repulsions and provided the substitution site is not obstructed by the macrocyclic ligand. An interchange mechanism, with appreciable but not dominant bond making to the entering group is inferred for the transition state for substitution at stereochemically unconjested sites in closely related Co(II) and Co(III) complexes with macrocyclic ligands. The aquo–methyl complexes are intermediate in this series, consistent with relatively incomplete transfer of electron density from Co(II) to the alkyl ligand.

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Registry No. [*trans*-Co([14]aneN_4)(OH_2)CH_3](ClO_4)$_2$, 51240-13-2; [*trans*-Co(Me_4[14]tetraeneN_4)(OH_2)CH_3](ClO_4)$_2$, 64942-11-6; [*trans*-Co(Me_4[14]tetraeneN_4)(OH_2)Cl](ClO_4)$_2$, 121675-81-8; [*trans*-Co(*ms*-(*H*)-Me_6[14]dieneN_4)(OH_2)CH_3](ClO_4)$_2$, 39611-20-6; [[*Pri*-CH_3]-*trans*-Co(*rac*-(*N*)-Me_6[14]dieneN_4)(OH_2)CH_3](ClO_4)$_2$, 39756-78-0; [[*Pri*-Cl]-*trans*-Co(*rac*-(*N*)-Me_6[14]dieneN_4)(OH_2)Cl](ClO_4)$_2$, 121701-58-4; [[*Sec*-CH_3]-*trans*-Co(*rac*-(*N*)-Me_6[14]-dieneN_4)(OH_2)-CH_3](ClO_4)$_2$, 121784-60-9; *trans*-Co(dimethylglyoximate)$_2$(OH_2)CH_3), 25360-55-8; [Co(*ms*-(*N*)-Me_6[14]dieneN_4)(OH_2)$_2$](ClO_4)$_2$, 121675-82-9; [Co(*rac*-(*N*)-Me_6[14]dieneN_4)(OH_2)$_2$](ClO_4)$_2$, 121784-62-1.

Supplementary Material Available: Summaries of MM2 input parameters and minimized energies (2 pages). Ordering information is given on any current masthead page.

Magnesium Dihalide Promoted Addition of Grignard Reagents to the Cyclopentadienyl Rings of Tungstenocene Dichloride

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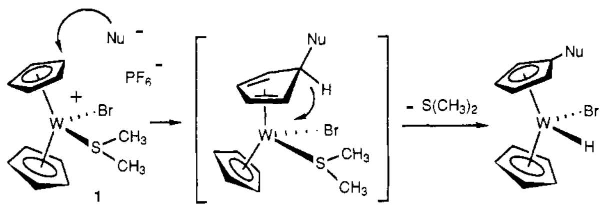
Abstract: Some Grignard reagents, including $CH_2{=}CHCH_2MgCl$, $CH_2{=}C(CH_3)CH_2MgCl$, and $PhCH_2MgCl$, add to a cyclopentadienyl ring of $[W(\eta\text{-}C_5H_5)_2Cl_2]$ (**2**) to give the ring-substituted hydrochlorides $[W(\eta\text{-}C_5H_4CH_2CH{=}CH_2)(\eta\text{-}C_5H_5)HCl]$ (**3**), $[W\{\eta\text{-}C_5H_4CH_2C(CH_3){=}CH_2\}(\eta\text{-}C_5H_5)HCl]$ (**4**), and $[W(\eta\text{-}C_5H_4CH_2Ph)(\eta\text{-}C_5H_5)HCl]$ (**5**). These reactions are promoted by the addition of $MgCl_2$, which is essential for the reproducible synthesis of **3**, **4**, or **5** in good yield. Grignards which react at the metal to give bis-alkyls $[W(\eta\text{-}C_5H_5)_2R_2]$, including CH_3MgCl and $(CH_3)_3SiCH_2MgCl$, were unaffected by added $MgCl_2$. The hydrochlorides **3**, **4**, and **5** can be converted to the corresponding dichlorides $[W(\eta\text{-}C_5H_4CH_2CH{=}CH_2)(\eta\text{-}C_5H_5)Cl_2]$ (**6**), $[W\{\eta\text{-}C_5H_4CH_2C(CH_3){=}CH_2\}(\eta\text{-}C_5H_5)Cl_2]$ (**7**), and $[W(\eta\text{-}C_5H_4CH_2Ph)(\eta\text{-}C_5H_5)Cl_2]$ (**8**) by reaction with CCl_4. Further reaction of **6** with $CH_2{=}CHCH_2MgCl$ in the presence of added $MgCl_2$ leads to substitution of the second cyclopentadienyl ligand and formation of $[W(\eta\text{-}C_5H_4CH_2CH{=}CH_2)_2HCl]$ (**10**). It is proposed that added magnesium dihalides promote Grignard addition to cyclopentadienyl rings of **2** by complexation of an intermediate cyclopentadiene complex. The presence of a double halide bridge in an adduct such as "$[W(\eta^4\text{-}C_5H_4CH_2CH{=}CH_2)(\eta\text{-}C_5H_5)Cl(\mu\text{-}Cl)(\mu\text{-}Br)MgBr]$" would account for the otherwise surprising observation that reaction of **2** with $CH_2{=}CHCH_2MgBr$ leads to predominant (64%) formation of the hydrobromide $[W(\eta\text{-}C_5H_4CH_2CH{=}CH_2)(\eta\text{-}C_5H_5)HBr]$ (**11**), with the hydrochloride **3** as a minor (7%) product.

Since the first report of electrophilic substitution of a cyclopentadienyl ligand of ferrocene under Friedel–Crafts conditions,[1] there has been continuing interest in the preparation of systems in which the cyclopentadienyl ligand carries additional functional groups, and this area is of particular current interest because additional functional groups can be used to incorporate cyclopentadienyl complexes into organometallic materials.[2] As pointed out in a recent review,[3] however, the extension of electrophilic substitution to the preparation of functionalized cyclopentadienyl complexes of other transition metals has been "severely limited in scope" by the relatively narrow range of complexes which are reactive under Freidel–Crafts conditions. Alternative approaches most typically involve functionalization of the cyclopentadienyl ligand prior to its introduction to the metal center,[3] but this has a number of intrinsic limitations, including the inevitable modification of the reactivity of the intermediate cyclopentadienides and the requirement that the new functional group be inert under the conditions required to produce these cyclopentadienides.

