Organometallics **1992**, *11*, 6–8

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$_2$CH$_3$), 137668-83-8; **5** (R = *n*–C$_4$H$_9$, 137668-84-9; **5** (R = *n*–C$_5$H$_{11}$, 137668-85-0; **5** (R = CH$_2$CH=CH$_2$), 137668-86-1; **5** ¥R = CH$_2$Ph), 137668-87-2; **5** (R = CH(OH)CH$_2$CH$_3$), 137668-88-3; **5** (R = CHPh), 137668-89-4; **5** (R = CH$_2$CH(OH)CH$_3$), 137695-57-9; [Cp(CO)$_2$Fe]$_2$, 12154-95-9; CH$_3$I, 74-88-4; CH$_3$CH$_2$I, 75-03-6; *n*–C$_4$H$_9$I, 542-69-8; *n*–C$_5$H$_{11}$OSO$_2$CF$_3$, 41029-43-0; H$_2$C=CHCH$_2$Br, 106-95-6; PhCH$_2$B4, 100-39-0; CH$_3$CH$_2$CHO, 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$_3$CN 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$_2$O to form Cp*W(NO)(CH$_2$SiMe$_3$)Cl (**2**), and (3) metathesis reactions of **2** with organomagnesium reagents, R$_2$Mg, 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$_3$CN 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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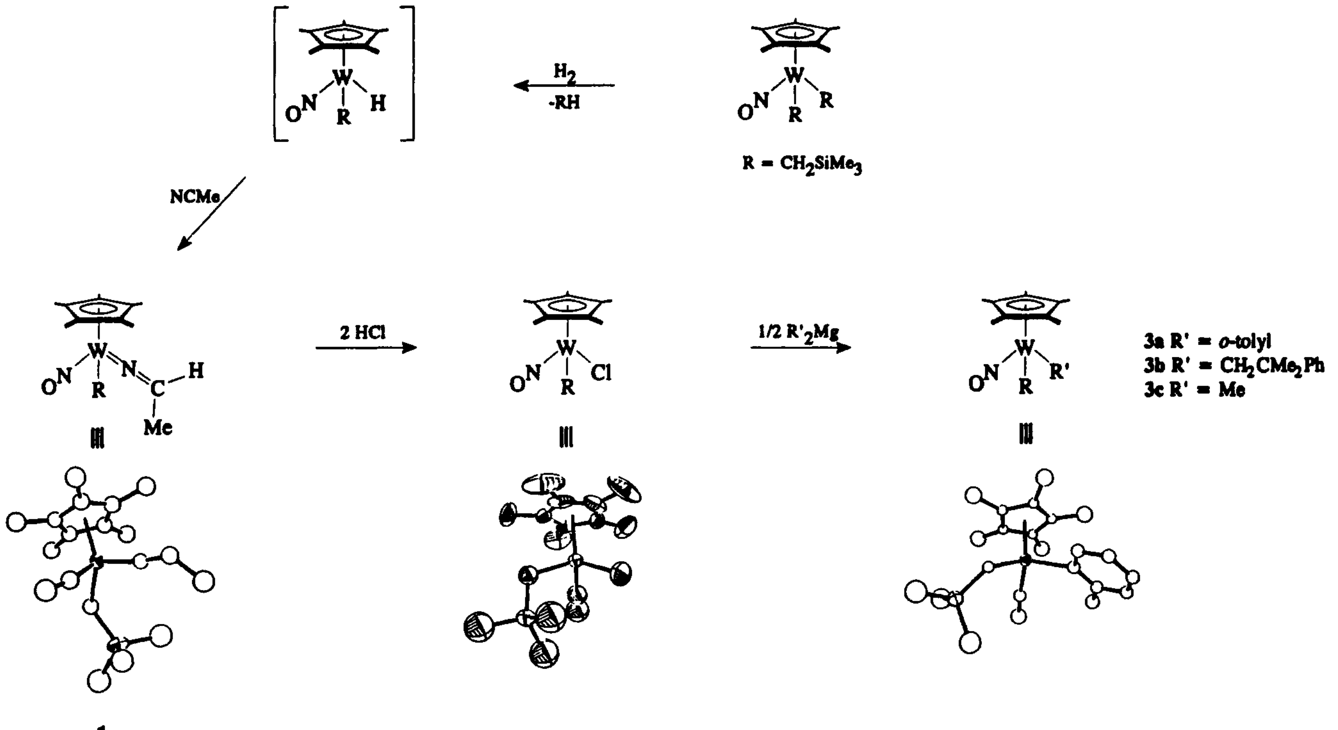
Scheme I



