Conclusions

The silylene-bridged dihydride complexes $[Ir_2(H)_2(CO)_2(\mu\text{-}SiRR')(dppm)_2]$ (R = R′ = Me (**2**), Et (**3**), Ph (**4**); R = Ph, R′ = H (**5**)) are readily obtained as the final products of the binuclear oxidative additions of two Si–H bonds of the appropriate silanes to $[Ir_2(CO)_3(dppm)_2]$ (**1**). These stable products cannot be induced to lose H_2 or to react with CO or additional silanes and so are much less labile than their dirhodium analogues, which do react further.[10] Although these iridium species (with the exception of **5**) are fluxional, this fluxionality differs substantially from that displayed by the dirhodium complexes in that hydride exchange between the metal and silicon atoms does not occur. These differences appear to reflect, in part, the greater strength of iridium–hydrogen vs rhodium–hydrogen bonds. The route by which these bridging silylene complexes are formed appears to involve a stepwise process, starting with attack of one Si–H bond of the silane substrate upon the coordinatively unsaturated d^8 Ir(I) center of $[Ir_2(CO)_3(dppm)_2]$ ($[(OC)Ir^+(\mu\text{-}dppm)_2Ir^-(CO)_2]$, as an alternate formulation), followed by loss of CO from, and coordination of the second silicon–hydrogen bond to, the second iridium center, as a prelude to the second oxidative addition and formation of the final silylene-bridged product. Studies of the mechanisms and products of reactions of low-valent binuclear Ir and Rh complexes with other "H_2X"-type substrates are presently underway in this group.

Acknowledgment. We wish to thank the University of Alberta and the Natural Sciences and Engineering Research Council of Canada for support of this work and the NSERC for partial support (through a grant to M.C.) of the diffractometer and structure determination package and for funding of the PE 883 infrared spectrometer. We also thank Prof. R. Eisenberg for a prepublication draft of ref 10b, Prof. U. Schubert for a copy of ref 25 prior to publication, and Dr. R. W. Hilts for advice on NMR simulations.

Supplementary Material Available: Tables of thermal parameters for the anisotropic atoms, idealized hydrogen parameters, and bond distances and angles within the phenyl rings and solvent molecules, along with a summary of crystal data and details of intensity collection for **4** and **5** (13 pages); listings of observed and calculated structure amplitudes for **4** and **5** (39 pages). Ordering information is given on any current masthead page.

Regioselectivity and Stereospecificity in (Trimethylsilyl)methyl Anion Additions to the Functionalized Tungstenocene Derivatives $[W(\eta\text{-}C_5H_4CH_2CR{=}CH_2)(\eta\text{-}C_5H_5)Cl_2]$ (R = H, CH_3)

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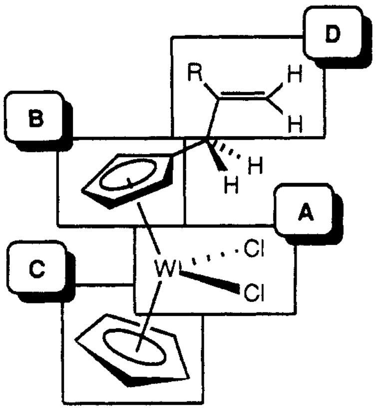
Addition of trimethylsilylmethyllithium to the allyl-substituted tungstenocene dihalides $[W(\eta\text{-}C_5H_4CH_2CR{=}CH_2)(\eta\text{-}C_5H_5)Cl_2]$ (R = H, **1**; R = CH_3, **2**) results in alkylation at the metal center to give $[W(\eta\text{-}C_5H_4CH_2CH{=}CH_2)(\eta\text{-}C_5H_5)\{CH_2Si(CH_3)_3\}_2]$ (**6**) and $[W\{\eta\text{-}C_5H_4CH_2C(CH_3){=}CH_2\}(\eta\text{-}C_5H_5)\{CH_2Si(CH_3)_3\}_2]$ (**8**), respectively. If $(CH_3)_3SiCH_2MgCl$ is used as the carbanion source, the reaction pathways are more complex: with fresh Grignard **2** is still alkylated at the metal to give **8**, but carbomagnesiation of the free double bond of **1** results in formation of a single diastereomer of the unusual carbocyclic $[\overline{W\{\eta\text{-}C_5H_4CH_2CH_2C}HCH_2Si(CH_3)_3\}(\eta\text{-}C_5H_5)Cl]$ (**4**). Addition of $MgCl_2$ to the Grignard reaction switches the locus of reactivity within **2** and results in alkylation of the cyclopentadienyl ring to form $[W\{\eta\text{-}C_5H_4CH_2Si(CH_3)_3\}\{\eta\text{-}C_5H_4CH_2C(CH_3){=}CH_2\}HCl]$ (**9**).

Introduction

One of the most important current challenges within organotransition-metal chemistry is the development of an understanding, comparable to that which exists in organic chemistry, of the factors controlling the reactivity of organometallic complexes. Our recent discovery[1] that magnesium halides promote the addition of Grignard reagents to the cyclopentadienyl ligands of $[W(\eta\text{-}C_5H_5)_2Cl_2]$ provides access to tungstenocene derivatives with functionalized cyclopentadienyl ligands and has provided us with an interesting opportunity to explore the reactivity of organometallic molecules that offer a number of potentially reactive sites. We have been particularly interested in the allyl-substituted complexes $[W(\eta\text{-}C_5H_4CH_2CH{=}CH_2)(\eta\text{-}C_5H_5)Cl_2]$ (**1**) and $[W\{\eta\text{-}C_5H_4CH_2C(CH_3){=}CH_2\}(\eta\text{-}C_5H_4)Cl_2]$ (**2**), both of which can be prepared conveniently on a multigram scale from $[W(\eta\text{-}C_5H_5)_2Cl_2]$ (**3**)[1]; see eq 1.

