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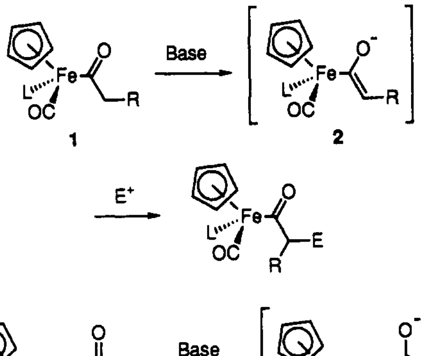
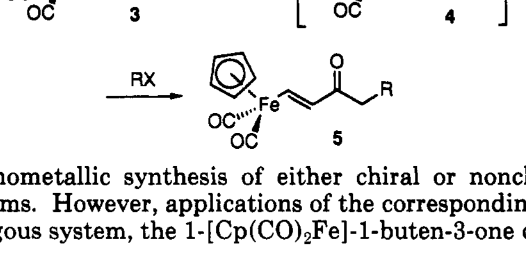
Summary: β-[$Cp(CO)_2Fe$]-alkenone derivatives, which have a number of potential applications in synthesis, are readily prepared by conversion of the parent 1-[$Cp(CO)_2Fe$]-1-buten-3-one complex (**3**) to the enolate **4** followed by reaction with various electrophilic reagents.

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)



(2)

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plex **3**[2] (Cp = η^5-C_5H_5) and the enolate **4**, have not been developed similarly. The resulting alkylation products **5** (eq 2) are potentially useful in several types of applications. In particular, these compounds are needed for other studies in our laboratory associated with uses of carbene complexes that can be derived as intermediates from these and related iron-containing systems.[1j,k,2c–e,3] In this communication, we give a preliminary account of the enolate chemistry of the parent compound of the β-[Cp(CO)$_2$Fe]-alkenone species.

The butenone complex **3** is obtained by reaction of sodium cyclopentadienyldicarbonylferrate with a mixture of 1-bromo- and 1-chloro-1-buten-3-one[4] in THF at −78 °C for 2 h followed by slow warming to 0 °C.[2,5] It is a fairly stable, crystalline compound that can be handled in the air for indefinitely long periods of time. A variety of bases were studied for conversion of **3** to the corresponding enolate **4**. The best results were obtained through use of lithium hexamethyldisilazide. Other bases such as lithium diisopropylamide led to side reactions such as substitutions on the cyclopentadienyl ligand. After having been generated as an intermediate, the enolate **4** is used immediately in reactions with various organic electrophiles, including alkyl halides, triflates, and aldehydes to give the corresponding chain-extended alkenone complexes **5** (eq 2). The results are summarized in Table I. The products are generally obtained as yellow oils that show good stability under normal laboratory conditions. However, the products obtained from aldehydes are prone to undergo dehydration to give cross-conjugated dienones that are not stable to silica gel chromatography. Product yields are good in the other cases, except for epoxides, which give unsatisfactorily low conversions.

Table I. Reaction of Enolate 4 with Organic Electrophiles (Eq 2)

RX	product	yield, %[a]
CH_3I	$Cp(CO)_2FeCH{=}CHC(O)CH_2CH_3$	82
CH_3CH_2I	$Cp(CO)_2FeCH{=}CHC(O)$-$CH_2CH_2CH_3$	70
n-C_4H_9I	$Cp(CO)_2FeCH{=}CHC(O)CH_2$-$n$-$C_4H_9$	53
n-$C_5H_{11}OSO_2CF_3$	$Cp(CO)_2FeCH{=}CHC(O)CH_2$-$n$-$C_5H_{11}$	48
$H_2C{=}CHCH_2Br$	$Cp(CO)_2FeCH{=}CHC(O)$-$CH_2CH_2CH{=}CH_2$	62
$PhCH_2Br$	$Cp(CO)_2FeCH{=}CHC(O)$-CH_2CH_2Ph	62
CH_3CH_2CHO	$Cp(CO)_2FeCH{=}CHC(O)CH_2CH$-$(OH)CH_2CH_3$	90[b]
PhCHO	$Cp(CO)_2FeCH{=}CHC(O)CH{=}CHPh$	11[c]
propylene oxide	$Cp(CO)_2FeCH{=}CHC(O)$-$CH_2CH_2CH(OH)CH_3$	40[d]

[a] Yields are given for pure, isolated products unless otherwise noted. [b] Yield of product of 92% purity without chromatographic purification. [c] See text. [d] $BF_3{\cdot}Et_2O$ (1.2 equiv) was used. The reaction went to only 40% conversion to give the product and **3** as an inseparable mixture.

