yield). Similarly, the *tert*-butyl-substituted nitrene complex **3** yields only amido complex **1**.

This system provides convenient access to gram quantities of electrophilic nitrene monomers of tungsten(IV). Efforts to utilize the reagents for nitrene transfer reactions are underway.

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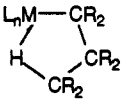
Supplementary Material Available: Full experimental details, including preparations and spectral and analytical data (infrared, ^{1}H NMR, ^{13}C NMR, elemental analyses) for complexes **1–4**, and X-ray diffraction data for **3** and **4**, including tables of crystal data, bond distances and angles, fractional atomic coordinates, and anisotropic thermal parameters (30 pages); tables of observed and calculated structure factors for **3** and **4** (26 pages). Ordering information is given on any current masthead page.

Chart I

Agostic $L_nM(CR_2)_n(CR)_mCR_2H$ Complexes

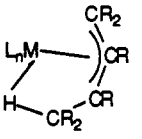
I. Agostic Alkyls (m=0; n=0, 1, 2, ...)

e.g. m=0, n=2:



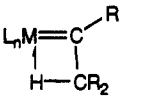
II. Agostic π-Complexes (n=1; m=1, 2, 3, ...)

e.g. n=1, m=2:



III. β-Agostic Carbene

n=0, m=1:



Reduction of Phenylacetylene in $[Tp'(CO)_2W(PhC_2H)][BF_4]$ To Form a β-Agostic Methylphenylcarbene Ligand

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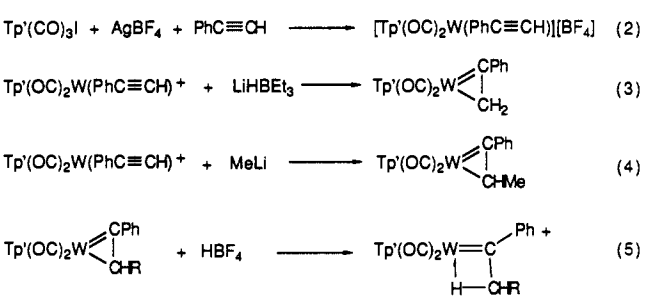
Agostic bonds have proliferated[1] since the first insightful review by Brookhart and Green in 1983.[2] Numerous α-agostic carbenes, alternatively described as protonated carbynes, of both groups V[3] and VI[4] have been reported by Schrock and co-workers. The paradigm for olefin insertion and polymerization reactions involves β-agostic alkyls.[5] Four-electron-donor alkyne ligands, common for group VI,[6] provide access to η^2-vinyl ligands[7] which are precursors to β-agostic carbene products as reported here.

Addition of a nucleophile (H^-, Me^-) to the terminal carbon of the phenylacetylene ligand in $[Tp'(CO)_2W(PhC{\equiv}CH)][BF_4]$ [Tp' = hydridotris(3,5-dimethylpyrazolyl)borate] forms an η^2-vinyl ligand which can be protonated to form an alkylphenylcarbene ligand. The agostic bond present in $[Tp'(CO)_2W{=}C(Ph)CH_2R][BF_4]$ (R = H, Me), described in detail below, complements the range of saturated and unsaturated agostic ligands represented in Chart I. In a sense, the β-agostic carbene resembles both agostic π-complexes with unsaturation in the organic ligand and Schrock α-agostic carbenes with unsaturation in the metal–carbon bond.

Oxidation of $[NEt_4][Tp'W(CO)_3]$[8] with iodine provides access to d^4 metal chemistry via the $Tp'W(CO)_3I$ monomer (eq 1).



(1)

(2)

(3)

(4)

(5)

Iodide removal with silver tetrafluoroborate in the presence of phenylacetylene yields a dark forest green cationic alkyne complex, $[Tp'(CO)_2W(PhC{\equiv}CH)][BF_4]$ (eq 2). This dicarbonyl derivative (ν_{CO} = 2057 and 1970 cm^{-1}) displays classic four-electrn-donor alkyne properties[6] (^{1}H NMR, δ = 14.0 ppm, ≡C*H*; ^{13}C NMR, 197 ppm, d, $^1J_{CH}$ = 223 Hz, ≡*C*H, 225 ppm, ≡*C*Ph).

Nucleophilic addition at the terminal acetylene carbon can be achieved with either $Li[Et_3BH]$ (eq 3) or MeLi (eq 4) to form neutral η^2-vinyl complexes. The carbenoid character of C_α, bearing the phenyl group, is evident in the low-field ^{13}C chemical shift (η^2-*C*Ph=CH_2, 234 ppm; η^2-*C*Ph=CHMe, 265 ppm). NMR data for these complexes is similar to data reported by Green and co-workers for η^2-vinyl ligands in a series of $(\pi\text{-}C_5H_5)[P(OMe)_3]_2Mo(\eta^2\text{-}CR{=}CR_2)$ complexes.[9]

Protonation of the original alkyne terminal carbon results from addition of tetrafluoroboric acid to the neutral η^2-vinyl monomers (eq 5). The net result of sequential H^-, H^+ addition to the terminal alkyne carbon is conversion of PhC≡CH to PhC̈CH_3. While electrophilic addition to the C_β site of η^1-vinyl ligands to form nonagostic carbenes maintains the metal electron count,[10] a similar

