Summary and Conclusions

The polyoxoanion $P_2W_{15}Nb_3O_{62}^{9-}$ was designed to provide three adjacent, B-type, edge-sharing NbO_6 octahedra as a C_{3v} symmetry site for support of organometallic moieties and, eventually, for catalytic studies. Work in this paper describes the synthesis and characterization of the previously unknown $H_4P_4W_{30}Nb_6O_{123}^{12-}$ as its Me_4N^+ salt or its organic-solvent-soluble Bu_4N^+ salt. In addition, deprotonation/cleavage of $(Bu_4N)_{12}H_4P_4W_{30}Nb_6O_{123}$ to $(Bu_4N)_9P_2W_{15}Nb_3O_{62}$ without decomposition has been demonstrated. Furthermore, two inner-sphere, regiospecifically attached, and covalently bonded organometallic derivatives, $(Bu_4N)_7[(C_5Me_5)Rh{\cdot}P_2W_{15}Nb_3O_{62}]$ and $(Bu_4N)_7[(C_6H_6)Ru{-}P_2W_{15}Nb_3O_{62}]$, have been synthesized and characterized in solution by a variety of spectroscopic techniques. These derivatives have C_{3v} symmetry. Efforts at the nontrivial task of producing crystalline salts of them for X-ray diffraction structural analysis are continuing.[8a,b]

Other studies with the $P_2W_{15}Nb_3O_{62}^{9-}$ polyoxoanion-support systems are in progress, notably the isolation and characterization of the catalyst precursor $\{(COD)Ir{\cdot}P_2W_{15}Nb_3O_{62}^{8-}\}_x$ and hydrogenolysis of its coordinated 1,5-COD to produce an interesting polyoxoanion-supported catalyst. These and other studies will be reported in due course.

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Registry No. $K_7HNb_6O_{19}$, 92762-45-3; Nb_2O_5, 1313-96-8; KOH, 1310-58-3; $Na_{12}P_2W_{15}O_{56}$, 84750-84-5; α-$K_6P_2W_{18}O_{62}$, 93240-37-0; $Na_{12}P_2W_{15}O_{56}{\cdot}18H_2O$, 114714-81-7; $(Me_4N)_{12}H_4P_4W_{30}Nb_6O_{123}$, 114594-66-0; $(Bu_4N)_{12}H_4P_4W_{30}Nb_6O_{123}$, 114594-65-9; $(Bu_4N)_9P_2W_{15}Nb_3O_{62}$, 114691-26-8; $(DBU{\cdot}H)_9P_2W_{15}Nb_3O_{62}{\cdot}11H_2O$, 114672-71-8; $(Bu_4N)_7[(C_5Me_5)Rh{\cdot}P_2W_{15}Nb_3O_{62}]$, 114594-64-8; $[Rh(C_5Me_5)Cl_2]_2$, 12354-85-7; $(Bu_4N)_7[(C_6H_6)Ru{\cdot}P_2W_{15}Nb_3O_{62}]$, 114594-63-7; $[Ru(C_6H_6)Cl_2]_2$, 37366-09-9; ^{183}W, 14265-81-7.

Supplementary Material Available: Spectrophotometric titration of $(Bu_4N)_{12}H_4P_4W_{30}Nb_6O_{123}$ with aqueous Bu_4NOH while the IR absorbances were monitored at 665, 800, 905, and 955 cm^{-1} (Figure A); plot of ln A vs r^2 (from ultracentrifugation molecular weight determinations) for $Li_{9-x}H_xP_2W_{15}Nb_3O_{62}$ (Figure B), for $(Bu_4N)_{12}H_4P_4W_{30}Nb_6O_{123}$ (Figure C), for the $P_2W_{15}Nb_3O_{62}^{9-} \rightleftharpoons 2H_2O + P_4W_{30}Nb_6O_{123}^{16-}$ equilibrium formed when H_2SO_4 is added (Figure D), for $(Bu_4N)_9P_2W_{15}Nb_3O_{62}$ (Figure H), and for $(Bu_4N)_7[(C_5Me_5)Rh{\cdot}P_2W_{15}Nb_3O_{62}]$ (Figure I); ^{183}W NMR spectrum and ^{31}P NMR spectrum (inset) of $(Bu_4N)_{12}H_4P_4W_{30}Nb_6O_{123}$ in dry acetonitrile (Figure E); successive ^{31}P NMR spectra of a dry acetonitrile solution $(Bu_4N)_{12}H_4P_4W_{30}Nb_6O_{123}$ after addition of 0–4 equiv of pyridine (Figure F); and ^{183}W and ^{31}P NMR spectra of $(Bu_4N)_{12}H_4P_4W_{30}Nb_6O_{123}$ plus 10 equiv H_2SO_4 in dry CD_3CN (Figure G) (9 pages). Ordering information is given on any current masthead page.

Mechanism of the Conversion of Intermediate 16-Electron Tungstenocene Alkyls into Alkene Hydrides and Fluxionality within $[W(\eta\text{-}C_5H_5)_2(CH_2{=}CHCH_3)H]PF_6$