Scheme I. Potential Electrophilic Zones of Reactivity within Allyl-Substituted Tungstenocene Dichlorides



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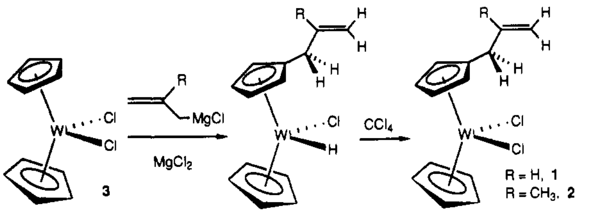
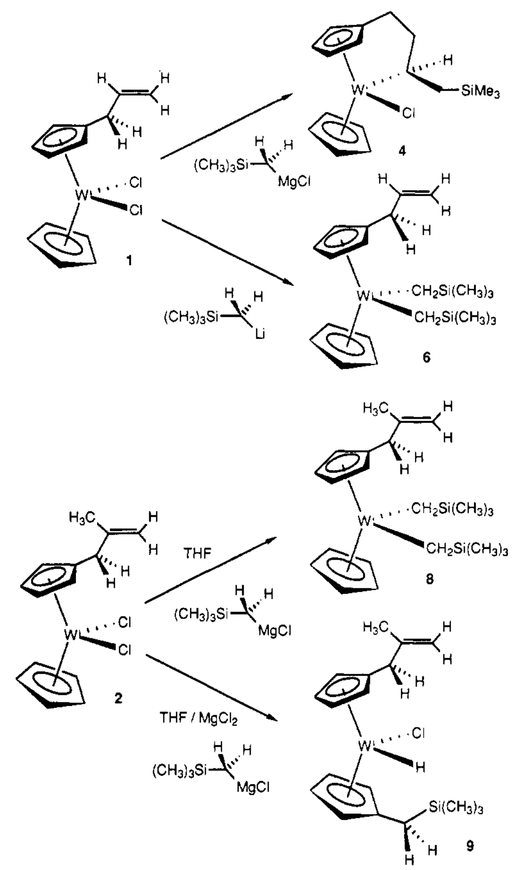
(1) Forschner, T. C.; Cooper, N. J. *J. Am. Chem. Soc.* **1989**, *111*, 7420–7424.



(1)

Complexes **1** and **2** could in principle react with nucleophiles within any one of four distinct zones of reactivity (Scheme I). The metal center offers the most obvious potentially electrophilic site (zone A), but the syntheses of these molecules by addition of allylmagnesium halides to **3** suggests that both the substituted and unsubstituted cyclopentadienyl ligands of **1** and **2** must also be considered potential zones of reactivity (zones B and C, respectively). The free double bonds of **1** and **2** offer a fourth potentially electrophilic site (zone D), and although carbon–carbon double bonds are not traditionally thought of as electrophilic centers, the literature on carbomagnesiation of homoallylic alcohols,[2] alkenyl ethers,[3] fulvenes,[4] alkenols,[5] alkenylamines,[6] and alkenes[7,8] does raise the possibility of nucleophilic attack at this site within the molecules. We now wish to report, as summarized in Scheme II, examples of the addition of the (trimethylsilyl)methyl anion to reactivity zones A, C, and D within these complexes. The most surprising of these reactions is the addition of [(trimethylsilyl)methyl]magnesium chloride to the allylic double bond in **1**—this ultimately results in the formation of metallacycle **4** as a single diastereomer, which we propose (on the basis of mechanistic arguments to be presented below) has the configuration shown in Scheme II.

Scheme II. Observed Outcomes of (Trimethylsilyl)methyl Anion Addition to 1 and 2



Experimental Section

General Data, Solvents, and Reagents. All manipulations were carried out under dry nitrogen using Schlenk tube techniques or a Vacuum Atmospheres Dri-lab glovebox. Glassware was oven dried or flamed under vacuum. Diethyl ether and tetrahydrofuran (THF) were freshly distilled from Na/benzophenone ketyl. CH_2Cl_2 was distilled from P_2O_5. Pentane and hexane were stirred over concentrated H_2SO_4 for 2 days and then over K_2CO_3 for 1 day before distillation from $LiAlH_4$. Reagent-grade ethanol was dried over 3-Å molecular sieves. $MgCl_2$ was prepared from Mg turnings (Baker) and anhydrous $HgCl_2$ (Aldrich).[9] Activity III alumina was prepared by addition of H_2O (60 mL/kg) to activity I Brockmann grade alumina (Aldrich). $[W(\eta\text{-}C_5H_4CH_2CH{=}CH_2)(\eta\text{-}C_5H_5)Cl_2]$ and $[W\{\eta\text{-}C_5H_4CH_2C(CH_3){=}CH_2\}(\eta\text{-}C_5H_5)Cl_2]$ were prepared as reported previously.[1] Grignard reagents were purchased from Aldrich or were prepared from alkyl chlorides (Aldrich Gold Label) and Mg turnings (Baker) in ether or THF and were standardized by titration with ethanol using 1,10-phenanthroline indicator.[10] Commercial $(CH_3)_3SiCH_2Li$ was used as received (Aldrich). Benzene-d_6 and CD_2Cl_2 were used as received from Aldrich.

NMR spectra were recorded on a Bruker WM 300 (^{1}H 300.10 MHz; ^{13}C 75.42 MHz). Microanalyses were performed as indicated by Desert Analytical, Tucson, AZ (Des) or Multichem, Lowell, MA (Mul). Molecular modeling studies were carried out using the CHEM-3-D program[11] and reasonable bond lengths and bond angles based on literature diffraction studies of tungstenocene complexes.[12] The supplementary material contains tables of the Cartesian coordinates of conformations of A, B, and C illustrated in Schemes V and VI (see the paragraph at the end of the paper).