We have recently observed that the cyclopentadienyl ring in the tungstenocene complex $[W(\eta\text{-}C_5H_5)_2(SEt_2)Br]^+$ (1^+) is sufficiently electrophilic to undergo substitution reactions of the type shown in eq 1, in which addition of a heteroanion to the cyclopentadienyl ring is followed by hydrogen migration to the metal center.[4] This reaction has enabled us to prepare differentially substituted tungstenocene complexes carrying a chiral substituent



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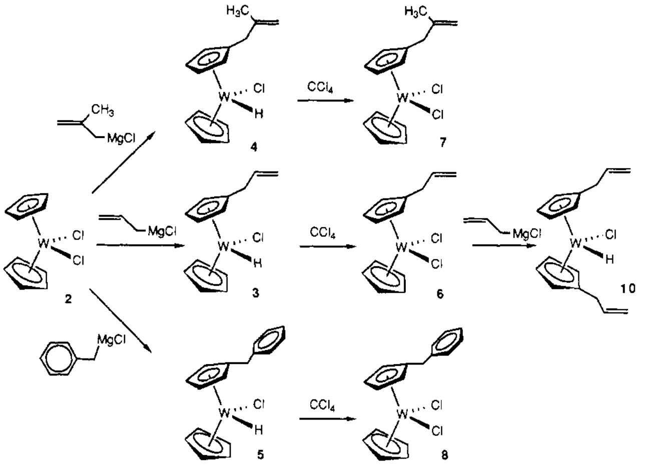
Scheme I. Addition of Grignard Reagents to a Cyclopentadienyl Ring of $[W(\eta\text{-}C_5H_5)_2Cl_2]$



on one of the cyclopentadienyl rings, and these have proved suitable for mechanistic studies of a number of fundamental organometallic reactions.[5] The reaction is, however, limited as a general approach to the preparation of functionalized cyclopentadienyl complexes of tungsten by the multistep synthesis of 1^{+} [6] and by the low and erratic yields observed for the addition of carbon-centered nucleophiles.[4]

The most readily available starting material in the tungstenocene system is the dichloride $[W(\eta\text{-}C_5H_5)_2Cl_2]$ (**2**),[7] and prior reports of the preparation of $[W(\eta\text{-}C_5H_5)_2X_2]$ derivatives from **2**[8] have established that many nucleophilic reagents attack **2** at the metal. Our results, however, together with prior reports of reactions **2** with C_6F_5Li[9a] and with $(Me_3Si)_3SiLi$[9b] which resulted in ring addition, raise the possibility that **2**, which is routinely prepared in our laboratory on a 150-g scale, might more commonly undergo ring substitution reactions with nucleophiles than had been assumed. This has led us to investigate the reactions of **2** with a number of carbon-based nucleophiles, and we now wish to report, as summarized in Scheme I, that **2** will undergo nucleophilic substitution reactions on a cyclopentadienyl ring with some Grignard reagents, and, most surprisingly, that some of these reactions can be promoted by addition of magnesium dihalides.

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. Toluene was distilled from CaH_2. Pentane was 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 and CCl_4 were dried over 3 Å molecular sieves. $MgCl_2$ and $MgBr_2$ were prepared from Mg turnings (Baker) and anhydrous $HgCl_2$ (Aldrich) or $HgBr_2$ (Aldrich).[10] Activity III alumina was prepared by addition of H_2O (60 mL/kg) to activity I Brockman grade alumina (Aldrich). $[W(\eta\text{-}C_5H_5)_2H_2]$ and $[W(\eta\text{-}C_5H_5)_2Cl_2]$ were prepared by the literature method.[7] $[W(\eta\text{-}C_5H_5)_2Br_2]$ was prepared by reaction of $[W(\eta\text{-}C_5H_5)_2H_2]$ in CH_2Cl_2/toluene (1:1) with CBr_4.[11] Grignard reagents were purchased from Aldrich or were prepared from alkyl bromides or chlorides (Aldrich Gold label) and Mg turnings (Baker) in ether or THF and were standardized by titration with ethanol with use of 1,10-phenanthroline indicator.[12] Commercial $(CH_3)_3SiCH_2Li$ was used as received (Aldrich), and $\{(CH_3)_3SiCH_2\}_2Mg$ was prepared by addition of 1.2 equiv of dioxane to a solution of $(CH_3)_3SiCH_2MgCl$ in diethyl ether (Aldrich). The precipitated $MgCl_2$·dioxane was separated by centrifugation.[13] Similar procedures were used to prepare $(CH_2{=}CHCH_2)_2Mg$ and $(PhCH_2)_2Mg$, and $CH_2{=}CHCH_2Li$ was prepared by reduction of $(CH_2{=}CHCH_2)_2Mg$ with Li/Hg.[14]

NMR spectra were recorded on a Bruker WM 300 (^1H 300.10 MHz). Electron impact mass spectra were recorded on a Kratos MS-50 with an ionizing voltage of 70 eV. Microanalysis were performed as indicated by Desert Analytical, Tucson, AZ (Des) or Multichem, Lowell, MA (Mul).