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$[W(\eta\text{-}C_5H_5)_2(\text{propene})H,D]^+$ (1^+-d_n) has been prepared from $[W(\eta\text{-}C_5H_5)_2Cl_2]$ and $(CD_3)_2CHMgBr$ to determine whether β-elimination within 16-electron tungstenocene alkyls can occur by an α-elimination/1,2-hydride shift mechanism. The complex isotopic distribution within the product arises from a combination of intermolecular exchanges during the workup and intramolecular scrambling reactions. Protonation of $[W(\eta\text{-}C_5H_5)_2(CD_2{=}CDCD_3)]$ has been used to monitor the latter. Spin population transfer (spt) studies have established magnetization transfer from the hydride into the propene methyne in 1^+-endo and into the methylene in 1^+-exo, consistent with rapid reversible insertion of the propene into the W–H bond in both isomers. E_a for insertion in 1^+-endo is 24.4 (7) kcal mol^{-1} with $\Delta H^\ddagger$ = 23.7 (7) kcal mol^{-1} and $\Delta S^\ddagger$ = 11.5 (1.8) eu (k_1 = 0.694 (18) s^{-1} at 79 °C). Insertion in 1^+-exo proceeds at ca. $^1/_6$ this rate with k_1 = 0.112 (25) s^{-1} at 79 °C. The absence of spt from the hydride into the exo methyl of 1^+-exo indicates that the methyl groups in the isopropyl intermediate do not exchange on the spt time scale, probably as a result of an agostic interaction between the methyl group formed in the insertion and the unsaturated metal center. Difference spt experiments on 1^+-endo indicate that reversible α-elimination/1,2-hydride shift processes, if they occur, must have a rate <2% of the observed insertion/β-elimination process. Photolysis of $[W(\eta\text{-}C_5H_5)_2(CH_2CH_2CH_3)(NCCH_3)]PF_6$ led to exclusive formation of 1^+-endo (>99%) and free CH_3CN, indicating that transient $[W(\eta\text{-}C_5H_5)_2(CH_2CH_2CH_3)]^+$ leads specifically to the isomer of 1^+ predicted by the β-elimination mechanism. Similarly, β-elimination within transient $[W(\eta\text{-}C_5H_5)_2\{CH(CH_3)_2\}]^+$, generated by chloride abstraction from $[W(\eta\text{-}C_5H_5)_2\{CH(CH_3)_2\}Cl]$, led exclusively to 1^+-exo. The interconversion of 1^+-endo and 1^+-exo, followed by ^1H NMR from both directions, occurs by a first-order reversible reaction with k_2 and k_{-2} of 0.102 (4) and 0.139 (5) h^{-1}, respectively, at 25 °C and E_a = 22.4 (0.4) kcal/mol, $\Delta H^\ddagger$ = 21.8 (0.4) kcal/mol, and $\Delta S^\ddagger$ = −2.4 (1.2) eu for the conversion of 1^+-endo to 1^+-exo. The isomerization is suggested to involve alkene rotation.

Introduction

Coordinatively unsaturated transition-metal alkyls are typically unstable and may undergo α-, β-, or γ-elimination reactions to generate alkylidene, alkene, or metallocyclic ligands respectively.[3] β-Elimination is much the best established of these processes,[4] and it is generally accepted

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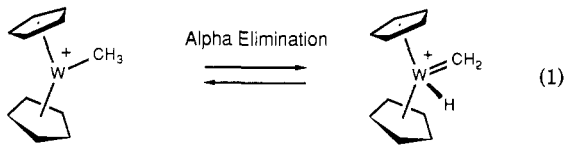
that, with few exceptions,[5] coordinatively unsaturated transition-metal alkyls in which the alkyl ligand carries an accessible β-hydride undergo β-elimination in preference to other conceivable decomposition reactions.

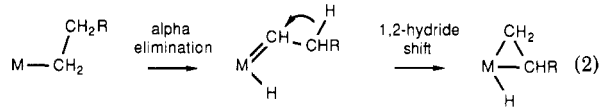
There are also, however, several examples of α-elimination reactions[6] which give alkylidene hydride complexes,[4b,5,8] and the reaction is particularly well-established as a characteristic reaction of 16-electron cationic alkyl complexes of tungstenocene (eq 1).[9] Alpha-elimination can



(1)

occur in tungstenocene complexes even in the presence of β-hydrides, as established by our recent observation that the alkene in $[W(\eta\text{-}C_5H_5)_2(CH_2{=}CH_2)H]^+$ can be converted into an alkylidene ligand by insertion of the alkene into the metal hydride bond and subsequent α-elimination.[10] Even in this system, however, it is assumed that β-elimination, if feasible, will occur in preference to α-elimination.

It has been generally assumed that the preference for β-elimination is essentially kinetic, but recent reports that cationic alkylidene complexes of iron undergo 1,2-hydride shifts under very mild conditions to generate alkene complexes[11,12] raise the possibility that interconversion of alkylidene and alkene ligands can be rapid and that the preference may be thermodynamic in origin. If alkylidene complexes were generally unstable with respect to alkene complexes and 1,2-hydride shifts were generally facile, this would account for the paucity of alkylidene complexes with β-hydrogens and would raise the possibility that overall β-elimination in some systems involves initial α-elimination followed by a 1,2-hydride shift (eq 2).



(2)

The importance of β-elimination as a fundamental mechanistic step in organometallic chemistry, and as a key step in some industrially important catalytic reactions,[13] has led us to explore the possibility that overall β-elimination in cationic tungstenocene alkyls occurs as shown in eq 2. There are three reasons why such a mechanism is particularly plausible in this system:

(1) α-Elimination is well-established in such systems[9] and can become part of the preferred reaction pathway, even if the alkyl carries a β-hydrogen, if the reaction is driven by subsequent halogenation of the metal hydride.[10]

(2) Preferential abstraction of an α-hydrogen from $[W(\eta\text{-}C_5H_5)_2(CH_2CH_3)_2]^+$ by trityl radical establishes that α-C–H bond breaking can be important in this system even in the presence of β-hydrogens.[14]

(3) The contrast between the facility of 1,2-hydride shift reactions in $[Fe(\eta\text{-}C_5H_5)(CO)_2\{C(CH_3)_2\}]^+$[11a,b] and the relative stability of $[Mn(\eta\text{-}C_5H_5)(CO)_2\{C(CH_3)_2\}]$[15] suggests that, not unreasonably, 1,2-hydride shifts may be facilitated by the electrophilic nature of the unsaturated carbon in *cationic* alkylidene complexes.