$[W(\eta\text{-}C_5H_4CH_2CH{=}CH_2)(\eta\text{-}C_5H_5)\{CH_2Si(CH_3)_3\}_2]$ (6). A solution of $(CH_3)_3SiCH_2Li$ (5 mmol in 5 mL of hexane) was syringed into a deep green ether (20 mL) slurry of $[W(\eta\text{-}C_5H_4CH_2CH{=}CH_2)(\eta\text{-}C_5H_5)Cl_2]$ (800 mg, 1.88 mmol) to give, after 45 min, a red–brown solution. The reaction was quenched with ethanol (5 mL) and filtered (15-cm pad of alumina), and the alumina washed with CH_2Cl_2. After removal of the volatiles under reduced pressure, the brown residue was extracted with hexane and filtered through alumina (15 cm). After evaporation of the hexane the product was isolated as a brown oil shown to be $[W(\eta\text{-}C_5H_4CH_2CH{=}CH_2)(\eta\text{-}C_5H_5)(CH_2Si(CH_3)_3)_2]$ (410 mg, 0.77 mmol ≡ 41%). Anal. Calcd for $C_{21}H_{36}Si_2W$: C, 47.72; H, 6.87. Found (Mul): C, 47.58; H, 7.13. ^{1}H NMR (300 MHz, benzene-d_6) δ −0.96 (d, J = 15 Hz, 2 H, $W\{C\mathit{H}HSi(CH_3)\}_2$), −0.80 (d, J = 15 Hz, 2 H, $W\{CH\mathit{H}Si(CH_3)\}_2$), 0.20 (s, 18 H, $W\{CH_2Si(C\mathit{H}_3)\}_2$), 2.53 (d, J = 7 Hz, 2 H, $C\mathit{H}_2CH{=}CH_2$), 4.00, 4.18 (m, 2 H, each, $\eta\text{-}C_5\mathit{H}_2\mathit{H}_2$), 4.10 (s, 5 H, $\eta\text{-}C_5H_5$), 4.94 (m, 2 H, $CH_2CH{=}C\mathit{H}_2$), 5.66 (m, 1 H, $CH_2C\mathit{H}{=}CH_2$).

$[\overline{W\{\eta\text{-}C_5H_4CH_2CH_2C}HCH_2Si(CH_3)_3\}(\eta\text{-}C_5H_5)Cl]$ (4). A freshly prepared solution of $(CH_3)_3SiCH_2MgCl$ (2 mmol in 2 mL

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of ether) was syringed in to a green THF solution (25 mL) solution of $[W(\eta\text{-}C_5H_4CH_2CH{=}CH_2)(\eta\text{-}C_5H_5)Cl_2]$ (0.50 g, 1.17 mmol) to give, after 24 h, a brown-yellow solution. The reaction was quenched with ethanol, the mixture filtered through a pad of alumina, and the alumina washed with CH_2Cl_2 until the filtrate was colorless. The filtrate was then concentrated (3 mL) and chromatographed on alumina with ether/CH_2Cl_2 (2:1) as the eluant to give two bands. The first fraction, a yellow band, was shown (^{1}H NMR) to be a complex mixture of organics and discarded. The second fraction, a brown band, was collected and evaporated to dryness. The resulting brown solid gave brown crystals after crystallization from ether at low temperatures (−78 °C) shown to be $[\overline{W\{\eta\text{-}C_5H_4CH_2CH_2C}HCH_2Si(CH_3)_3\}(\eta\text{-}C_5H_5)Cl]$ (0.421 g, 0.88 mmol ≡ 68%). Anal. Calcd for $C_{17}H_{25}ClSiW$: C, 42.83; H, 5.29. Found (Des): C, 42.83; H, 5.31. ^{1}H NMR (300 MHz, CD_2Cl_2) δ 0.00 (s, 9 H, $Si(CH_3)_3$), 0.53 (dd, $J_{CHH} = 14.4$ Hz, $J_{CH_2CH} = 7.0$ Hz, 1 H, $CHHSi(CH_3)_3$), 0.69 (dd, $J_{CHH} = 14.4$ Hz, $J_{CH_2CH} = 7.0$ Hz, 1 H, $CHHSi(CH_3)_3$), 1.67 (dt, $J_{CHH} = 11.8$ Hz, $J_{CHHCHH} = 3.0$ Hz, $J_{CHHCHW} = 3.2$ Hz, 1 H, C_5H_4CHH), 1.87 (pseudotriplet, $J_{CHH} = 11.6$ Hz, $J_{CHHCHW} = 11.6$ Hz, $J_{CHHCHH} = 3.0$ Hz, 1 H, CHHCHW), 2.27 (pseudotriplet, $J_{CHH} = 11.8$ Hz, $J_{CHHCHW} = 8.8$ Hz, $J_{CHHCHH} = 3.0$ Hz, 1 H, $\eta\text{-}C_5H_4CHH$), 2.64 (m, $J_{CHH} = 11.6$ Hz, $J_{CHHCHW} = 5.9$ Hz, 1 H, CHHCHW), 2.79 (m, 1 H, WCH), 3.83, 4.62, 4.76, 5.64 (m, 1 H each, $\eta\text{-}C_5H_4CH_2$), 4.86 (s, 5 H, $\eta\text{-}C_5H_5$). ^{13}C NMR (75.4 MHz, CD_2Cl_2) δ −0.3 (q, $J = 118$ Hz, $SiCH_3)_3$, 18.5 (t, $J = 130$ Hz, CH_2Si), 31.4 (t, $J = 116$ Hz, CH_2CHW), 37.3 (t, $J = 127$ Hz, $C_5H_4CH_2$), 55.5 (d, $J = 131$ Hz, CHW), 71.4 (d, $J = 187$ Hz, 1 of 4 C, $\eta\text{-}C_4H_4C$), 75.2 (d, $J = 181$ Hz, 1 of 4 C, $\eta\text{-}C_4H_4C$), 78.1 (d, $J = 181$ Hz, 1 of 4 C, $\eta\text{-}C_4H_4C$), 90.5 (d, $J = 182$ Hz, $\eta\text{-}C_5H_5$), 111.5 (d, $J = 178$ Hz, 1 of 4 C, $\eta\text{-}C_4H_4C$), 132.4 (s, $\eta\text{-}C_4H_4C$).