$[W(\eta\text{-}C_5H_4CH_2CH{=}CH_2)(\eta\text{-}C_5H_5)HCl]$ (3). A THF solution of $MgCl_2$ (20.0 mmol in 20 mL) and a THF solution of $CH_2{=}CHCH_2MgCl$ (20.0 mmol in 20 mL) were syringed into a green slurry of $[W(\eta\text{-}C_5H_5)_2Cl_2]$ (4.00 g, 10.31 mmol) in THF (15 mL) to give, after 1.5 h, a dark orange solution. The reaction was quenched at 0 °C with ethanol (15 mL), and the solvent was removed under reduced pressure. The resulting brown-orange residue was extracted with CH_2Cl_2 (8 × 10 mL portions) and filtered through a pad (20 cm) of activity III alumina (for analytical samples this procedure was repeated). After removal of the volatiles from the clear red-brown filtrate, the brown solids were dissolved in ether (minimum volume) and cooled to −78 °C to give brown air-sensitive crystals of $[W(\eta\text{-}C_5H_4CH_2CH{=}CH_2)(\eta\text{-}C_5H_5)HCl]$ (3.22 g, 8.24 mmol ≡ 80%): ^1H NMR (300 MHz, benzene-d_6, geminal, cis and trans coupling constants from narrow band decoupling experiments): δ −11.26 (s, satellites $J_{W-H} = 66$ Hz, 1 H, W-H), 3.06 (d, $J = 6.7$ Hz, 2 H, $\eta\text{-}C_5H_4CH_2$), 3.89, 4.10, 4.20, 4.72 (m, 1 H each, $\eta\text{-}C_5HHHH$), 4.41 (s, 5 H, $\eta\text{-}C_5H_5$), 5.03 (m, $J_{\text{geminal}} = 5.7$ Hz, 1 H, CH=CHH), 5.05 (m, $J_{\text{geminal}} = 5.7$ Hz, 1 H, CH=CHH), 5.90 (m, $J_{\text{cis}} = 11$ Hz, $J_{\text{trans}} = 18$ Hz, 1 H, $CH_2CH{=}CH_2$). Anal. Calcd for $C_{13}H_{15}ClW$: C, 39.98; H, 3.87. Found (Mul): C, 39.75; H, 3.75.

$[W(\eta\text{-}C_5H_4CH_2CH{=}CH_2)(\eta\text{-}C_5H_5)Cl_2]$ (6). A dark red-brown solution of $[W(\eta\text{-}C_5H_4CH_2CH{=}CH_2)(\eta\text{-}C_5H_5)HCl]$ (3.00 g, 7.68 mmol) dissolved in CH_2Cl_2 (10 mL) and ether (15 mL) was treated with CCl_4 (2 mL). As the reaction proceeded, dark green crystals slowly precipitated from solution. After 24 h the solids were filtered off and washed with ether. The dark green microcrystals were shown to be $[W(\eta\text{-}C_5H_4CH_2CH{=}CH_2)(\eta\text{-}C_5H_5)Cl_2]$ (2.66 g, 6.25 mmol ≡ 81%). ^1H NMR (300 MHz, acetone-d_6) δ 3.13 (d, $J = 6.6$ Hz, 2 H, $\eta\text{-}C_5H_4CH_2$), 5.06 (d, $J = 12$ Hz, 1 H, $CH{=}CH_{\text{cis}}H$), 5.08, 5.51 (m, 2 H each, $\eta\text{-}C_5H_2H_2CH_2$), 5.16 (d, $J = 17$ Hz, $CH_2CH{=}CHH_{\text{trans}}$), 5.54 (s, 5 H, $\eta\text{-}C_5H_5$), 5.91 (m, 1 H, $CH{=}CH_2$). Anal. Calcd for $C_{13}H_{14}Cl_2W$: C, 36.74; H, 3.32. Found (Des): C, 36.62; H, 3.08.

$[W\{\eta\text{-}C_5H_4CH_2C(CH_3){=}CH_2\}(\eta\text{-}C_5H_5)HCl]$ (4). A stirred suspension of $[W(\eta\text{-}C_5H_5)_2Cl_2]$ (4.00 g, 10.31 mmol) in THF (15 mL) was treated with THF solutions of $MgCl_2$ (20 mmol in 20 mL) and $CH_2{=}C(CH_3)CH_2MgCl$ (20 mmol in 20 mL) to give, after 1 h, a brown-orange solution. The reaction was quenched with ethanol (15 mL), and the volatiles were removed under reduced pressure. The reaction was worked up as described above for $[W(\eta\text{-}C_5H_4CH_2CH{=}CH_2)(\eta\text{-}C_5H_5)HCl]$. The crude product was recrystallized by slowly cooling an ether solution to precipitate $[W(\eta\text{-}C_5H_4CH_2C(CH_3){=}CH_2\}(\eta\text{-}C_5H_5)HCl]$ (3.50 g, 8.66 mmol ≡ 84%) as brown needles: ^1H NMR (benzene-d_6 300 MHz) δ −11.23 (s, satellites, $J_{W-H} = 66$ Hz, 1 H, W-H), 1.64 (s, 3 H, CH_3), 2.85 (d, $J = 15.8$ Hz, 1 H, $\eta\text{-}C_5H_4CHH$), 3.00 (d, $J = 15.8$ Hz, 1 H, $\eta\text{-}C_5H_4CHH$), 3.91, 4.13, 4.62, 4.77 (m, 1 H each, $\eta\text{-}C_5H_4$), 4.40 (s, 5 H, $\eta\text{-}C_5H_5$), 4.80 (m, 2 H, $C(CH_3){=}CH_2$). Anal. Calcd for $C_{14}H_{17}ClW$: C, 41.59; H, 4.24. Found (Des): C, 41.52; H, 4.22.