1 2 3a

an ethylideneamido ligand attached via a W═N link which is disordered between two diastereomeric orientations in a 3:2 ratio, the principal one being shown in the ORTEP diagram in Scheme I. The existence of two sets of signals in the ^1H and ^{13}C NMR spectra of 1[4] indicates that these isomers also persist in solution in approximately the same ratio. The presence of the two diastereomers can be attributed to the existence of a large rotational barrier about the W═N bond. This observation, along with the essentially linear W-N-C angles (168.4 and 171.7°), is consistent with the views that the ethylideneamide functions as a formal 3-electron donor and that 1 is an 18-valence-electron complex. The intramolecular dimensions of 1 are comparable to those of other complexes possessing linear alkylideneamido ligands.[8]

Treatment of 1 with 2 equiv of HCl in Et_2O leads to the formation of the deep blue alkyl chloro complex 2,[4] and an air-sensitive white precipitate which is presumably the $CH_3C(H){=}NH_2^+Cl^-$ salt. This conversion is without precedent for an alkylideneamido complex and is a key step on the route to the ultimately desired organometallic complexes. A crystallographic analysis of 2[7] has established that the complex is a 16-electron monomer rather than a halide-bridged 18-electron dimer. The intramolecular dimensions of 2 generally resemble those of the related 16-electron complex $CpW(NO)(CH_2SiMe_3)_2$.[3a]

Isolation of the alkyl chloro complex, 2, by crystallization from pentane and its subsequent utilization in metathesis reactions with organomagnesium reagents (Scheme I) produce the mixed alkyl and alkyl–aryl complexes **3a**, **3b**, and **3c**.[4] The asymmetric **3a** has been subjected to a single-crystal X-ray crystallographic analysis[7] as a representative example of the mixed complexes. This analysis has confirmed its monomeric, three-legged piano-stool molecular structure, as depicted in Scheme I. Again, its intramolecular parameters are similar to those of $CpW(NO)(CH_2SiMe_3)_2$.[3a]

The mixed $Cp^*W(NO)(CH_2SiMe_3)R$ complexes are interesting in their own right since they provide an opportunity to compare directly the reactivities with various substrates of different alkyl and aryl groups on the same metal center. Equally significant is the fact that the synthetic route followed to produce them is unique, but may be quite generally applicable, and so we are currently investigating the trapping of the reactive hydride, $Cp^*W(NO)(CH_2SiMe_3)H$, by other unsaturated substrates in order to produce otherwise inaccessible ligands at the metal center. Furthermore, we are also extending the three-step synthetic methodology portrayed in Scheme I to encompass other dialkyl and diaryl analogues of $Cp^*W(NO)(CH_2SiMe_3)_2$.

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Supplementary Material Available: A textual presentation

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(7) X-ray diffraction data were collected using an Enraf-Nonius CAD-4F diffractometer with a modified low-temperature attachment; radiation, Mo Kα, graphite monochromatized ($\lambda = 0.71069$ Å). Data for $Cp^*W(NO)(CH_2SiMe_3)(NC(H)CH_3)$ (1): monoclinic; $P2_1/n$; $T = 200$ K; $a = 9.515$ (2) Å, $b = 21.946$ (3) Å, $c = 9.552$ (2) Å; $\beta = 102.57$ (2)°; $V = 1946.8$ Å^3; $Z = 4$; μ(Mo Kα) = 61.2; transmission, 0.260–0.392; reflections = 2035 ($4° \le 2\theta \le 48°$, $I_o \ge 2.5\sigma(I_o)$); $R = 0.029$, $R_w = 0.028$; 106 parameters. Data for $Cp^*W(NO)(CH_2SiMe_3)Cl$ (2): $P2_1/c$; $T = 200$ K; $a = 11.068$ (3) Å, $b = 9.092$ (3) Å, $c = 18.128$ (4) Å; $\beta = 96.76$ (2)°; $V = 1811.9$ Å^3; $Z = 4$; μ(Mo Kα) = 67.2 cm^{-1}; relative transmission, 0.79–1.00; reflections = 2403 ($4° \le 2\theta \le 50°$, $I_o \ge 2.5\sigma(I_o)$); $R = 0.031$, $R_{wF} = 0.036$; 145 parameters. Data for $Cp^*W(NO)(CH_2SiMe_3)$(*o*-tolyl) (**3a**): orthorhombic; $Pc2_1b$; $T = 195$ K; $a = 14.079$ (3) Å, $b = 15.114$ (2) Å, $c = 41.524$ (5) Å; $V = 8835.9$ Å^3; $Z = 16$; μ(Mo Kα) = 54.0 cm^{-1}; transmission, 0.220–0.739; 4121 reflections ($4° \le 2\theta \le 45°$, $I_o \ge 25\sigma(I_o)$); 281 restraints; 349 variables; $R_F = 0.055$; $R_{wF} = 0.067$ (unit weights); our current model is highly restrained with chemically reasonable parameters and relatively few variables. A false least-squares minimum, which we attribute to pseudosymmetry involving the heavy-atom coordinates has not been entirely resolved at this stage. Further work is in progress. Results of the structure determinations are provided as supplementary material.