$[W\{\eta\text{-}C_5H_4CH_2C(CH_3){=}CH_2\}(\eta\text{-}C_5H_5)\{CH_2Si(CH_3)_3\}_2]$ (8). I. An ether solution of $(CH_3)_3SiCH_2MgCl$ (5 mmol in 5 mL) was syringed into a green THF (20 mL) solution of $[W(\eta\text{-}C_5H_4CH_2C(CH_3){=}CH_2)(\eta\text{-}C_5H_5)Cl_2]$ (800 mg, 1.82 mmol) to give, after 45 min, a red-brown solution. The reaction was then quenched with ethanol (5 mL) and filtered (15-cm pad of alumina), and the alumina washed with CH_2Cl_2 until the filtrate was colorless. After removal of the volatiles from the filtrate, the brown residue was dissolved into hexane and filtered through alumina (15-cm pad), and the pad washed with hexane until the filtrates were colorless (a brown band remained on the column). The hexane was removed to leave a brown oil shown to be $[W\{\eta\text{-}C_5H_4CH_2C(CH_3){=}CH_2\}(\eta\text{-}C_5H_5)\{CH_2Si(CH_3)_3\}_2]$ (532 mg, 0.98 mmol ≡ 47%). ^{1}H NMR (300 MHz, benzene-d_6) δ −0.95 (d, $J = 14.8$ Hz, 2 H, $W\{CHHSi(CH_3)\}_2$), 0.79 (d, $J = 14.8$ Hz, 2 H, $W\{CHHSi(CH_3)\}_2$), 0.20 (s, 18 H, $CH_2Si(CH_3)$), 1.60 (s, 3 H, $C(CH_3){=}CH_2$), 2.44 (s, 2 H, CH_2), 4.00, 4.19 (m, 2 H each, $\eta\text{-}C_5H_2H_2$), 4.10 (s, 5 H, $\eta\text{-}C_5H_5$), 4.78 (m, 2 H, $C(CH_3){=}CH_2$).

II. A hexane solution of $(CH_3)_3SiCH_2Li$ (5 mmol in 5 mL) was syringed into a green THF (20 mL) solution containing $[W\{\eta\text{-}C_5H_4CH_2C(CH_3){=}CH_2\}(\eta\text{-}C_5H_5)Cl_2]$ (1.12 g, 2.55 mmol) to give, after 15 min, a red-brown solution. The reaction was then quenched with ethanol (5 mL) at 0 °C, and the product $[W\{\eta\text{-}C_5H_4CH_2C(CH_3){=}CH_2\}(\eta\text{-}C_5H_5)\{CH_2Si(CH_3)_3\}_2]$ (0.815 g, 1.50 mmol ≡ 59%) was isolated by using the procedure described above.

$[W\{\eta\text{-}C_5H_4CH_2Si(CH_3)_3\}\{\eta\text{-}C_5H_4CH_2C(CH_3){=}CH_2\}HCl]$ (9). An ether solution of $(CH_3)_3CH_2SiMgCl$ (15 mmol in 15 mL) was syringed into a deep green slurry of $[W\{\eta\text{-}C_5H_4CH_2C(CH_3){=}CH_2\}(\eta\text{-}C_5H_5)Cl_2]$ (2.75 g, 6.26 mmol) in a THF solution of $MgCl_2$ (15 mmol in 25 mL) to give, after 2 h, a dark red-brown mixture. The reaction was quenched with ethanol (10 mL) at −78 °C, and the volatiles were removed as the vessel warmed to room temperature. The brown solids were extracted with CH_2Cl_2 (4 × 15 mL) and filtered (through a 15-cm pad alumina), and the clear red-brown filtrate was concentrated (5 mL) and transferred to a column (4.5 cm × 25 cm, activity III alumina). The column was developed with CH_2Cl_2/pentane (1:3) to give two overlapping broad brown bands. A 20-mL fraction was collected that included all of the first band and a small amount of the second band, and this product was shown by ^{1}H NMR to be >85% $[W\{\eta\text{-}C_5H_4CH_2C(CH_3){=}CH_2\}(\eta\text{-}C_5H_5)\{CH_2Si(CH_3)_3\}_2]$ (108 mg) contaminated by some of the second fraction. Further development with CH_2Cl_2/pentane (1:1) resulted in elution of the second band. The second fraction was evaporated to dryness and dissolved in a minimum volume of ether. The clear red-brown ether solution was cooled to −78 °C for 5 days to give brown crystals shown to be $[W\{\eta\text{-}C_5H_4CH_2Si(CH_3)_3\}\{\eta\text{-}C_5H_4CH_2C(CH_3){=}CH_2\}HCl]$ (2.04 g, 4.15 mmol ≡ 64%). Anal. Calcd for $C_{18}H_{27}ClSiW$: C, 44.05; H, 5.55. Found (Mul): C, 44.17; H, 5.93. ^{1}H NMR (300 MHz, benzene-d_6) δ −10.53 (s, 1 H, W—H), 0.00 (s, 9 H, $CH_2Si(CH_3)_3$), 1.65 (d, $J = 13.4$ Hz, 1 H, $CHHSi(CH_3)_3$), 1.67 (s, 3 H, $C(CH_3){=}CH_2$), 1.71 (d, $J = 13.4$ Hz, 1 H, $CHHSi(CH_3)_3$), 2.94 (d, $J = 15.2$ Hz, 1 H, $CHHC(CH_3){=}CH_2$), 3.10 (d, $J = 15.2$ Hz, 1 H, $CHHC(CH_3){=}CH_2$), 3.36, 4.06 (2 H), 4.12, 4.39, 4.50, 4.70–4.90 (m, 2 H, overlapping with $\eta\text{-}C_5H_4CH_2C(CH_3){=}CH_2$) (m, 1 H each, $\eta\text{-}C_5HHHHCH_2Si(CH_3)_3$ and $\eta\text{-}C_5HHHHCH_2C(CH_3){=}CH_2$), 4.83 (m, 2 H, $\eta\text{-}C_5H_4CH_2C(CH_3){=}CH_2$ overlapping with the diastereotopic cyclopentadienyl protons).