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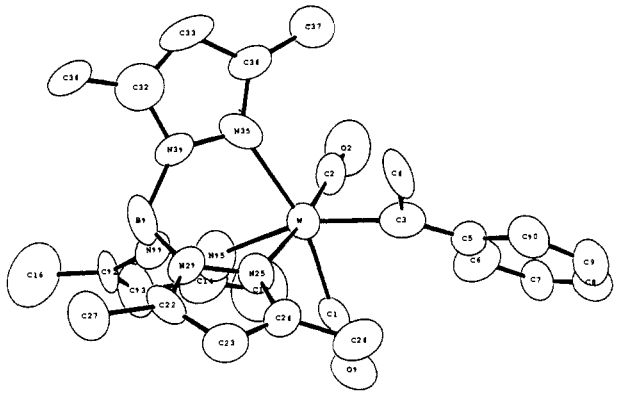

Figure 1. $[Tp'(CO)_2W{=}C(Ph)Me]^+$ with the β-agostic carbene lying between the two carbonyl ligands: W-C3, 1.94 (2) Å; C3-C4, 1.50 (3) Å; C3-C5, 1.45 (3) Å; W-C3-C4, 91 (1)°; W-C3-C5, 149 (2)°; C1-W-C2, 96 (1)°.

result from protonation of an η^2-vinyl ligand would leave the metal unsaturated.

The only unusual piece of spectral data we obtained for the methylphenylcarbene complex was a high-field ^{13}C chemical shift for the methyl carbon (-22.8 ppm). The $^1J_{CH}$ value of 132 Hz for this group could result either from a normal CH_3 moiety or from averaging one agostic C-H coupling constant with two olefin-like C-H coupling constants.[1] Partial deuterium incorporation did not cause a substantive change in either the methyl ^1H chemical shift or the methyl $^1J_{CH}$ coupling constant down to -70 °C.[11] Facile rotation of agostic methyl groups is known to obscure NMR evidence for agostic bonding in some complexes.[12]

The ethylphenylcarbene displays an unusually high field shift for the methylene carbon (-11.4 ppm), suggesting a close structural analogy to the methyl derivative. (In contrast, agostic spectral properties present in a scandium ethyl derivative disappear in the analogous propyl complex.[13]) The methylene $^1J_{CH}$ value of 121 Hz and several broad room-temperature NMR signals for $[Tp'(OC)_2W{=}C(Ph)CH_2Me][BF_4]$ encouraged us to undertake low-temperature NMR studies. Distinct proton signals for the methylene group of the ethyl substituent were evident at -60 °C (1.76 and 3.48 ppm, $^2J_{HH}$ = 17.5 Hz, $^3J_{HH}$ = 5.2 Hz). The absence of a mirror plane in the solution structure was also evident in the low-temperature ^{13}C spectrum as two carbonyl carbon signals were detected (211 ppm, $^1J_{WC}$ = 161 Hz; 215 ppm, $^1J_{WC}$ = 134 Hz).

The keystone that definitively characterizes the cationic ethylcarbene complex as agostic was the doublet of doublets revealed at -60 °C for the methylene carbon. The smaller $^1J_{CH}$ value of 96 Hz is the signature of an agostic bond,[1] and the larger value of 145 Hz reflects rehybridization from sp^3 toward sp^2 for the methylene carbon. The $^1J_{WC}$ value of 41 Hz to the carbene carbon is also noteworthy. Coalescence of the methylene protons at -5 °C indicates a barrier of 11.7 kcal/mol for enantiomer interconversion.

The X-ray structure[14] of $[Tp'(OC)_2W{=}C(Ph)CH_3][BF_4]$ is compatible with an agostic formulation (Figure 1). The Tp' and carbonyl ligands are unremarkable; details of the carbene geometry are the focus of attention here. The W=C distance of 1.942 Å lies near high oxidation state Schrock alkylidenes and below low oxidation state Fischer carbenes[15] $[Bu^tCH{=}W(dmpe)(CBu^t)(CH_2Bu^t)]$, 1.94 Å;[16] $Ph_2C{=}W(CO)_5$, 2.14 Å[17]). The metal to methyl carbon distance of 2.49 Å is consistent with a three-center, two-electron linkage tying the W-H-C unit together. The W=C—C angles of 149° to the phenyl ipso carbon and 91° to the methyl carbon are reminiscent of protonated carbynes,[3,4] the analogy here being a methylated phenylcarbyne ligand.

The classical limits accessible to $[Tp'(OC)_2W{=}C(Ph)CH_2R][BF_4]$ are either an 18-electron η^2-vinyl hydride complex or a 16-electron carbene monomer. We believe that the steric requirements of the Tp' ligand[18] inhibit the formation of $[Tp'(OC)_2HW(\eta^2\text{-}CPh{=}CHR)]^+$, and thus this cationic third row metal complex adopts an agostic structure.

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Supplementary Material Available: Synthetic details and complete characterization data as well as tables of X-ray structural parameters for $[Tp'(CO)_2WC(Ph)Me][BF_4]$ (19 pages); observed and calculated structure factors for $[Tp'(CO)_2WC(Ph)Me][BF_4]$ (14 pages). Ordering information is given on any current masthead page.

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Total Synthesis of the Oligosaccharide Fragment of Calicheamicin γ_1^I

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Model studies recently reported from these laboratories[1] suggested a strategy for the construction of the oligosaccharide fragment of calicheamicin γ_1^I (**1**),[2] which has been suggested as the main DNA-binding domain of this molecule.[3] We now report the first total synthesis of this unusual oligosaccharide as its methyl glycoside (**2**). The stereocontrolled synthesis reported herein is based on a novel 3,3-sigmatropic rearrangement that established the essential elements of the central ring B as presented in Scheme I and delivered the target molecule in enantiomerically pure form and high overall yield.

Designated on structure **2** are the strategic bond disconnections that allowed the tracing of the requisite intermediates to the readily available starting materials, L-rhamnose (ring D), 3,4,5-tri-

† Visiting scientist from Ono Pharmaceutical Co., Japan, 1989-1990.
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