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of complete experimental details concerning the synthesis and characterization of complexes **1**, **2**, **3a**, **3b**, and **3c** and ORTEP diagrams and tables of data acquisition and refinement details, fractional coordinates, selected intramolecular distances and angles, anisotropic thermal parameters, and isotropic or equivalent isotropic thermal parameters for **1**, **2**, and **3a** (24 pages); listings of structure factors for **1**, **2**, and **3a** (65 pages). Ordering information is given on any current masthead page.

Double-Insertion Reaction of Alkynes with $[Cp'_2ZrMe]^+$: Formation of an Unusual Distorted η^5-Pentadienyl Ligand

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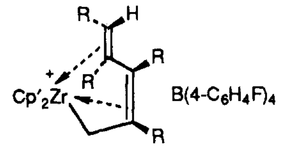
Summary: Reaction of $[Cp'_2ZrMe(NMe_2Ph)][X]$ (**1**; Cp' = C_5H_5 (**a**), $(Me_3Si)C_5H_4$ (**b**), $(Me_3C)C_5H_4$ (**c**), *rac*-C_2H_4(indenyl)$_2$ (**d**); $[X]^- = [B(4\text{-}C_6H_4F)_4]^-$) with excess 2-butyne gives $[Cp'_2Zr(\eta^5\text{-}CH_2C(Me){=}C(Me)C(Me){=}CHMe)][X]$ (**2a–d**); an X-ray structure analysis of **2c** shows that novel pentadienyl coordination occurs via a σ-bond and two weak unconjugated η^2-interactions with the double bonds. The reaction proceeds via observable, but unstable, alkenyl and 1,3-alkadienyl complexes, followed by a 1,5-hydrogen shift. Double alkyne insertion is unfavorable for crowded $(C_5Me_5)_2ZrMe(X)$, which instead gives $[(C_5Me_5)_2Zr(\eta^3\text{-}CH_2C{\equiv}CMe)][X]$ via a σ-bond metathesis reaction.

In contrast to the high polymerization reactivity of electrophilic d^0 complexes, $[Cp'_2MR]^{n+}$ (n = 0,[1] 1[2]), with alkenes, *multiple* alkyne insertion into such M–alkyl bonds has not previously been reported. Either single alkyne insertion (into the M–R bond[3] or an M–H bond formed on β-hydrogen elimination)[4] to give alkenyl complexes or σ-bond metathesis to give 1-alkynyl ($HC{\equiv}CR'$)[3c,5] or 2-alkynyl ($MeC{\equiv}CR'$)[6] complexes (followed by further reaction) takes place. Our recent isolation of cationic *Lewis-base-free* alkenyl complexes, $[Cp'_2ZrC(R^1){=}C(R^2)Me]^+$,[7] from the reaction of highly electrophilic cations with $Me_3SiC{\equiv}CMe$ or $PhC{\equiv}CPh$, led us to believe that with more reactive alkynes novel multiple-insertion products, of relevance to alkyne oligomerization and polymerization,[8] could be obtained. We now report that double insertion of 2-butyne occurs for all but the most sterically crowded methylzirconocene cations studied, to give remarkable η^5-pentadienyl compounds via ligand isomerization.

Scheme I

$$Cp'_2ZrMe_2 + [PhMe_2NH][B(4\text{-}C_6H_4F)_4] + 2RC{\equiv}CR \xrightarrow[-30\text{ to }+25\ ^\circ C]{C_6H_5Br}$$



Cp'	R = Me	R = Et
C_5H_5	**2a**	**3a**
$(Me_3Si)C_5H_4$	**2b**	
$(Me_3C)C_5H_4$	**2c**	**3c**
rac-C_2H_4(indenyl)$_2$	**2d**	

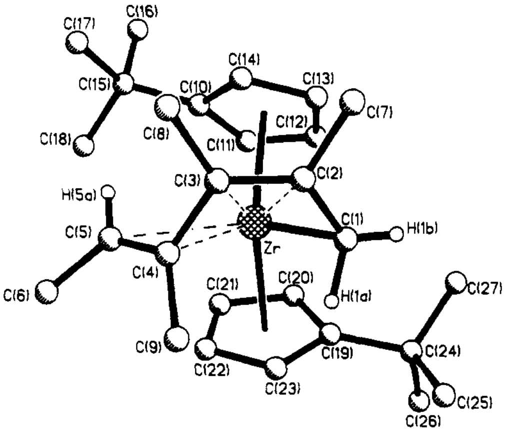


Figure 1. Molecular geometry of **2c**. Hydrogen atoms, except for those on C(1) and C(5), have been omitted for clarity.

Protonolysis[7] of Cp'_2ZrMe_2 using $[PhMe_2NH][B(4\text{-}C_6H_4F)_4]$ gives unstable electrophilic complexes $[Cp'_2ZrMe(NMe_2Ph)_n][B(4\text{-}C_6H_4F)_4]$ (**1a–e**), in which *N,N*-dimethylaniline (n = 1; **1a–d**) or the anion (Cp' = C_5Me_5; n = 0; **1e**) is weakly coordinated. In situ reaction

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