Results and Discussion

(Trimethylsilyl)methyl Anion Additions to $[W(\eta\text{-}C_5H_4CH_2CH{=}CH_2)(\eta\text{-}C_5H_5)Cl_2]$. We have previously reported that the reaction of $[W(\eta\text{-}C_5H_5)_2Cl_2]$ (**3**) with a variety of main-group sources of the (trimethylsilyl)methyl anion resulted in alkylation at the metal center to give $[W(\eta\text{-}C_5H_5)_2\{CH_2Si(CH_3)_3\}_2]$ (**5**),[1] and addition of $(CH_3)_3SiCH_2Li$ to **1** resulted in a similar alkylation at the metal center to give the bis-alkyl $[W(\eta\text{-}C_5H_4CH_2CH{=}CH_2)(\eta\text{-}C_5H_5)\{CH_2Si(CH_3)_3\}_2]$ (**6**). This provides an interesting contrast with the reaction of **1** with $CH_2{=}CHCH_2MgCl/MgCl_2$, which results in addition to the cyclopentadienyl ring to give $[W(\eta\text{-}C_5H_4CH_2CH{=}CH_2)_2HCl]$ (**7**).[1]

It is clear that there is a fine balance in the reactivity of **1** toward electrophiles, and changing the source of $[(CH_3)_3SiCH_2]^-$ from $(CH_3)_3SiCH_2Li$ to $(CH_3)_3SiCH_2MgCl$ switched the principal zone of reactivity from the metal (zone A) to the free double bond (zone D) and resulted in a surprising carbomagnesiation reaction which ultimately gives the remarkable metallacyclic product $[\overline{W(\eta\text{-}C_5H_5)\{\eta\text{-}C_5H_4CH_2CH_2C}HCH_2Si(CH_3)_3\}Cl]$ (**4**). We have been unable to obtain crystals of **4** suitable for X-ray diffraction, but we have formulated it as the metallacycle shown in Scheme II on the basis of the analytical and ^{1}H and ^{13}C NMR data reported in detail in the Experimental Section.

It was obvious from inspection of the ^{1}H NMR spectrum illustrated in Figure 1 that the compound was a tungstenocene derivative containing one C_5H_5 ligand and a second monosubstituted cyclopentadienyl which gives rise to a characteristic ABCD pattern[13] in the range δ 3.8–5.8. The absence of a high-field resonance established that there was no hydride attached to the W atom, and the presence of a further five complex peaks with intensities corresponding to a single hydrogen indicated that the complex had a carbocyclic structure. It was not, however, immediately apparent whether this was a structure with an ethylene bridge between the ring and the methine group (as illustrated) or a single methylene bridge in this position.

As will be clear from the mechanistic discussion below, a single methylene bridge was a more attractive initial hypothesis, but the ^{1}H NMR data unambiguously establishes the structure as that in Figure 1, primarily because a doublet of doublets is observed for each of the diastereotopic hydrogens of the methylene group α to Si. These resonances have a characteristically high chemical shift and form part of an ABC coupling system indicating that they are also α to the methine group bonded to tungsten. The remaining assignments were confirmed by narrow-band

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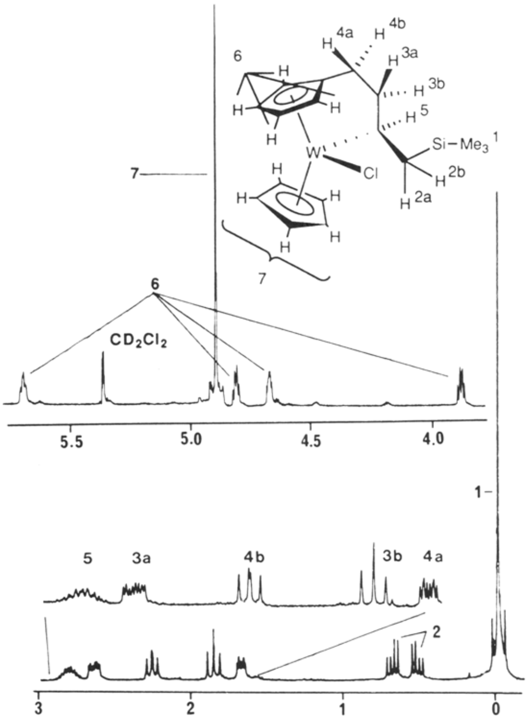
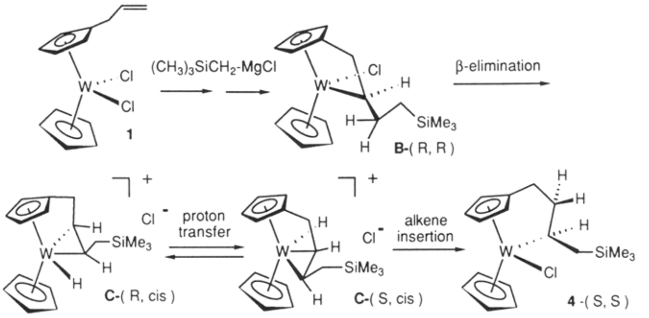


Figure 1. ^{1}H NMR spectrum of $[\overline{W\{\eta\text{-}C_5H_4CH_2CH_2C}HCH_2Si(CH_3)_3\}(\eta\text{-}C_5H_5)Cl]$ (4) at 300 MHz.