A general procedure follows. To a yellow-brown solution of **3** (1.00 mmol) in THF (2.2 mL) and *N,N'*-dimethylpropyleneurea (DMPU, 1.7 mL) at −78 °C under nitrogen is added $LiN(SiMe_3)_2$ (1.1 mL, 1.0 N in THF) dropwise. After being stirred at −78 °C for 20 min, the dark brown solution is warmed to −20 °C and stirred for 10 min before the electrophile (1.2 mmol) is added dropwise. Upon completion of the reaction (0.5–8 h) as indicated by TLC, aqueous NH_4Cl (0.2 mL or alternatively aqueous $NaHCO_3$ when $BF_3{\cdot}Et_2O$ is present) is added. The product mixture is partitioned repeatedly between 1:1 hexane–EtOAc and water under nitrogen followed by concentration of the organic phase and flash column chromatography (silica gel, 5:1 to 1:1.5 gradient of hexane–EtOAc) under nitrogen. The pure product is obtained from the distinctly yellow band.[6,7]

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(5) The preparation of $FpCH{=}CHCOCH_3$ was as follows:[2a] After sodium amalgam (15 mL of Hg, 2.124 g of Na) was generated under N_2 and sufficiently cooled (~20 min), a solution of $[Cp(CO)_2Fe]_2$ (Fp_2, 10.62 g, 30.0 mmol) in THF (160 mL) was immediately transferred to the amalgam flask. This dark reddish brown reaction mixture was stirred for 15 h at 22 °C to produce a dark yellowish brown NaFp solution. In a Schlenk tube, the ether solution of 1-bromo-1-buten-3-one–1-chloro-1-buten-3-one[4] (~66 mmol vinyl halide) was concentrated under vacuum. THF (140 mL) was added, and the solution was cooled to −78 °C. The NaFp solution was cooled to 0 °C and transferred via cannula to the Schlenk tube over 10 min. The dark-colored reaction mixture was stirred at −78 °C for 2 h and then gradually (2 h) warmed to 0 °C. Solvent was removed under vacuum, and the dark residue was dissolved in deoxygenated 5:1 hexane–ethyl acetate and the solution transferred to an anaerobic silica gel column (8 cm wide × 12 cm high) via cannula and initially eluted with 5:1 hexane–ethyl acetate. After a reddish brown band (Fp_2) was eluted, a bright yellow band was eluted with 1:1.5 hexane–ethyl acetate and collected under N_2. Concentration under vacuum provided 10.54 g (71.4% overall yield from Fp_2) of brownish yellow solid: mp 82.5–83.0 °C (hexane–ethyl acetate) (lit.[2a] mp 83 °C); FTIR (KBr) 3126, 3103, 2985, 2962, 2032, 1975, 1642, 1527, 1361, 1251, 1183 (w), 981, 856, 629 cm^{-1} (lit.[2a] IR (KBr) 3105 (w), 3090 (w), 2030 (s), 1975 (s), 1635 (s), 1600 (w), 1525 (s), 1430 (w), 1420 (m), 1360 (s), 1250 (s), 1165 (m), 1115 (m), 1060 (w), 1050 (w), 1025 (w), 985 (s), 945 (w), 860 (s), 800 (w) cm^{-1}); ^1H NMR (200 MHz) δ 9.26 (d, J = 16.5 Hz, 1 H, FeC*H*), 6.64 (d, J = 16.5 Hz, 1 H, FeCH=C*H*), 4.94 (s, 5 H, C_5H_5), 2.15 (s, 3 H, CH_3) (lit.[2a] ^1H NMR (100 MHz, CCl_4) δ 8.77 (d, J = 16.4 Hz), 6.36 (d, J = 16.4 Hz), 4.86 (s), 1.98 (s)); ^{13}C NMR δ 213.79, 191.79 (CH*C*O, obsd in NMR of propylene oxide adduct), 172.17, 148.39, 85.88, 26.41. Anal. Calcd for $C_{11}H_{10}FeO_3$ (246.05): C, 53.70; H, 4.10. Found: C, 53.46; H, 4.29.