The only factor that might not favor an α-elimination/1,2-hydride mechanism in this system is that the alkylidene ligand would probably adopt the electronically preferred orientation[16] perpendicular to the plane between the cyclopentadienyl ligands in the intermediate alkylidene complex, as established experimentally for several isoelectronic Ta complexes,[17] and that this geometry might limit the participation of the metal in the subsequent 1,2-hydride shift.

In practice the reactions involved in the conversion of cationic tungstenocene alkyls into alkene hydrides are

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(6) The term α-elimination is also sometimes applied to the α-hydride abstraction reaction which Schrock has used to prepare an extensive range of alkylidene complexes of the group 5 and 6 metals from d^0 precursors.[7] This concerted reaction is more common than α-elimination to an alkylidene hydride complex, but the reactions are mechanistically distinct and α-hydride abstraction will not be discussed in this paper.

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complex, and our studies have led to a detailed examination of the fluxional processes within $[W(\eta\text{-}C_5H_5)_2(CH_3CH{=}CH_2)H]^+$. Our results complement the elegant study by Doherty and Bercaw of insertion within $[Nb(\eta\text{-}C_5Me_5)_2RCH{=}CH_2)H]$ complexes[18] and indicate that while *exo*- and *endo*-$[W(\eta\text{-}C_5H_5)_2(CH_3CH{=}CH_2)H]^+$ are involved in rapid insertion/β-elimination, base-catalyzed deprotonation/protonation, and alkene rotation equilibria, it is unlikely that they are formed by α-elimination/1,2-hydride shift mechanisms.

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 was freshly distilled from Na/benzophenone ketyl. 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 $LiAlH_4$. Acetonitrile was distilled from CaH_2 under a $CaSO_4$ drying tube. Reagent grade acetone, pyridine, ethanol, and chloroform were dried over 3-Å molecular sieves. Deuterium oxide (Aldrich Gold Label, 99.8 atom %) was used as received.

$[W(\eta\text{-}C_5H_5)_2Cl_2]$ and $[W(\eta\text{-}C_5H_5)_2H_2]$ were prepared by the literature method.[19] Grignard reagents were prepared from alkyl bromides (Aldrich Gold Label) and sublimed Mg (Alfa) in diethyl ether[20] and were standardized by titration with ethanol using 1,10-phenanthroline indicator. The 99.8 atom % $(CD_3)_2CO$ and 99.2 atom % $(CD_3)_2CDOD$ were used as supplied by MSD Isotopes.

NMR spectra were recorded on Bruker AM300 (^1H 300.10 MHz, ^{13}C 75.5 MHz), Bruker AM500 (^1H 500.13 MHz, ^{13}C 125.8 MHz), JEOL 270 (^1H 270 MHz, ^{13}C 67.5 MHz), and Varian CFT-20 (^1H 80 MHz) spectrometers. Infrared spectra were recorded on a Perkin-Elmer 683 spectrophotometer and calibrated by using the 1601 cm^{-1} absorption of polystyrene. Electron-impact mass spectra were recorded on an AEI MS-9 with an ionizing voltage of 40 eV. Photolyses were performed by using a 75-W sunlamp or a 450-W Hanovia medium pressure Hg arc lamp in a water-cooled jacket. Microanalyses were performed as indicated by Schwarzkopf Microanalytical Laboratory, Woodside, NY (Sch) or Galbraith Laboratories, Knoxville, TN (Gal).

The Arrhenius equation $\ln k = \ln A - E_a/RT$ was used to determine values of A and E_a. $\Delta H^\ddagger$ and $\Delta S^\ddagger$ were calculated from the equations $\Delta H^\ddagger = E_a - RT$ and $\Delta S^\ddagger = R \ln (ehA/k_bT)$.

$(CD_3)_2CHMgBr$. A solution of $(CD_3)_2CO$ (12.0 g, 0.19 mol) in 20 mL of H_2O was added via a dropping funnel over 30 min to a stirred solution of 4.1 g (0.11 mol) of $NaBH_4$ in 70 mL of H_2O in a 150-mL three-neck flask equipped with a reflux column. After 3 h, the alcohol was distilled and then refluxed over CaO for 3 h. Redistillation yielded 10.2 g (0.15 mol ≡ 81%) of $(CD_3)_2CHOH$. The alcohol was converted to the bromide as follows:[21] neat Br_2 (29.5 g, 0.18 mol) was slowly added through a dropping funnel into a 50-mL three-neck round-bottom flask containing $(CD_3)_2CHOH$ (10.2 g, 0.15 mol) and phosphorus (1.3 g of red + 0.88 g of yellow, 70 mmol). The mixture was heated in a 90 °C oil bath for 3 h and then distilled. The light yellow liquid that distilled below 145 °C was washed with 3 mL of 5% NaOH solution (0 °C) and 2 × 3 mL of H_2O (0 °C). The organic layer was redistilled from $CaCl_2$ to give 10.4 g (81 mmol ≡ 54%) of $(CD_3)_2CHBr$. The bromide was converted into 33 mL of $(CD_3)_2CHMgBr$ in diethyl ether (2.0 M ≡ 83%).

The isotopic purity of the Grignard was determined by conversion to 1-(1-naphthyl)-2-methyl-1-propanol-d_6 by reaction with 1-naphthaldehyde in diethyl ether and subsequent protonolysis with aqueous NH_4Cl. ^1H NMR of the product indicated >98 atom % D in the methyl groups.