Scheme III. Summary of the Proposed Mechanism of Formation of the *S*,*S* Enantiomer of 4

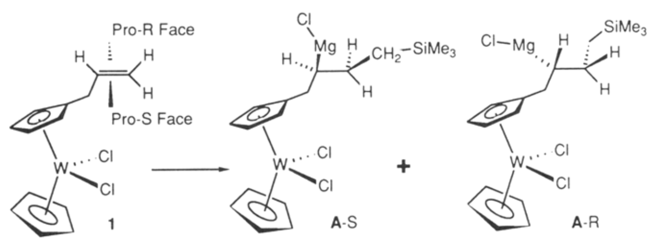


decoupling of each of the resonances between δ 0.5 and 3.0 and by COSY experiments,[14] which allowed determination of the coupling constants listed in the Experimental Section. The magnitudes of the coupling constants are qualitatively consistent with those that would be expected on the basis of the Karplus relationship[15] and the restricted conformations accessible to the ring.

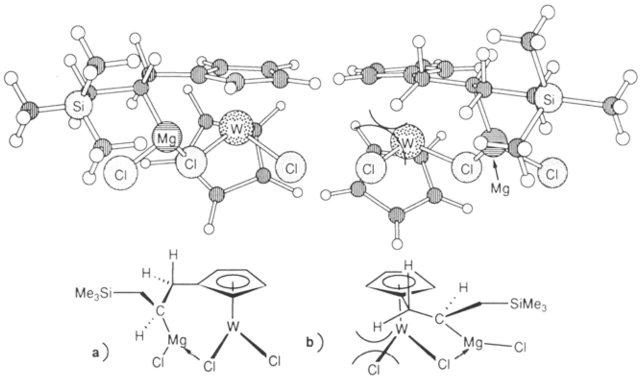
Mechanism of the Stereospecific Formation of $[\overline{W(\eta\text{-}C_5H_5)\{\eta\text{-}C_5H_4CH_2CH_2C}HCH_2Si(CH_3)_3\}Cl]$ (4).

Our previous work on differentially substituted tungstenocene systems has established that the ^{1}H NMR chemical shifts of the ABCD patterns of the substituted cyclopentadienyl rings provide a sensitive probe for the identification of diastereomers differing in chirality at the metal center.[13] The appearance of a single ABCD pattern in the cyclopentadienyl range of the ^{1}H NMR spectrum of 4 establishes that the addition of (trimethylsilyl)methyl anion to the allylic double bond in 1 has resulted in formation of 4 as a *single* enantiomeric diastereomer. We were at first surprised by this diastereospecificity, but our recent investigations of the stereochemistry of reactions in this system[16] enable us to provide a mechanistic description of the reaction (summarized in Scheme III[17]) which, in addition to accounting for this diastereospecificity, allows us to predict that the product is formed as the *SS*, *RR* diastereomer[18] (Figure 1 and Scheme III).

Scheme IV. Initial Grignard Addition to 1



Scheme V. Proposed Origin of Diastereoselectivity in Cyclization of A: Intramolecular Coordination of Mg to (a) Pro-*S* W–Cl and (b) Pro-*R* W–Cl



The most reasonable first step in the sequence leading to formation of 4 is C–C bond formation by addition of the Grignard to the allylic C=C bond. Although C=C bonds are not normally thought of as electrophilic sites, there are previous examples of carbomagnesiation reactions,[2-8] some of which involve addition to unactivated C=C bonds.[8] Some of these are driven by subsequent cyclizations, as in the intramolecular metallo–ene reactions reported by Oppolzer,[7] and the potential for cyclization may be a significant factor leading to carbomagnesiation of 1.

There is no reason for the addition to achiral 1 to be stereoselective, and we would expect, as shown in Scheme IV, that this would give rise to the intermediate Grignard (A) as a 1:1 mix of the enantiomers with *R* and *S* configurations at the carbon β to the ring and hence ultimately to the formation of 4 as an enantiomeric diastereomer.

The most reasonable next step in the reaction sequence is cyclization to form metallacycle B (Scheme III) in which there is a *single* methylene bridge between the cyclopentadienyl ring and the methine group bonded to tungsten, and it is this step that we propose is responsible for the observed diastereospecificity of the reaction. Although

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[14] DISNMRD, Version 87 101.0; Bruker Instruments: Billerica, MA 1987.

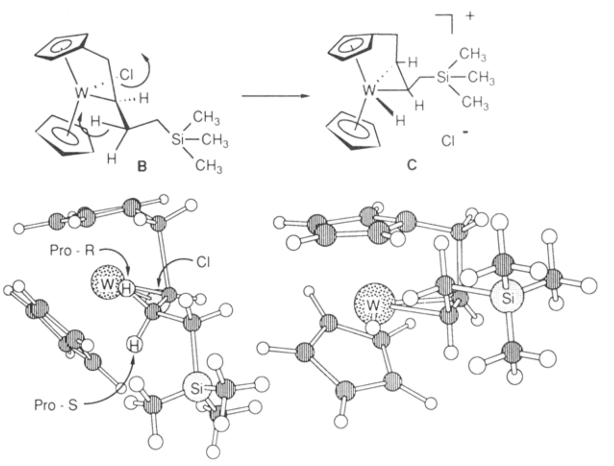
[15] Karplus, M. *J. Am. Chem. Soc.* **1964**, *85*, 5561.