(6) A more detailed experiment follows. (*E*)-1-[(η^5-Cyclopentadienyl)dicarbonylferrio]-5-phenyl-1-penten-3-one: A 10-mL round-bottomed flask was charged with a stirring bar and the yellow-brown solid $FpCH{=}CHCOCH_3$ (123 mg, 0.50 mmol), capped with a septum and placed under nitrogen. THF (1.12 mL) and DMPU (0.83 mL) were added via syringe. The solution was cooled to −78 °C, and $LiN(Si(CH_3)_3)_2$ solution (0.55 mL, 0.55 mmol) was added dropwise via syringe to yield a dark brown solution. Benzyl bromide (71 μL, 0.60 mmol) was then added dropwise via syringe. TLC (1:1 hexane–ethyl acetate) after 0.5 h revealed most of the $FpCH{=}CHCOCH_3$ (R_f 0.30) was consumed, and a new spot at R_f 0.49 was formed. After 1.5 h the reaction was terminated by addition of 100 μL of saturated aqueous NH_4Cl solution and the mixture was warmed to 20 °C. In a 25-mL flask under nitrogen, the reaction mixture in 14 mL of deoxygenated 1:1 hexane–ethyl acetate was extracted with 6 × 5 mL of deoxygenated distilled water. The volatile materials were removed under vacuum (0.1 mmHg) to produce an orange-brown oil that was flash-chromatographed (2.3 × 20 cm) with 5:1 hexane–ethyl acetate. After a faint reddish band (Fp_2) reached the bottom of the column, elution was continued with 2:1 hexane–ethyl acetate until the bright yellow-orange band of product was 14 cm down the column. Elution with 2:3 hexane/ethyl acetate furnished the fraction of product, which was collected under nitrogen. Removal of solvent under vacuum (0.1 mmHg) yielded 104 mg (62%) of yellow-orange oil: FTIR 3030, 2030 (s), 1978 (vs), 1663, 1637, 1533, 1521, 1498 (w), 1193, 837 cm^{-1}; ^1H NMR δ 9.27 (d, J = 16.5 Hz, 1 H, FeC*H*), 7.31–7.15 (m, 5 H, C_6H_5) 6.63 (d, J = 16.5 Hz, 1 H, FeCH=C*H*), 2.95–2.87 (m, 2 H, COCH_2), 2.83–2.77 (m, 2 H, C$H_2C_6H_5$); ^{13}C NMR δ 213.84, 192.73, 171.51, 146.93, 141.93, 128.43, 128.36, 125.84, 85.92 (C_5H_5), 40.71, 30.76; high-resolution EIMS m/z calcd for $C_{18}H_{16}FeO_3$ 336.04488, found 336.0446. Anal. Calcd: C, 64.31; H, 4.80. Found: C, 64.11; H, 5.00

As our results indicate, the chain-extension reactions of enolate 4 provide convenient access to a wide range of β-[Cp(CO)$_2$Fe]-alkenone derivatives. We are presently investigating applications of these compounds. Various cycloadditions and chiral modifications are the subjects of ongoing studies. The results of this further work will be reported in due course.

Acknowledgment. We thank Dr. Bruce Plashko for obtaining mass spectral data for the compounds reported in this work. We are very grateful to the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for providing financial support of this work. We thank Professor Jan-E. Bäckvall for providing a Visiting Scholar position to M.N.M. at the University of Uppsala, Uppsala, Sweden, during the summer of 1990. M.N.M. also acknowledges the award of a Reilly Fellowship for 1990–1991.

Registry No. **3**, 137668-90-7; **5** (R = CH_3), 137668-82-7; **5** (R = CH_2CH_3), 137668-83-8; **5** (R = n–C_4H_9, 137668-84-9; **5** (R = n–C_5H_{11}, 137668-85-0; **5** (R = $CH_2CH{=}CH_2$), 137668-86-1; $\bar{5}$ ¥R = CH_2Ph), 137668-87-2; **5** (R = CH(OH)CH_2CH_3), 137668-88-3; $\bar{5}$ (R = CHPh), 137668-89-4; **5** (R = CH_2CH(OH)CH_3), 137695-57-9; [Cp(CO)$_2$Fe]$_2$, 12154-95-9; CH_3I, 74-88-4; CH_3CH_2I, 75-03-6; n–C_4H_9I, 542-69-8; n–$C_5H_{11}OSO_2CF_3$, 41029-43-0; $H_2C{=}CHCH_2Br$, 106-95-6; $PhCH_2B4$, 100-39-0; CH_3CH_2CHO, 123-38-6; PhCHO, 100-52-7; propylene oxide, 75-56-9; (*E*)–1–bromo–1–buten–3–one, 38302-93-1; (*E*)–1–chloro–1–buten–3–one, 4643-20-3.