$[W\{\eta\text{-}C_5H_4CH_2C(CH_3){=}CH_2\}(\eta\text{-}C_5H_5)Cl_2]$ (7). A dark red-brown solution of $[W\{\eta\text{-}C_5H_4CH_2C(CH_3){=}CH_2\}(\eta\text{-}C_5H_5)HCl]$ (3.00 g, 7.41 mmol) in CH_2Cl_2 (10 mL) and ether (15 mL) was treated with CCl_4 (2 mL) and left undisturbed for 24 h. The long green needles which formed were filtered, washed with ether, and shown to be $[W\{\eta\text{-}C_5H_4CH_2C(CH_3){=}CH_2\}(\eta\text{-}C_5H_5)Cl_2]$ (3.17 g, 7.22 mmol ≡ 97%): ^1H NMR (300 MHz, CD_2Cl_2) δ 1.74 (s, 3 H, $C(CH_3){=}CH_2$), 2.86 (s, 2 H, $\eta\text{-}C_5H_4CH_2$), 5.41–5.33 (m, (overlapping) 4 H, $\eta\text{-}C_5H_4$), 5.21 (s, 5 H,

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η-C_5H_5), 5.50 (m, 2 H, =CH_2). Anal. Calcd for $C_{14}H_{16}Cl_2W$: C, 38.30; H, 3.67. Found (Mul): C, 39.18; H, 3.38.

[W(η-$C_5H_4CH_2Ph$)(η-C_5H_5)HCl] (5). A THF solution of $MgCl_2$ (5.0 mmol in 5 mL) and a THF solution of $PhCH_2MgCl$ (5.0 mmol in 5.0 mL) were syringed into a green slurry of [W(η-C_5H_5)$_2$$Cl_2$] (1.00 g, 2.57 mmol) in THF (10 mL) to give, after 1 h, a red-brown solution. The reaction was quenched with saturated aqueous ammonium chloride at 0 °C, and the THF layer was removed (using a syringe). The aqueous layer was washed with CH_2Cl_2 (3 × 15 mL). The THF and CH_2Cl_2 extracts were filtered (5 cm $MgSO_4$, 5 cm alumina), collected, and concentrated (5 mL). The concentrate was chromatographed (activity III alumina, 2.5 cm × 25 cm column). The column was developed with CH_2Cl_2/pentane (1:2) to give two closely spaced bands. The first (light yellow) was shown, by ^1H NMR, to be a complex mixture of organics. The second broad brown band was collected, and the volatiles were removed to leave a brown oil, which was crystallized (4 days at −78 °C) from ether to give brown platelets of [W(η-$C_5H_4CH_2Ph$)(η-C_5H_5)HCl] (0.65 g, 1.47 mmol ≡ 57%). ^1H NMR (300 MHz, CD_3CN) δ −11.71 (s, satellites, J_{W-H} = 66 Hz, 1 H, W-H), 3.61 (d, J = 15 Hz, 1 H, (η-C_5H_4CHH), 3.76 (d, J = 15 Hz, 1 H, (η-C_5H_4CHH), 4.53, 4.86, 4.93, 5.11 (m, 1 H each, η-C_5H_4), 4.96 (s, 5 H, η-C_5H_5), 7.42 (m, 5 H, C_6H_5). Anal. Calcd for $C_{17}H_{17}ClW$: C, 46.34; H, 3.89. Found (Mul): C, 47.14; H, 3.89.

[W(η-$C_5H_4CH_2Ph$)(η-C_5H_5)Cl_2] (8). A brown solution of [W(η-$C_5H_4CH_2Ph$)(η-C_5H_5)HCl] (0.15 g, 0.34 mmol) dissolved in CH_2Cl_2 (3 mL) and diluted with ether (10 mL) was treated with CCl_4 (4 mL). The reaction was stirred for 1 min and then allowed to precipitate green crystals shown to be [W(η-$C_5H_4CH_2Ph$)(η-C_5H_5)Cl_2] (0.085 g, 0.18 mmol ≡ 53%). ^1H NMR (300 MHz, CD_3CN) δ 3.82 (s, 2 H, η-$C_5H_4CH_2$), 5.09, 5.44 (m, 2 H each, (η-$C_5H_2H_2CH_2$), 5.53 (s, 5 H, (η-C_5H_5), 7.46 (m, 5 H, C_6H_5). Anal. Calcd for $C_{17}H_{16}Cl_2W$: C, 42.98; H, 3.39. Found (Mul): C, 42.77; H, 3.41.

[W(η-C_5H_5)$_2${$CH_2Si(CH_3)_3$}$_2$] (9). I. A solution of [$(CH_3)_3SiCH_2Li$] in hexane (5 mmol in 5 mL) was syringed into a green ether (20 mL) slurry of [W(η-C_5H_5)$_2$$Cl_2$] (0.80 g, 2.08 mmol) to give, after 2 h, a brown-yellow solution. The reaction was quenched with ethanol (5 mL) and filtered (through a 15-cm pad of activity III alumina), and the alumina was washed with CH_2Cl_2 until the filtrate was colorless. The volatiles were evaporated under reduced pressure, leaving a brown residue, which was extracted with hexane and filtered again through alumina (15 cm). Evaporation of the hexane from the filtrates gave brown needles which were shown to be [W(η-C_5H_5)$_2${$CH_2Si(CH_3)_3$}$_2$][15] (0.69 g, 1.41 mmol ≡ 68%) by comparison with the ^1H NMR data in the literature.

II. A solution of [$(CH_3)_3SiCH_2MgCl$] in ether (5 mmol in 5 mL) was syringed into a green ether slurry (20 mL) of [W(η-C_5H_5)$_2$$Cl_2$] (1.50 g, 3.91 mmol) to give, after 2 h, a brown-yellow solution. The reaction was then quenched at 0 °C with water, and the ether layer was filtered through activity III alumina (5 cm, first layer) and $MgSO_4$ (5 cm, second layer). The aqueous layer was washed with CH_2Cl_2 (3 × 20 mL) and filtered as above. After the volatiles were removed, the residue was extracted with hexane and filtered through alumina (10 cm), and the filtrate was concentrated to 15 mL. The brown concentrate was slowly cooled to −78 °C to precipitate brown needles shown (^1H NMR) to be [W(η-C_5H_5)$_2${$CH_2Si(CH_3)_3$}$_2$][15] (1.50 g, 3.08 mmol ≡ 78%).