[16] (a) McNally, J. P.; Cooper, N. J. *Organometallics* **1988**, *7*, 1704–1715. (b) McNally, J. P.; Cooper, N. J. Submitted to *J. Am. Chem. Soc.*

[17] Scheme III shows the formation of a single (*SS*) enantiomer of 4, which is formed as the *SS*, *RR* enantiomeric diastereomer.

[18] *R* and *S* designations are based on the pseudoatom approach: Stanley, K.; Baird, M. C. *J. Am. Chem. Soc.* **1975**, *97*, 6598–6599. This leads to the priority sequence W > substituted cyclopentadienyl > C_5H_5 > Cl > alkene > alkyl, and the chirality at W is given first in accord with: Attig, T. G.; Teller, R. G.; Wu, S.-M.; Bau, R.; Wojcicki, A. *J. Am. Chem. Soc.* **1979**, *101*, 619–628.

Scheme VI. Most Probable Conformation for β-Push Hydride Elimination from B



the structure of A could be more complex, Grignards are typically monomeric in THF,[19] and cyclization would most reasonably involve the transient coordination of a W–Cl to the Mg of the Grignard, followed by $MgCl_2$ extrusion and ring closure to form B. Diastereoselectivity in this ring closure would imply that the *R* and *S* enantiomers of A must exhibit a preference for coordination to either the pro-*R* or pro-*S* W–Cl.

Molecular modeling studies confirmed that A-*R* and A-*S* should indeed be able to discriminate between the pro-*S* and pro-*R* W–Cl groups, as illustrated by the representations in Scheme V of the 3-D structures of the intramolecular complex of A-*R* with the pro-*S* and pro-*R* W-Cl groups. Complexation of the pro-*R* W-Cl group results in an unfavorably close approach (2.45 Å) between the pro-*S* H of the methylene group α to the cyclopentadienyl ring and the pro-*S* W–Cl group (this is analogous to the 1,3-diaxial interaction in the chair conformation of a six-membered ring). None of the nonbonding contacts in the analogous complex with the pro-*R* W–Cl group are as unfavorable, and we suggest that B is formed exclusively as the *RR*, *SS* diastereomer.

It was clear that the tungsten atom could be "walked" along the hydrocarbon chain to expand the metallacycle to that in the observed product **4**, as shown in Scheme III, but it was not immediately obvious whether it was reasonable to suggest that this reaction should be stereospecific and lead from a single diastereomer of B to a single diastereomer of **4**. We have, however, obtained evidence that halide loss and β-elimination within the diastereomeric tungstenocene alkyl halide $[W(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4\{OCH(CHMe_2)Ph\})(\eta^1\text{-}C_2H_5)I]$, a sequence closely related to that required to convert B to C, is a stereoselective reaction resulting in formal inversion at the metal center.[16b] We have proposed that this occurs by a "β-push" mechanism, which would suggest that the *RR* enantiomer of B leads to the *R*-cis enantiomer of *C* shown in Scheme III. This assumes that the transition state for "β-push" hydride elimination within B will occur preferentially from the conformation illustrated in Scheme VI in which it is the pro-*R* hydrogen that is transferred to the metal to generate the cis isomer of the alkene. A β-hydride elimination in which the pro-*S* hydrogen is transferred to the metal is unlikely to be favorable since it would have to occur from a conformation in which the trimethylsilyl group would have dramatic steric interactions with the cyclopentadienyl ligand.

Migration of the tungsten along the hydrocarbon chain could be completed by a base-catalyzed proton transfer that inverts the configuration at the metal center, and we have previously observed similar proton transfers to be facile in $[W(\eta\text{-}C_5H_5)_2(CH_2{=}CHCH_3)H]^+$ when it is generated in the presence of a Grignard reagent.[16a] Reinsertion of the alkene into the W–H bond together with recoordination of the halide (a reaction that is the microscopic reverse of the "β-push" hydride elimination) would ultimately result in formation of **4** as the *SS*, *RR* diastereomer.

The sequence by which we propose that **4** is formed is complex, and we have sought supporting evidence by looking for reaction intermediates. ^1H NMR spectra of material obtained by quenching the reaction before it was complete (after 1 h) did indeed indicate the formation of observable intermediates, but the complexity of the mixture (and of the spectra of its components) precluded speculation on the nature of the intermediates, and we have been unable to isolate pure compounds other than **4** from these mixtures.

(Trimethylsilyl)methyl Anion Additions to $[W\{\eta\text{-}C_5H_4CH_2C(CH_3){=}CH_2\}(\eta\text{-}C_5H_5)Cl_2]$ (2). As might expected from the reactivity of **1**, complex **2** reacts with $(CH_3)_3SiCH_2Li$ at the metal to give a 59% yield of $[W\{\eta\text{-}C_5H_4CH_2C(CH_3){=}CH_2\}(\eta\text{-}C_5H_5)\{CH_2Si(CH_3)_3\}_2]$ (**8**), as established by the characterization data in the Experimental Section.

In the case of **1**, switching from the lithio reagent to the Grignard resulted in a switch from reaction at W to initial addition to the free double bond (followed by cyclization and isomerization to **4**). In sharp contrast, freshly prepared $(CH_3)_3SiCH_2MgCl$ shows no tendency to add to the methallyl group of **2** but, as in the case of the lithio reagent, gives **8** in reasonable (47%) yield. Although unexpected, this result is reasonable. It suggests that the reactivity of the system is finely balanced, and that the +I effect of the methyl substituent sufficiently disfavors the buildup of negative charge on the carbon β to the ring to prevent carbomagnesiation.