$(CD_3)_2CDMgBr$. A procedure similar to that used to prepare $(CD_3)_2CHBr$ was used to convert $(CD_3)_2CDOD$ (10.0 g, 0.15 mol) into $(CD_3)_2CDBr$ (10.7 g, 82 mmol ≡ 55%). Conversion to the Grignard derivative yielded 40 mL of $(CD_3)_2CDMgBr$ in diethyl ether (1.6 M ≡ 80%). Formation of 1-(1-naphthyl)-2-methyl-1-propanol-d_7 and analysis by ^1H NMR indicated <1% incorporation of ^1H in the Grignard.

$(CH_3)_2CHOTs$. On the basis of a general procedure for the synthesis of tosylates,[22] reaction of $(CH_3)_2CHOH$ (2.4 g, 40 mmol) with TsCl (12.8 g, 68 mmol) in 40 mL of pyridine afforded 7.3 g (34 mmol ≡ 85%) of $(CH_3)_2CHOTs$ as a white crystalline solid (melting point approximately 25 °C). Purity and structure were confirmed by IR and ^1H NMR.

$[W(\eta\text{-}C_5H_5)_2(CH_3CH{=}CH_2)H]PF_6$ (1-PF_6) and Partially Deuteriated Derivatives. Compound 1-PF_6 was prepared as an equilibrium mixture of the exo and endo isomers by reaction of $[W(\eta\text{-}C_5H_5)_2Cl_2]$ with either *i*-PrMgBr or *n*-PrMgBr (yields from the two reagents were similar) by procedures similar to those previously described.[23,24] In a typical preparation, 20 mL of $(CH_3)_2CHMgBr$ in diethyl ether (54 mmol) was slowly syringed into a stirred suspension of $[W(\eta\text{-}C_5H_5)_2Cl_2]$ (3.0 g, 7.8 mmol) in 100 mL of toluene to give, after 12 h, a bright orange solution over pale tan solids. The solvent was removed under vacuum and 10 mL of EtOH added at −196 °C. The vessel was warmed to room temperature, and the volatiles were removed under vacuum. The orange-brown residue was extracted with 100 mL of H_2O and filtered through a pad of Celite 545 on a medium-porosity 5-cm glass frit. Immediate addition of 1 g of NH_4PF_6 to the light brown solution yielded a flocculent tan precipitate of 1-PF_6 which was collected by filtration, washed with 3 × 50 mL of H_2O, and dried under vacuum for 6 h. Crystallization from acetone/H_2O afforded 1.40 g (2.8 mmol ≡ 38%) of spectroscopically pure 1-PF_6 as a 4:3 mixture of the endo and exo isomers (^1H NMR). The identity of 1-PF_6 was confirmed by comparison with an authentic sample (^1H NMR and IR). ^1H NMR ($(CD_3)_2CO$, 500 MHz): 1^+-endo, δ 5.62 (d, 5 H, J = 0.6 Hz, η-C_5H_5), 5.55 (d, 5 H, J = 0.6 Hz, η-C_5H_5), 3.00 (d of d of d of q, 1 H, J = 13.6, 10.3, 1.1, 6.4 Hz, CH_2CHCH_3), 2.21 (d of d, 1 H, J = 10.3, 4.4 Hz, $CHHCHCH_3$-trans), 2.03 (d, 3 H, J = 6.4 Hz, CH_2CHCH_3), 1.73 (d of d, 1 H, J = 13.6, 4.4 Hz, $CHHCHCH_3$-cis), −7.01 (s, 1 H, satellites $J_{W\text{-}H}$ = 54 Hz, W-*H*); 1^+-exo, δ 5.55 (d, 5 H, J = 0.6 Hz, η-C_5H_5), 5.49 (d, 5 H, J = 0.6 Hz, η-C_5H_5), 2.68 (d of d of q, 1 H, J = 13.4, 10.5, 6.5 Hz, CH_2CHCH_3), 2.06 (d of d of d, 1 H, J = 10.5, 5.5, 1.6 Hz, $CHHCHCH_3$-trans), 1.93 (d, 3 H, J = 6.5 Hz, CH_2CHCH_3), 1.59 (d of d of d, 1 H, J = 13.4, 5.5, 1.4 Hz, $CHHCHCH_3$-cis), −7.11 (s, 1 H, satellites $J_{W\text{-}H}$ = 46 Hz, W-*H*). ^{13}C NMR ($(CD_3)_2CO$, 67.5 MHz): both isomers, δ 90.80 (d of quin, J = 187, 6 Hz, η-C_5H_5-endo), 90.45 (d of quin, J = 187, 6 Hz, η-C_5H_5-exo), 89.94 (d of quin, J = 187, 6 Hz, η-C_5H_5-endo), 89.53 (d of quin, J = 185, 6 Hz, η-C_5H_5-exo), 35.76 (d of d, J = 150, 4 Hz, CH_2CHCH_3-endo), 31.04 (d, J = 126 Hz, CH_2CHCH_3-exo), 24.38 (q, J = 126 Hz, CH_2CHCH_3-endo), 23.27 (t, J = 160 Hz, CH_2CHCH_3-endo), 21.65 (q, J = 127 Hz, CH_2CHCH_3-exo), 13.64 (t, J = 158 Hz, CH_2CHCH_3-exo).

Partially deuteriated derivatives of 1-PF_6 were prepared from $[W(\eta\text{-}C_5H_5)_2Cl_2]$ by reaction with $(CD_3)_2CHMgBr$ in diethyl ether in a procedure similar to that used to prepare the protio complex. A workup using EtOH and H_2O (as in the case of the protio material) resulted in the formation of material with ^1H NMR resonances assigned to the propene ligand and the metal hydride that integrated as 1.9 ± 0.2 protons relative to the resonances assigned to the 10 cyclopentadienyl protons, indicating that the material was predominantly 1-d_5-PF_6. The use of D_2O to quench the reaction mixture (in place of ethanol) and to extract the crude halide salt (in place of H_2O) resulted in formation of material with ^1H NMR resonances assigned to the propene ligand and the metal hydride that integrated as 1.1 ± 0.2 protons relative to the res-

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(24) Hayes, J. C. Ph.D. Thesis, Harvard University.

onances assigned to the 10 cyclopentadienyl protons, indicating that the material was predominantly 1-d_6-PF_6. The isotope distributions in these partially deuterated materials are described in the Results and Discussion.