III. A freshly prepared sample of [{$(CH_3)_3SiCH_2$}$_2$Mg] (10 mmol in 10 mL of ether) was transferred to solid [W(η-C_5H_5)$_2$$Cl_2$] (0.50 g, 1.3 mmol) in a Schlenk tube to give, after 16 h, a red-brown solution. The reaction was quenched at 0 °C with water, and the ether layer was filtered through activity III alumina (5 cm, first layer) and $MgSO_4$ (5 cm, second layer). The aqueous layer was washed with CH_2Cl_2 (3 × 20 mL) and filtrated as above. After the volatiles were removed, the residue was extracted with hexane and filtered through alumina (10 cm), and the filtrate was concentrated to 15 mL. The brown concentrate was slowly cooled to −78 °C to precipitate brown needles, shown (^1H NMR) to be [W(η-C_5H_5)$_2${$CH_2Si(CH_3)_3$}$_2$][15] (0.38 g, 0.79 mmol ≡ 61%).

[W(η-$C_5H_4CH_2CH$=CH_2)$_2$HCl] (10). A green THF solution (25 mL) of [W(η-$C_5H_4CH_2CH$=CH_2)(η-C_5H_5)Cl_2] (500 mg, 1.28 mmol) was treated with THF solutions of CH_2=$CHCH_2MgCl$ (5 mmol in 5 mL) and $MgCl_2$ (5 mmol in 5 mL). After 30 min the red-brown solution was quenched with saturated ammonium chloride at 0 °C, and the THF layer was removed with a syringe. The aqueous layer was washed with CH_2Cl_2 (3 × 15 mL), and the extracts were filtered (5-cm $MgSO_4$ on top of 5-cm alumina), collected, concentrated, and chromatographed on an alumina column (2.5 cm × 25 cm). The column was developed with CH_2Cl_2/pentane (1:2), and two fractions were collected. The first (light yellow) was a complex mixture of organics which was discarded, and the second (a broad brown band) was collected, and the volatiles were removed. The brown residue was dissolved in ether (10 mL) and cooled to −78 °C to give (4 days) brown-yellow crystals which were shown to be [W(η-$C_5H_4CH_2CH$=CH_2)$_2$HCl] (372 mg, 0.86 mmol ≡ 63%). ^1H NMR (300 MHz, benzene-d_6) δ −10.91 (s, satellites J_{W-H} = 68 Hz, 1 H, W-H), 3.08 (d, J = 6.4 Hz, 4 H, η-$C_5H_4CH_2$−), 3.93, 4.07, 4.22, 4.71 (m, 2 H each, η-C_5H_4−), 5.00 (m, 4 H, −CH=CH_2), 5.78 (m, 2 H, −CH=CH_2). Anal. Calcd for $C_{16}H_{19}ClW$: C, 44.63; H, 4.45. Found (Mul): C, 44.55; H, 4.75.

[W(η-$C_5H_4CH_2CH$=CH_2)(η-C_5H_5)HBr] (11). A THF solution of $MgBr_2$ (10.0 mmol in 20 mL) and CH_2=$CHCH_2MgBr$ (10.0 mmol in 10 mL) were transferred to a slurry of [W(η-C_5H_5)$_2$$Br_2$] (1.00 g, 2.11 mmol) in THF (10 mL) to give, after 30 min, a brown solution. The crude reaction product was purified as described above to give dark brown crystals shown to be [W(η-$C_5H_4CH_2CH$=CH_2)(η-C_5H_5)HBr] (0.720 g, 1.64 mmol ≡ 78%) by comparison with an authentic sample (see below).

Reaction of [W(η-C_5H_5)$_2$$Cl_2$] with CH_2=$CHCH_2MgBr$. A green slurry of [W(η-C_5H_5)$_2$$Cl_2$] (0.80 g, 2.07 mmol) in THF (8 mL) was treated with CH_2=$CHCH_2MgBr$ (15.0 mmol in 15 mL of ether) to give, after 1 h, a brown-orange solution. The reaction was quenched with ethanol (15 mL) at 0 °C before the volatiles were removed under reduced pressure. The dark orange oil was extracted with CH_2Cl_2 (5 × 10 mL) and filtered through alumina (20-cm plug), and the combined filtrates were concentrated (ca. 3 mL) and then placed on a second alumina column (2.5 × 25 cm) prepared in ether. The column was developed with 2:3 CH_2Cl_2/ether to give three closely spaced colored bands: fraction I, a yellow oil, was discarded; fraction II, a brown-orange solid was shown to be [W(η-$C_5H_4CH_2CH$=CH_2)(η-C_5H_5)HCl] (0.056 g, 0.14 mmol ≡ 7%); fraction III, a brown-orange solid, was shown to be [W(η-$C_5H_4CH_2CH$=CH_2)(η-C_5H_5)HBr] (0.58 g, 1.33 mmol ≡ 64%): ^1H NMR (300 MHz, benzene-d_6) −11.68 (s, satellites, J_{W-H} = 78 Hz, 1 H, W-H), 3.09 (d, J = 6.4 Hz, 2 H, η-$C_5H_4CH_2$), 4.00, 4.15, 4.36, 4.55 (m, 1 H each, η-C_5H_4), 4.41 (s, 5 H, η-C_5H_5), 4.99 (m, 2 H, CH=CH_2), 5.86 (m, 1 H, CH=CH_2). Anal. Calcd for $C_{13}H_{15}BrW$: C, 35.89; H, 3.48. Found (Mul): C, 35.70; H, 3.47.

