields of the pyrolysates from $In(Bu\text{-}i)_3$ higher than those from $InBu_3$ are inconsistent with this concept. However, it is found that $In(Bu\text{-}s)_3$ decomposed as smoothly as $In(Bu\text{-}i)_3$ does with respect to the yields of the pyrolysates. This suggests that the acceleration effect of α-fission on the pyrolysis of $In(Bu\text{-}s)_3$ should precede that of β-elimination, which is perhaps related to the large steric repulsion among the α-substituents surrounding the In center. The repulsion may contribute significantly in weakening the In–C bonds and preventing the conformation necessary for β-elimination. The presence of an electronic absorption band near 350 nm[12] also suggests such a conformational deformation in $In(Bu\text{-}s)_3$. Therefore, the pyrolysis of $In(Bu\text{-}s)_3$ predominately proceeds via α-fission.

The similar pyrolysis of $In(Bu\text{-}s)_3$ in several methylarenes, including tetralin and indane, gave the corresponding dimers **2b–i** in good yields, as shown in Table III. As judged from the yields of **2a,e,f**, the order of the abstraction rate of the benzylic hydrogen can be explained by the "polar effect",[13] because an electron-withdrawing substituent such as Cl at the para position leads to higher yields of **2** than electron-releasing substituents such as Me and MeO. Incidentally, this order agrees with that observed in the general abstraction of secondary alkyl radical.[14] Another interesting feature should be pointed out. The pyrolysis of $In(Bu\text{-}s)_3$ and $In(Pr\text{-}i)_3$ in methylarenes gave lustrously metallic indium deposition.

Overall, it should be concluded that *s*-Bu and *i*-Pr attached to In effectively lower the decomposition temperature and accelerate the deposition of metallic indium. In addition, we propose here the further use of *s*-Bu or *i*-Pr derivatives in semiconductor processes.

Registry No. **1a**, 106-42-3; **1b**, 108-38-3; **1c**, 95-47-6; **1d**, 100-41-4; **1e**, 106-43-4; **1f**, 104-93-8; **1h**, 496-11-7; **1i**, 119-64-2; **1** (R′ = X = H), 108-88-3; **2a**, 538-39-6; **2b**, 4662-96-8; **2c**, 952-80-7; *dl*-**2d**, 2726-21-8; *meso*-**2d**, 4613-11-0; **2e**, 5216-35-3; **2f**, 1657-55-2; *dl*-**2h**, 81523-13-9; *meso*-**2h**, 84735-48-8; *dl*-**2i**, 137628-11-6; *meso*-**2i**, 75421-54-4; $In(Bu\text{-}s)_3$, 101749-61-5; $InBu_3$, 15676-66-1; $In(Bu\text{-}i)_3$, 6731-23-3; $In(Pr\text{-}i)_3$, 17144-80-8; $Al(Bu\text{-}s)_3$, 13282-35-4; $Sb(Bu\text{-}s)_3$, 99715-44-3; *s*-BuMgCl, 15366-08-2; 1-butene, 106-98-9; isobutene, 115-11-7; butane, 106-97-8; 2-butene, 107-01-7; 3,4-dimethylhexane, 583-48-2.

Supplementary Material Available: Text detailing the experimental procedure and analytical and spectral data for **2a–i** (2 pages). Ordering information is given on any current masthead page.

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Enolate Chemistry of the $Cp(CO)_2FeCH{=}CHC(O)CH_3$ System

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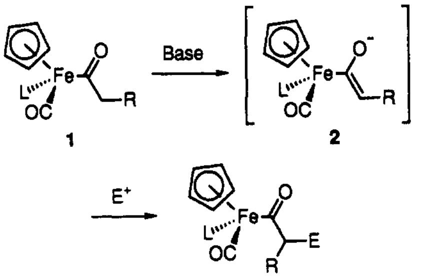
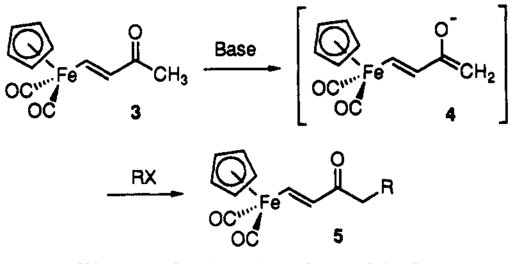
Summary: β-$[Cp(CO)_2Fe]$-alkenone derivatives, which have a number of potential applications in synthesis, are readily prepared by conversion of the parent 1-$[Cp(CO)_2Fe]$-1-buten-3-one complex (**3**) to the enolate **4** followed by reaction with various electrophilic reagents.

The acyliron complexes **1** and their derived enolates **2**, which undergo reactions with a number of electrophilic species E^+ (eq 1; L = CO, phosphine, or other ligands), have been the subjects of numerous reports.[1] These complexes have proven to be very useful in organic and organometallic synthesis of either chiral or nonchiral systems. However, applications of the corresponding vinylogous system, the 1-$[Cp(CO)_2Fe]$-1-buten-3-one com-



(1)



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