[W(η-C_5H_5)$_2$(CD_3CD=CD_2)D]PF_6 (1-d_7-PF_6). A slurry of [W(η-C_5H_5)$_2$$Cl_2$] (0.30 g, 0.78 mmol) in toluene (100 mL) was treated with 2.5 mL of $(CD_3)_2CDMgBr$ in diethyl ether (4.0 mmol) in a procedure similar to that used to prepare 1-PF_6. The mixture was quenched with D_2O, and the crude halide salt was extracted with D_2O before addition of NH_4PF_6 to give 1-PF_6 in 36% yield (0.14 g, 0.28 mmol) after recrystallization. ^1H NMR showed no integrable resonances in the alkene or metal hydride regions.

[W(η-C_5H_5)$_2$(CH_3CH=CH_2)] (2) and [W(η-C_5H_5)$_2$-(CD_3CD=CD_2)] (2-d_6). The propene hydride 1-PF_6 was deprotonated by the procedure of Benfield and Green[23] to give [W(η-C_5H_5)$_2$(CH_3CH=CH_2)] (2) in 78% recrystallized yield. Mass spectrum, parent ion (^{184}W): m/e 356. A similar procedure beginning with 1-d_7-PF_6 gave 2-d_6, as established by ^1H NMR spectra that contained no integrable resonances in the alkene region. Mass spectrum, parent ion (^{184}W): m/e 362.

Protonation of 2-d_6 with HPF_6. A magnetically stirred solution of 2-d_6 in 15 mL of toluene was treated with 15 mL of HPF_6 in H_2O (Alfa, 1 M) to give a two-phase mixture which began to precipitate an off-white flocculent solid within a few seconds. After 10 min, the solids were collected by filtration, washed with toluene (2 × 15 mL), and dried under vacuum for 8 h. Confirmation of the primary formation of 1-d_6-PF_6 as [W(η-C_5H_5)$_2$-(CD_3CD=CD_2)H]PF_6, and observation of subsequent proton migrations, was accomplished by ^1H NMR.

Protonation of 2-d_6 with CF_3COOH. In a typical NMR experiment 2-d_6 (10 mg, 0.03 mmol) was dissolved in 0.5 mL of acetone-d_6 in a 5-mm NMR tube in the glovebox. CF_3COOH (2 μL, 0.03 mmol) was injected into the solution and the tube capped and shaken to decolorize the initial orange solution and give [W(η-C_5H_5)$_2$(CD_3CD=CD_2)H]$^+$ (^1H NMR). Subsequent migration of the proton was monitored by ^1H NMR.

[W(η-C_5H_5)$_2$($CH_2CH_2CH_3$)($NCCH_3$)]PF_6 (3-PF_6). An equilibrium mixture of endo and exo isomers of 1-PF_6 (0.250 g, 0.498 mmol) was dissolved in 20 mL of triply distilled CH_3CN. During the following 24 h, the color of the solution changed from pale yellow to a deep red brown. The solvent was then removed under vacuum and the material redissolved in acetone. Analytically pure [W(η-C_5H_5)$_2$($CH_2CH_2CH_3$)($NCCH_3$)]PF_6 (3PF_6, 0.240 g, 0.442 mmol ≡ 89%) precipitated as deep red needles after this solution was diluted with an equal volume of diethyl ether which was diffused into the reaction vessel over a period of 1 week at atmospheric pressure and room temperature. ^1H NMR ($(CD_3)_2CO$, 300 MHz): δ 5.37 (s, 10 H, η-C_5H_5), 2.82 (s, 3 H, $NCCH_3$), 1.43 (m, 2 H, $CH_2CH_2CH_3$), 0.85 (m, 5 H, $CH_2CH_2CH_3$). $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$, 125.8 MHz): δ 92.19 (η-C_5H_5), 32.04 (CH_3CN), 20.85 ($CH_2CH_2CH_3$), 4.89 ($CH_2CH_2CH_3$), -3.23 ($CH_2CH_2CH_3$). Anal. Calcd for $C_{15}H_{20}F_6NPW$: C, 33.17; H, 3.71. Found (Sch): C, 33.34; H, 3.64.