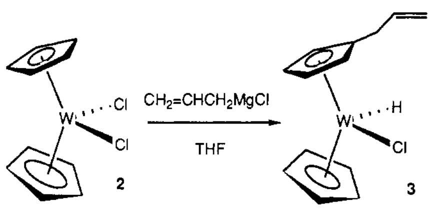
Reaction of [W(η-$C_5H_4CH_2CH$=CH_2)(η-C_5H_5)HCl] with $MgBr_2$. Brown-orange crystals of [W(η-$C_5H_4CH_2CH$=CH_2)(η-C_5H_5)HCl] (0.50 g, 1.28 mmol) were transferred to a clear THF solution of $MgBr_2$ (10 mL, 10.0 mmol). The resulting brown-orange solution was stirred for 48 h without any visible changes. After removal of the THF, the brown solids were extracted with CH_2Cl_2 and filtered (alumina, 20-cm pad). Removal of the CH_2Cl_2 under reduced pressure left a brown solid (0.44 g) corresponding to a 97% recovery of [W(η-$C_5H_4CH_2CH$=CH_2)(η-C_5H_5)HCl] as determined by ^1H NMR.

Reaction of [W(η-C_5H_5)$_2$$Cl_2$] with $MgBr_2$. A green slurry of [W(η-C_5H_5)$_2$$Cl_2$] (0.50 g, 1.30 mmol) in THF (10 mL) was mixed with 4 equiv of $MgBr_2$ in THF (5.2 mmol in 10.4 mL). The mixture was stirred for 4 h, and the green solids were filtered, washed with THF (3 × 20 mL), and vacuum dried. The green powder was shown by ^1H NMR to be [W(η-C_5H_5)$_2$$Cl_2$] by comparison with an authentic sample.

Reaction of [W(η-$C_5H_4CH_2CH$=CH_2)(η-C_5H_5)HCl] with CH_2=$CHCH_2MgBr/MgBr_2$. A red-brown solution of [W(η-$C_5H_4CH_2CH$=CH_2)(η-C_5H_5)HCl] (0.50 g, 1.28 mmol) in THF (10 mL) was mixed with THF solutions of CH_2=$CHCH_2MgBr$ (5 mmol in 5 mL) and $MgBr_2$ (5 mmol in 5 mL). After 1 h there was no observable color change or precipitate formation. The reaction was quenched with ethanol (15 mL) at 0 °C, and the volatiles were removed under reduced pressure at room temperature. The oil was extracted with CH_2Cl_2 (5 × 10 mL), filtered (alumina, 20 cm plug), concentrated (3 mL), and chromatographed (alumina activity III; 2.5 cm × 25 cm column prepared in ether). The column was developed with 2:3 CH_2Cl_2/ether to give two bands: fraction I, yellow band, a complex mixture of organics, was discarded; fraction II, brown band. The brown solids from the second fraction were shown (^1H NMR) to consist of 96% [W(η-C_5H_5)(η-$C_5H_4CH_2CH$=CH_2)HCl] and 4% [W(η-C_5H_5)($C_5H_4CH_2CH$=CH_2)HBr] as determined by integration of the tungsten hydride resonances (0.37 g, 0.95 mmol ≡ 74% recovery).

Results and Discussion

Preliminary experiments established that **2** undergoes more complex reactions than simple halide replacement with a variety of common alkylating reagents, including vinylmagnesium chloride, phenyllithium, and phenylmagnesium chloride, and ^1H NMR indicated that the product mixtures included substituted cyclopentadienyl derivatives. Allylmagnesium chloride gave relatively simple product mixtures, and ^1H NMR indicated that the principal product of the reaction with **2** in THF (eq 2) was the addition product [W(η-$C_5H_4CH_2CH$=CH_2)(η-C_5H_5)HCl] (**3**). Yields were, however, erratic, ranging from 20 to 80% depending on the history of the particular sample of Grignard. The allyl group is a particularly interesting functionality to add to **2** since the unsaturation in the functional group could potentially be used in a



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variety of further reactions, and we therefore decided to focus on optimization of the reaction in eq 2.

It is well-established that the solution structures of Grignard reagents are complex and dependent on the alkyl group, halide, temperature, and solvent.[16] In strongly donating solvents such as THF, however, bromo and chloro Grignard reagents are monomeric at the concentrations used in our experiments,[16h,i] and the Schlenck equilibrium (eq 3) will be the most important

$$2RMgCl \rightleftarrows R_2Mg + MgCl_2 \qquad (3)$$

variable. This raised the possibility that $(CH_2{=}CHCH_2)_2Mg$ might be the true alkylating reagent in the reaction with **2**, but experiments in which **2** was reacted directly with $(CH_2{=}CHCH_2)_2Mg$ resulted in lower yields of **3** (^1H NMR) together with a number of unidentified side products. The reaction of allyllithium with **2** was also disappointing and resulted in complex and intractable reaction mixtures.

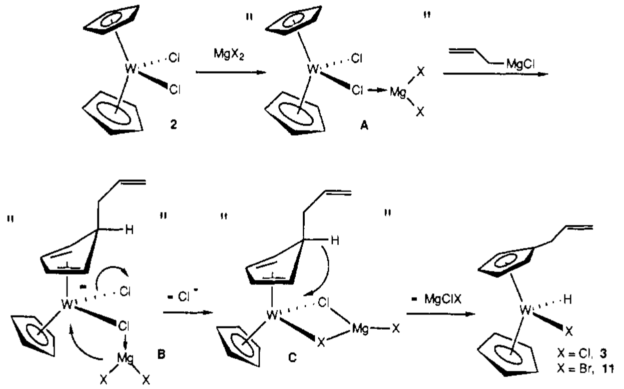
The only consistent pattern in the varying yields for the formation of **3** was that "aged" Grignards, with reduced titers, added more cleanly and in higher yield to **2**. This led us to examine the reaction of **2** with $CH_2{=}CHCH_2MgCl$ in the presence of an equimolar quantity of $MgCl_2$, and we have observed that added $MgCl_2$ results in reproducible alkylation of **2** to **3** in 80% yield. Similar high yield additions of carbanions to a cyclopentadienyl ring of **2** were observed with methallylmagnesium chloride and benzylmagnesium chloride in the presence of equimolar magnesium dichloride to give, respectively, the ring-substituted products $[W\{\eta\text{-}C_5H_4CH_2C(CH_3){=}CH_2\}(\eta\text{-}C_5H_5)HCl]$ (**4**) and $[W(\eta\text{-}C_5H_4CH_2Ph)(\eta\text{-}C_5H_5)HCl]$ (**5**) in good yield. In the case of the reaction of **2** with $PhCH_2MgCl$ it was also confirmed (^1H NMR) that reaction with $(PhCH_2)_2Mg$ alone gave lower yields of **5**, contaminated with other unidentified products.