Supplementary Material Available: Experimental details and ^{1}H NMR, ^{13}C NMR, IR, and high-resolution EIMS spectral data for all new compounds (8 pages). Ordering information is given on any current masthead page.

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(7) All new compounds gave satisfactory C, H elemental analysis or high-resolution mass spectral data, with the exception of the propanal adduct, which could not be satisfactorily purified.

New Synthetic Methodology Leading to 16-Electron Asymmetric Complexes of Tungsten: Cp*W(NO)(CH$_2$SiMe$_3$)R (R = Alkyl or Aryl)[1,2]

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Summary: An unprecedented three-step synthetic route leading from Cp*W(NO)(CH$_2$SiMe$_3$)$_2$ [Cp* = (η^5-C$_5$Me$_5$)] to the asymmetric species Cp*W(NO)(CH$_2$SiMe$_3$)R (R = alkyl or aryl), is described. The three steps are (1) exposure of Cp*W(NO)(CH$_2$SiMe$_3$)$_2$ to H_2 (1 atm) in acetonitrile to afford Cp*W(NO)(CH$_2$SiMe$_3$)(N=C(H)CH$_3$) (**1**), probably via hydrotungstation of CH_3CN by the initially formed hydrido complex, Cp*W(NO)(CH$_2$SiMe$_3$)H, (2) treatment of **1** with 2 equiv of HCl in Et_2O to form Cp*W(NO)(CH$_2$SiMe$_3$)Cl (**2**), and (3) metathesis reactions of **2** with organomagnesium reagents, R_2Mg, to produce the mixed alkyl and alkyl-aryl complexes, Cp*W(NO)(CH$_2$SiMe$_3$)R (**3a**, R = *o*-tolyl; **3b**, R = CH$_2$CMe$_2$Ph; **3c**, R = Me).

We have reported the synthesis and aspects of the rich chemistry of 16-electron dialkyl complexes of tungsten of the type Cp′W(NO)R$_2$ [Cp′ = Cp (η^5-C$_5$H$_5$) or Cp* (η^5-C$_5$Me$_5$); R = alkyl].[3] Until now, however, we have been unable to produce systematically the analogous 16-electron asymmetric species, Cp′W(NO)(R)R′. We now wish to report an unprecedented three-step synthetic route (summarized in Scheme I) that leads from Cp*W(NO)(CH$_2$SiMe$_3$)$_2$ to the desired complexes, Cp*W(NO)(CH$_2$SiMe$_3$)R (R = alkyl or aryl). This route involves the novel hydrotungstation of a nitrile and new reactivity of the resulting alkylideneamido complex.

As shown in Scheme I, the ethylideneamido complex, **1**, is preparable in high yields by exposure of Cp*W(NO)(CH$_2$SiMe$_3$)$_2$ to H_2 (1 atm) in acetonitrile. The transformation probably proceeds via the 16-electron hydrido alkyl intermediate Cp*W(NO)(CH$_2$SiMe$_3$)H, which effects hydrotungstation of CH_3CN to afford the yellow ethylideneamido complex, **1**.[4] Support for the intermediacy of Cp*W(NO)(CH$_2$SiMe$_3$)H in this process is provided by our previous observation that treatment of Cp*W(NO)(CH$_2$SiMe$_3$)$_2$ with H_2 in the presence of Lewis bases, L, produces the 1:1 adducts *trans*-Cp*W(NO)(CH$_2$SiMe$_3$)(H)L (L = P(OPh)$_3$ or PMePh$_2$).[3b] Addition of a metal hydride across a nitrile is more common for the early transition metals[5] than for the later ones,[6] but to our knowledge the initial step in Scheme I is the first example involving tungsten. The crystal structure of **1**[7] revealed

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[1] Organometallic Nitrosyl Chemistry. 50. For part 49, see: Herring, F. G.; Legzdins, P.; McNeil, W. S.; Shaw, M. J.; Batchelor, R. J.; Einstein, F. W. B. *J. Am. Chem. Soc.* **1991**, *113*, 7049.

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