[W(η-C_5H_5)$_2${CH(CH_3)$_2$}H] (4). [W(η-C_5H_5)$_2H_2$] (2.0 g, 6.3 mmol) was converted into [{W(η-C_5H_5)$_2$HLi}$_4$] by using the literature procedure,[25] in which n-BuLi in hexanes (Aldrich; 2.0 mL, 6.8 mmol) is added to the dihydride to precipitate [{W(η-C_5H_5)$_2$HLi}$_4$] as yellow crystals (2 h). The collected and washed solids were suspended in toluene (120 mL) and cooled to -78 °C, and $(CH_3)_2CHOTs$ (1.35 g, 6.3 mmol) in precooled toluene (20 mL) was added over a period of 5 min. The slurry was slowly warmed to room temperature and stirred for 12 h to give an orange-yellow solution over a gray precipitate. The solution was collected by filtration and the solvent removed under vacuum to leave slightly oily orange yellow crystals of [W(η-C_5H_5)$_2${CH(CH_3)$_2$}H] (4). The crude product was used directly in subsequent reactions, but analytically pure 4 could be obtained by fractional precipitation of [W(η-C_5H_5)$_2H_2$] and $(CH_3)_2CHOTs$ from pentane at -80 °C and subsequent recrystallization of the product from a concentrated pentane solution at -80 °C and then from ethanol at -80 °C. The yield of 4 after the fractional precipitation was 0.46 g (1.3 mmol ≡ 21%; ca. 95% spectroscopically pure with [W(η-C_5H_5)$_2H_2$] as the principal impurity). IR (KBr, selected): 1898 (s br, ν_{M-H}) cm^{-1}. ^1H NMR (C_6D_6, 300 MHz): δ 4.21 (s, 10 H, η-C_5H_5), 1.96 (septet, 1 H, J = 7.2 Hz, $CH(CH_3)_2$), 1.60 (d, 6 H, J = 7.2 Hz, $CH(CH_3)_2$), -10.38 (s, 1 H, satellites J_{W-H} = 94 Hz, W-H). ^{13}C NMR (C_6D_6, 125.8 MHz): δ 79.28 (d of quin, J = 180, 7.5 Hz, η-C_5H_5), 35.12 (q, J = 121 Hz, $CH(CH_3)_2$), -12.65 (d, J = 121 Hz, $CH(CH_3)_2$). Mass spectrum, parent ion: overlapping W isotope envelopes at m/e 358 and 357 (^{184}W; 85:15). Anal. Calcd for $C_{13}H_{18}W$: C, 43.60; H, 5.07. Found (Gal): C, 43.46; H, 5.12.

Complex 4 decomposes rapidly upon exposure to air in solution (seconds) and in the solid state (minutes). It is also thermally unstable as evidenced by a gradual darkening of the crystals over a period of days in an inert atmosphere at room temperature. Decomposition is arrested if the solid is stored at -80 °C.

[W(η-C_5H_5)$_2${CH(CH_3)$_2$}Cl] (5). Crude 4 (0.42 g, 1.1 mmol) was dissolved in 50 mL of $CHCl_3$. Over a period of 30 min, the clear orange-yellow solution became a deep burgundy red. The volatiles were removed under vacuum to give a dark red-brown slightly oily crystalline solid. Recrystallization from diethyl ether by slow vacuum removal of solvent afforded dark red crystals (needles and plates) of [W(η-C_5H_5)$_2${CH(CH_3)$_2$}Cl] (5) (0.39 g, 0.99 mmol ≡ 90%). ^1H NMR ($(CD_3)_2CO$, 300 MHz): δ 4.94 (s, 10 H, η-C_5H_5), 1.97 (septet, 1 H, J = 7.0 Hz, $CH(CH_3)_2$), 1.29 (d, 6 H, J = 7.0 Hz, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$, 75.5 MHz): δ 92.14 (η-C_5H_5), 30.52 ($CH(CH_3)_2$), -6.85 ($CH(CH_3)_2$). Anal. Calcd for $C_{13}H_{17}ClW$: C, 39.77; H, 4.36. Found (Sch): C, 39.89; H, 4.50.

***endo*-[W(η-C_5H_5)$_2$(CH_3CH=CH_2)H]PF_6 (1-endo-PF_6).** In a typical bulk preparation, a 10-mL acetone solution of 3-PF_6 (0.250 g, 0.460 mmol) in a 25-mL Schlenk tube equipped with a stir bar was placed in a -20 °C cold bath (dry ice/i-PrOH). Irradiation of the stirred solution with a sunlamp for 2 h resulted in a color change from deep red-brown to pale yellow. The volatiles were removed under vacuum at 0 °C to give an essentially quantitative yield of 1-PF_6 in an isomeric ratio of 93% 1-endo-PF_6 to 7% 1-exo-PF_6 (^1H NMR). The product was either used directly or after rapid precipitation (<5 min) from a saturated acetone solution (10 mL) with diethyl ether (20 mL).

Photolysis of an NMR tube sample of 3-PF_6 in acetone-d_6 with a medium-pressure Hg arc lamp for 10 min resulted in exclusive formation of 1-endo-PF_6 (>99%). Nonequilibrium isomeric mixtures of 1-PF_6 were stored under N_2 at -80 °C to avoid isomerization.

***exo*-[W(η-C_5H_5)$_2$(CH_3CH=CH_2)H]PF_6 (1-exo-PF_6).** Compound 5 (0.110 g, 0.280 mmol) was dissolved in 25 mL of acetone. Excess $TlPF_6$ (ca. 300 mg) was added and the brown suspension stirred for 20 min. After the mixture had settled, the pale tan solution was separated from the white solids by filtration. Solvent was removed under vacuum and the residue extracted with 10 mL of acetone and filtered to give a clear yellow-brown solution which became cloudy on standing. Rapid addition of 30 mL of diethyl ether precipitated 1-exo-PF_6 as a pale yellow solid that was collected by filtration and dried under vacuum (total time in solution approximately 30 min). Tl impurities prevented an accurate yield determination, but ^1H NMR showed no other significant cyclopentadienyl-containing products and an isomeric ratio of 90% 1^+-exo to 10% 1^+-endo.

An NMR tube reaction between 5 (5 mg, 0.01 mmol) and $TlPF_6$ (5 mg, 0.02 mmol) was conducted by loading the two reactants into a 5-mm tube and then adding 0.5 mL of acetone-d_6. The tube was capped and shaken for 1 min. The solids were centrifuged to the top of the tube to leave a faintly cloudy tan solution. A ^1H NMR spectrum of the fresh solution showed the almost exclusive presence of the exo isomer of 1^+ with <2% 1^+-endo.