Our experiments indicate that added magnesium halide is essential to the high yield and reproducible preparation of **3**, **4**, and **5** from **2**, but $MgCl_2$ addition is not a general recipe for the alkylation of a cyclopentadienyl ligand of **2** with Grignard reagents. We have, for example, established that addition of an equivalent of $MgCl_2$ to a mixture of **2** and CH_3MgCl does not have a significant effect on the reported methylation of **2** to $[W(\eta\text{-}C_5H_5)_2(CH_3)_2]$,[8k] and we have also observed, as reported in the Experimental Section, that the known bis-alkyl $[W(\eta\text{-}C_5H_5)_2\{CH_2Si(CH_3)_3\}]_2$[15] (**9**) is the product of the reaction of **2** with many potential sources of the trimethylsilylmethyl anion, including $(CH_3)_3SiCH_2Li$, $(CH_3)_3SiCH_2MgCl$ in diethyl ether, $(CH_3)_3SiCH_2MgCl$ in THF with added $MgCl_2$, and $\{(CH_3)_3SiCH_2\}_2Mg$.

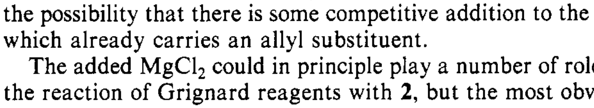
The hydrochlorides **3**, **4**, and **5** are potentially valuable substrates for incorporation in novel inorganic materials, but since much of the chemistry of the tungstenocene system has used the dichloride **2** as a starting material[8] we also confirmed (Scheme I) that these hydrochlorides can be converted in high yield to the corresponding dichlorides $[W(\eta\text{-}C_5H_4CH_2CH{=}CH_2)(\eta\text{-}C_5H_5)Cl_2]$ (**6**), $[W\{\eta\text{-}C_5H_4CH_2C(CH_3){=}CH_2\}(\eta\text{-}C_5H_5)Cl_2]$ (**7**), and $[W(\eta\text{-}C_5H_4CH_2Ph)(\eta\text{-}C_5H_5)Cl_2]$ (**8**) by reaction with CCl_4 in CH_2Cl_2. The dichlorides should prove to be versatile starting materials for development of the chemistry of these functionalized systems and have the added advantage that they are indefinitely air stable in the solid state.

The utility of **6** as a starting material for further synthesis is illustrated by its reaction with allylmagnesium chloride in the presence of added magnesium dichloride, which resulted in the formation of $[W(\eta\text{-}C_5H_4CH_2CH{=}CH_2)_2HCl]$ (**10**). In light of the reaction of **2** with allylmagnesium chloride, it is not surprising that we see no evidence in this reaction for allylation of **6** at the metal center, but the moderate yield does not allow us to rule out the possibility that there is some competitive addition to the ring which already carries an allyl substituent.

Scheme II. Possible Role of Added Magnesium Halide in Promotion of Grignard Addition to a Cyclopentadienyl Ring of $[W(\eta\text{-}C_5H_5)_2Cl_2]$



The added $MgCl_2$ could in principle play a number of roles in the reaction of Grignard reagents with **2**, but the most obvious of these seem unlikely to produce the observed effect on the course of the reaction. The addition of $MgCl_2$ should, for example, drive the Schlenk equilibrium (eq 3) from the magnesium dialkyl toward the Grignard itself, but this should not significantly increase the yields of ring-substituted products since the reactions were carried out with an excess of the Grignard and the Schlenck equilibrium is rapid in THF.[16k,l] It is also unlikely that the role of the $MgCl_2$ is to modify the reactivity of the Grignard by formation of a halide-bridged adduct of the RMg_2X_3 type, since ^1H and ^{25}Mg NMR studies rule out the possibility of such equilibria in THF solutions of $CH_2{=}CHCH_2MgCl$ and $PhCH_2MgCl$.[16l,m] The added magnesium dihalide might, finally, facillitate the reaction by Lewis acid complexation of the relatively electron-rich transition-metal center in **2** or by formation of a π complex with the cyclopentadienyl ring, but neither of these possibilities could easily account for the observation that the reaction of **2** with $CH_2{=}CHCH_2MgBr$ resulted in formation of a mixture in which **3** was the minor product and $[W(\eta\text{-}C_5H_4CH_2CH{=}CH_2)(\eta\text{-}C_5H_5)HBr]$ (**11**) was the major product (eq 4).



(4)

The isolated yields of **3** and **11** were 7 and 64%, respectively, after separation by chromatography on alumina, and the identity of **11** was confirmed by independent synthesis from the reaction of $[W(\eta\text{-}C_5H_5)_2Br_2]$ (**12**) with $CH_2{=}CHCH_2MgBr$.

Control experiments established that this surprising metathesis of bromide for chloride did not result from reaction of **2** with $MgBr_2$ and that $MgBr_2$ did not induce metathesis of **3** in the

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presence or absence of $CH_2{=}CHCH_2MgBr$, suggesting that the added $MgBr_2$ had an active role in the addition reaction. One possibility, as outlined in Scheme II, is that chloride loss from an intermediate cyclopentadiene complex such as B is facilitated by the ability of a magnesium dihalide to stabilize a potentially unsaturated intermediate as shown in C. The double halide bridge in C could result in halide exchange concurrent with hydrogen migration from the cyclopentadiene ligand to the metal to give **11**. We have no direct evidence for initial magnesium halide complexation of **2**, but Lewis acid complexation of a chloride in **2** to form A would be a natural first step in the sequence and should enhance the electrophilicity of the cyclopentadienyl ligand.