We have previously reported that magnesium dihalides can promote the addition of Grignard reagents to cyclopentadienyl ligands in the tungstenocene system,[1] and this led us to also examine the reaction of **2** with $(CH_3)_3SiCH_2MgCl$ in the presence of added $MgCl_2$. Under these conditions complex **8** was only a minor product (3%), and the principal product of the reaction was the ring addition product $[W\{\eta\text{-}C_5H_4CH_2C(CH_3){=}CH_2\}\{\eta\text{-}C_5H_4CH_2Si(CH_3)_3\}HCl]$ (**9**), isolated in 64% yield after chromatography and crystallization. This is in accord with our previous observations,[1] but the reaction of **2** with $(CH_3)_3SiCH_2MgCl$ is the first example in which added $MgCl_2$ not only promotes ring addition (to give reproducible high yields) but can actually switch the primary regioselectivity for alkylation of a single substrate from the metal (zone A) to the cyclopentadienyl ring (zone C).

We have suggested[1] that added magnesium halides promote nucleophilic alkylation of $[W(\eta\text{-}C_5H_5)_2Cl_2]$ by a Lewis acidic interaction with the chlorides on tungsten which enhances the electrophilicity of the cyclopentadienyl ligand. This then allows exo addition of a carbanion to a cyclopentadienyl ligand, followed by hydride migration to tungsten to give products of the type $[W(\eta\text{-}C_5H_4R)(\eta\text{-}C_5H_5)HCl]$, and this mechanism is supported by the halide exchange observed when $MgBr_2$ is used to promote allylation of $[W(\eta\text{-}C_5H_5)_2Cl_2]$ to give, predominantly, $[W(\eta\text{-}$

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[19] (a) Ashby, E. C. *Pure Appl. Chem.* **1980**, *52*, 544–569. (b) Ashby, E. C. *Bull. Soc. Chim. Fr.* **1972**, 2133. (c) Wakefield, B. J. *Organomet. Chem. Rev.* **1966**, *1*, 131–156.

$C_5H_4CH_2CH{=}CH_2)(\eta\text{-}C_5H_5)HBr]$.[1]

It seems reasonable to propose that a similar mechanism accounts for the nucleophilic alkylation of **2** by $(CH_3)_3SiCH_2MgCl$ in the presence of $MgCl_2$ to give **9**, but exo nucleophilic addition to cyclopentadienyl ligands is not as well established for *neutral* tungstenocene complexes as it is for the *cationic* complex $[W(\eta\text{-}C_5H_5)_2(SMe_2)Br]^+$,[13a] (although Norton has reported that $Na[AlD_2(OCH_2CH_2OCH_3)_2]$ reduces $[W(\eta\text{-}C_5H_5)_2(OCOPh)(CH_3)]$ to $[W(\eta\text{-}C_5H_4D)(\eta\text{-}C_5H_5)(CH_3)H]$[20]). We have, therefore, considered alternative possibilities, such as initial alkylation at tungsten followed by magnesium halide induced migration of the $(CH_3)_3SiCH_2$ group to the cyclopentadienyl ligand. This seemed unlikely, since the regiospecific migration[21] would lead to an endo-alkylated cyclopentadiene ligand that would have to subsequently lose an exo-hydride, and we also have established experimentally that **8** (which would be closely related to any tungsten alkylated intermediate) is stable to added $MgCl_2$ under the experimental conditions. This argues against initial alkylation at tungsten followed by magnesium dihalide induced migration to the ring.

A second possibility is that migration of a $(CH_3)_3SiCH_2$ ligand from W to the cyclopentadienyl ligand is induced by metalation of the ring by excess Grignard, in a reaction similar to those reported recently in the Fp system by Berryhill[22] and Pannell[23] and in a Re system by Gladysz.[24] This would imply that the hydride in **9** originates from the ethanol used to quench the reaction. We do not have experimental data excluding this possibility, but we feel that a mechanism involving exo addition of the (trimethylsilyl)methyl anion to the cyclopentadienyl ligand of **2** is more probable and allows a simple explanation of the ability of the $MgCl_2$ to enhance the electrophilicity of the ring.[1]

Conclusion

From the present results and our prior report[1] it would appear that the use of alkyllithium reagents favors alkylation of tungstenocene dihalides at the metal, as indicated by formation of **6** and **8** from the reaction of $(CH_3)_3SiCH_2Li$ with **1** and **2**, respectively, while Grignards exhibit a diverse reactivity pattern.

In the case of the allyl complex **1**, for example, the initial site of carbanion addition from $(CH_3)_3SiCH_2MgCl$ would appear to be the free double bond, to give an intermediate that then undergoes a diastereospecific cyclization that eventually lends to the metallacycle **4**. Addition of a methyl substituent to the allyl group of **1** is, however, sufficient to suppress carbomagnesiation of the free double bond and leads to alkylation of **2** at the metal, while addition of $MgCl_2$ to the reaction of $(CH_3)_3SiCH_2MgCl$ with **2** further switches the primary site of alkylation from the metal to the free cyclopentadienyl ring. The implication is that reactions of carbanions with functionalized tungstenocene dihalides are surprisingly diverse but that it is reasonable to anticipate that rational variation of reaction condtions and substituents can be used to target selected zones of reactivity. This should allow the planning and execution of relatively complex multistep syntheses and opens a wide range of synthetic possibilities in this system.

Acknowledgment. We thank the National Science Foundation for financial support through Grant CHE-8722424.

Registry No. **1**, 121524-56-9; **2**, 121524-57-0; **4**, 126541-18-2; **6**, 126502-73-6; **8**, 126502-74-7; **9**, 126502-75-8; $(CH_3)_3SiCH_2Li$, 1822-00-0; $(CH_3)_3SiCH_2MgCl$, 13170-43-9.

Supplementary Material Available: Listings of Cartesian coordinates of conformations of A, B, and C illustrated in Schemes V and VI (9 pages). Ordering information is given on any current masthead page.

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