Kinetics of the Isomerization of 1^+ in Solution. Isomerization of 1^+ was monitored by observation of (500-MHz ^1H NMR) the independent conversion of 1^+-endo and 1^+-exo to the equilibrium mixture. Reaction temperatures were maintained by the temperature controller of the Bruker AM500 and were calibrated by means of a Cu–constantan thermocouple inserted into an NMR tube containing 0.5 mL of toluene and lowered into the probe. Temperatures were found to be constant within ±0.5 °C for the range studied (21–54 °C). In a typical experiment a sample of one isomer of 1-PF_6 in acetone-d_6 would be sealed under vacuum in a 5-mm NMR tube and stored at -80 °C until the beginning of the experiment. Concentrations of 1^+-endo and 1^+-exo were monitored by integration of the nonoverlapping cyclopentadienyl

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resonances (see Figure 1). In all cases, the total concentration of 1^+—as conveniently determined by integration of the two overlapping cyclopentadienyl resonances of the endo and exo isomers in the absolute intensity scaling mode of the DISNMR software package[26]—was unchanged throughout the experiment. Reactions were followed to equilibrium, but only data sufficiently far from equilibrium to have acceptable errors for the quantities $\{[1^+\text{-endo,exo}](t) - [1^+\text{-endo,exo}](\text{equil})\}$ were used in calculations. This typically permitted usable data to be acquired for 4–5 half-lives. The rate equations $\ln \{[1^+\text{-endo,exo}](t) - [1^+\text{-endo,exo}](\text{equil})\} = -(k_2 + k_{-2})t + \ln \{[1^+\text{-endo,exo}](t = 0) - [1^+\text{-endo,exo}](\text{equil})\}$ were derived on the assumption of first-order reversible kinetics. The equilibrium constant $K = k_2/k_{-2}$ determined during each experiment, together with a non-weighted least-squares analysis of the fit of the data to the appropriate rate equation, gave values of k_2 and k_{-2}.

Spin Population Transfer (spt) within 1^+. Spin population transfer within 1^+-exo and 1^+-endo was monitored at 500 MHz by established procedures.[18,27] Reaction temperatures were controlled and monitored as described above and were stable to ±1 °C within the range studied (64–91 °C). In a typical experiment 40 mg of 1-PF_6 (0.08 mmol) in acetone-d_6 in a partially evacuated, sealed NMR tube was equilibrated in the spectrometer at the reaction temperature for at least 30 min. Decoupler-power and pulse width settings were optimized to produce a 180° pulse for the resonance whose migration was to be monitored. A microprogram based on standard software commands[26] was used to invert the target resonance and irradiate the sample with a $\pi/2$ observation pulse after a time delay τ. Twenty delay intervals between 0 and 20 s were used in a random sequence to minimize systematic errors. Both the inverted resonance and any exchanging resonances were monitored by integration relative to a nonexchanging peak. No decomposition of 1^+ was observed during the typical 4 h of data collection per experiment at temperatures up to 90 °C. Temperatures above 90 °C led to gradual degradation, and the exchange rate was too slow to monitor below 64 °C.

The data were analyzed by a three-parameter nonlinear least-squares fit of the population of the noninverted exchanging resonance(s) as a function of delay time τ to the magnetization equations[28] using a modified version of a Simplex curve fitting program[30] on an IBM PC. The optimized values of T_{1a}, T_{1b}, and

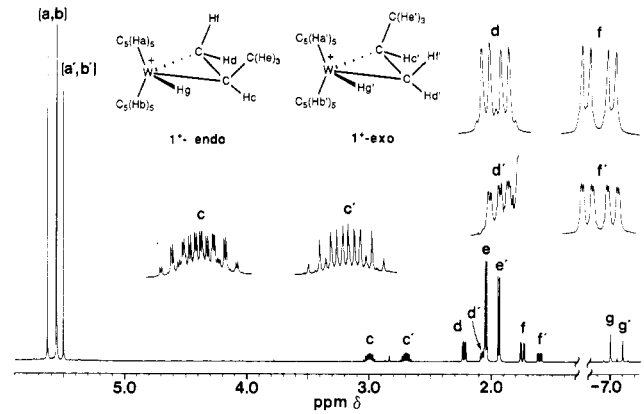
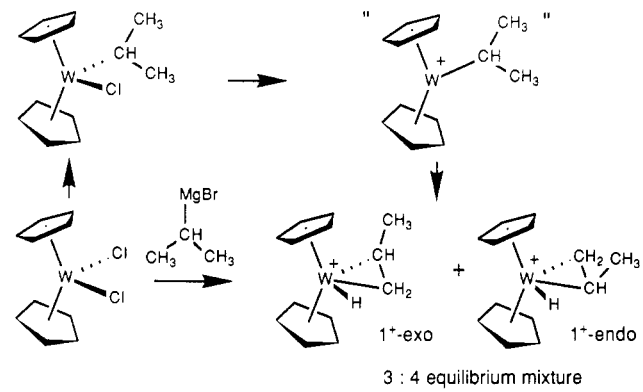
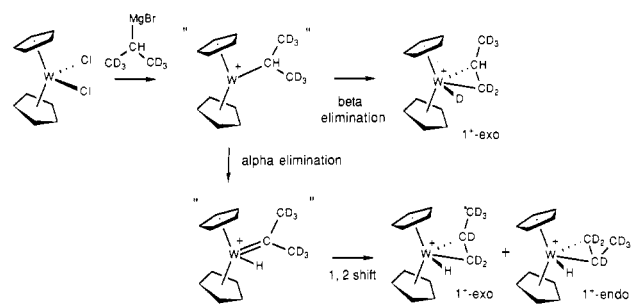


Figure 1. ^1H NMR spectrum of $[W(\eta\text{-}C_5H_5)_2(CH_3CH{=}CH_2)H]PF_6$ at 500 MHz in $(CD_3)_2CO$.