Conclusion

The results above establish that the nucleophilic alkyls in some Grignard reagents can be induced to add cleanly and in high yield to a cyclopentadienyl ligand in $[W(\eta\text{-}C_5H_5)_2Cl_2]$. These reactions offer convenient access to tungstenocene derivatives containing functionalized cyclopentadienyl ligands and suggest that the potential of nucleophilic alkylation as an approach to the functionalization of cyclopentadienyl ligands should be explored in other systems. Further experiments along these lines, and exploring the factors controlling the regioselectivity of a variety of nucleophiles with **2**, are underway in our laboratories.

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Registry No. **2**, 12184-26-8; **3**, 121524-53-6; **4**, 121524-54-7; **5**, 121524-55-8; **6**, 121524-56-9; **7**, 121524-57-0; **8**, 121524-58-1; **9**, 61089-07-4; **10**, 121524-59-2; **11**, 121524-60-5; $W(\eta\text{-}C_5H_5)_2Br_2$, 12184-19-9; $CH_2{=}CHCH_2MgCl$, 2622-05-1; $MgCl_2$, 7786-30-3; $PhCH_2MgCl$, 6921-34-2; $(CH_3)_3SiCH_2Li$, 1822-00-0; $(CH_3)_3SiCH_2MgCl$, 13170-43-9; $\{(CH_3)_3SiCH_2\}_2Mg$, 51329-17-0; $CH_2{=}CHCH_2MgBr$, 1730-25-2; $CH_2{=}C(CH_3)CH_2MgCl$, 5674-01-1.

Formation of Metalloheterocycles by Addition of Heteroallenes to the Electron-Rich Carbonyl Complex $[W(\eta\text{-}C_5H_5)_2(CO)]$

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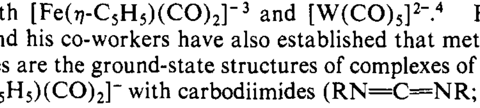
Abstract: The reactions of $[W(\eta\text{-}C_5H_5)_2(CO)]$ (**1**) with a range of heteroallenes establish that four-membered metalloheterocycles can be formed by addition of heteroallenes to an electron-rich neutral carbonyl complex. Metallocycloimides $[W(\eta\text{-}C_5H_5)_2\{C(O)N(R)C(O)\}]$ (**2**, R = CH_3; **3**, R = Ph) are formed by addition of methyl and phenyl isocyanate to **1**, and the metallocycloacylamidine $[W(\eta\text{-}C_5H_5)_2\{C(O)N(Ph)C(NPh)\}]$ (**4**) is formed by addition of diphenylcarbodiimide to **1**. In surprising contrast, addition of phenyl isothiocyanate to **1** leads to formation of a four-membered metalloheterocycle determined by single-crystal X-ray diffraction (R_W = 3.77%) to be the metallocyclothioacylamidine $[W(\eta\text{-}C_5H_5)_2\{C(S)N(Ph)C(NPh)\}]$ (**5**). The complex crystallizes in the monoclinic space group $P2_1/n$ with a = 7.816 (2) Å, b = 19.838 (5) Å, c = 13.066 (3) Å, β = 92.33 (2)°, d_{calcd} = 1.81 g mL^{-1}, Z = 4. It is proposed that initial $S{=}C{=}NPh$ addition to **1** results in ring closure through S to give a metallocycle which eliminates COS (GC) to form an intermediate isonitrile complex. Addition of a second $S{=}C{=}NPh$ with ring closure through N then leads to **5**. There is a fine balance between ring closure through S and N in isothiocyanate addition to **1**, and $S{=}C{=}NCH_3$ forms predominantly the metallocycloacylthioamide $[W(\eta\text{-}C_5H_5)_2\{C(S)N(CH_3)C(O)\}]$ (**8**) in diethyl ether and a mixture of **8** (53%) and the bis adduct $[W(\eta\text{-}C_5H_5)_2\{C(NCH_3)N(CH_3)C(S)\}]$ (**9**) (27%) in pentane.

It is now well-established that coordination of heteroallenes to anionic transition-metal complexes containing carbonyl ligands can result in incorporation of heteroallenes into metalloheterocycles as shown in eq 1. In the case of CO_2, for example, we have



(1)

suggested that the accessibility of metalloanhydrides (X = Y = O) is responsible for the facile scrambling of labeled oxygens between coordinated CO_2 and coordinated CO in η^1-C complexes of CO_2 with $[Fe(\eta\text{-}C_5H_5)(CO)_2]^{-}$[3] and $[W(CO)_5]^{2-}$.[4] Fehlhammer and his co-workers have also established that metalloheterocycles are the ground-state structures of complexes of salts of $[Fe(\eta\text{-}C_5H_5)(CO)_2]^-$ with carbodiimides ($RN{=}C{=}NR$; R = *i*-Pr, *t*-Bu, C_6H_{11}, Ph)[5] and ketenimines ($R_2C{=}C{=}NR'$; R = Ph, R′ = CH_3; R = CH_3, R′ = Ph)[6] and that the η^1-C complex of the isothiocyanate CH_3NCS with $Na[Fe(\eta\text{-}C_5H_5)(CO)_2]$ is in equilibrium with the metalloheterocycle $Na[Fe(\eta\text{-}C_5H_5)(CO)\{C(S)N(CH_3)C(O)\}]$.[7]

Fehlhammer's results suggested that, under some circumstances, the addition of CO_2 to CO complexes might lead to the formation of isolable metalloanhydride complexes analogous to those which we had proposed as reactive intermediates, and this has led us to further examine the reactivity of CO_2 and other heteroallenes with electron-rich carbonyl complexes. We were particularly interested in the possibility that metalloheterocycles might be more stable if they were formed by the addition of heteroallenes to a CO complex which, although nucleophilic, was not anionic, and the tungsten complex $[W(\eta\text{-}C_5H_5)_2(CO)]$ (**1**)[8] was a promising

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