Scheme I. Probable Mechanism for the Formation of $[W(\eta\text{-}C_5H_5)_2(CH_3CH{=}CH_2)H]^+$ from $[W(\eta\text{-}C_5H_5)_2Cl_2]$



Scheme II. Labeling Study To Distinguish Direct β-Elimination from α-Elimination Followed by a 1,2-Hydride Shift



$k_{exchange}$ converged in less than 200 iterations in all cases and were found to be independent of starting guesses used by the Simplex algorithm. No NOE enhancement was observed for any of the exchanging resonances upon inversion of either an olefin or hydride peak at 25 °C (all exchange rates are negligible at this temperature).

In magnetization transfer experiments involving the irradiation of either the endo methyne or hydride resonances it was impossible to separate the T_1 values for the two sites, the independent parameters T_{1a} and T_{1b} invariably optimizing at identical values. This can be explained at least in part by noting $k_{exchange} \geq 1/T_1$ for most of these experiments. As the exchange rate becomes faster than spin–lattice relaxation, information about the individual relaxation rates is lost and the two T_1's approach an averaged value.[31] For the insertion reaction of the exo isomer, $k_{exchange} \ll 1/T_1(\text{av})$ and T_{1a} and T_{1b} converged to discrete values.

Error Analysis. Errors in $\Delta H^\ddagger$, $\Delta S^\ddagger$, E_a, A, and k_1 represent one standard deviation calculated from the propagation of one

(26) *DISNMRP, Version 830701.2*; Bruker Instruments Inc.: Billerica, MA, 1984.

(27) (a) Forsen, S.; Hoffman, R. A. *J. Chem. Phys.* **1963**, *11*, 2892–2901. (b) Sandstrom, J. *Dynamic NMR Spectroscopy*; Academic: London, England, 1982; Chapter 4 and references therein. (c) Campbell, I. D.; Dobson, C. M.; Ratcliffe, R. G.; Williams, R. J. P. *J. Magn. Reson.* **1978**, *29*, 397–417.

(28) For a first-order exchange process between two sites[29]

$$A \underset{k_B}{\overset{k_A}{\rightleftharpoons}} B$$

$$M_A^*(t) = \frac{M_A^\infty - M_A^0}{\lambda_1 - \lambda_2}[(\lambda_2 + k_{1A})e^{\lambda_1 t} - (\lambda_1 + k_{1A})e^{\lambda_2 t}] + M_A^\infty \quad \text{(a)}$$

$$M_B(t) = \frac{(M_A^\infty - M_A^0)k_A}{\lambda_1 - \lambda_2}[e^{\lambda_2 t} - e^{\lambda_1 t}] + M_B^\infty \quad \text{(b)}$$

where

$$\lambda_1 = \tfrac{1}{2}\{-(k_{1A} + k_{1B}) + [(k_{1A} - k_{1B})^2 + 4k_Ak_B]^{1/2}\}$$

$$\lambda_2 = \tfrac{1}{2}\{-(k_{1A} + k_{1B}) - [(k_{1A} - k_{1B})^2 + 4k_Ak_B]^{1/2}\}$$

$$k_{1A} = 1/T_{1A} + k_A$$

$$k_{1B} = 1/T_{1B} + k_B$$

$M_{A,B}^\infty$ = magnetization at site A,B at $t = \infty$. M_A^0 = magnetization at site A at $t = 0$. $T_{1A,B} = T_1$ for site A,B. The asterisk (*) indicates inverted resonance. No perturbation at site B is assumed at $t = 0$. In this case, since sites A and B are on the same molecule, k_A and k_B are related by a simple statistical factor. In the absence of significant NOE (vide infra), spin population at site B (measured in arbitrary units) can be fitted to the three parameters T_{1a}, T_{1b}, and k_A[27c] as a function of the variable delay τ. Since integrations of the resonances into which exchange was occurring were more accurate, eq b was used to analyze the data. A combination of the two equations (eq a − eq b) did, however, give similar values for k_A.

(29) McConnel, H. M. *J. Chem. Phys.* **1958**, *28*, 430–431.

(30) Caceci, M. S.; Cacheris, W. P. *Byte* **1984**, *9*(5), 340–362.

(31) Led, J. L.; Gesmar, H. *J. Magn. Reson.* **1982**, *49*, 444–463.

standard deviation in the slope and y intercept of the appropriate linear regression analysis generated either from the random variation of the data within its error limits or from an analysis of the residuals of the line. In all cases the errors determined from both methods were similar in magnitude and the larger was used. Concentrations as determined by integration were considered to be accurate within ±5%.

Errors in $k_{exchange}$ were evaluated by allowing the data to vary within its error limits with subsequent optimization of T_{1a}, T_{1b}, and $k_{exchange}$. A total 50 sets of varied data were processed with the Simplex program for each experiment to determine the standard deviations.

Results and Discussion

The principle distinction between direct and indirect β-elimination is the origin of the hydrogen atom transferred to the metal center, and the literature suggested that this could be simply determined in the tungstenocene system. Benfield and Green have reported that reaction of $[W(\eta\text{-}C_5H_5)_2Cl_2]$ with isopropylmagnesium bromide leads to the propene hydride complex $[W(\eta\text{-}C_5H_5)_2(CH_3CH{=}CH_2)H]PF_6$ (1-PF_6) as a mixture of exo and endo isomers,[23] and, although there have been no detailed mechanistic studies, the reaction most reasonably involves initial formation of an alkyl chloride that converts to a 16-electron alkyl cation by halide loss (Scheme I).[32] This suggests that a suitably labeled Grignard reagent would allow the pathway for overall β-elimination to be determined as shown in Scheme II,[33] provided that there were not rapid subsequent scrambling of the labels, and two features of the system suggested that scrambling would not be a significant problem.

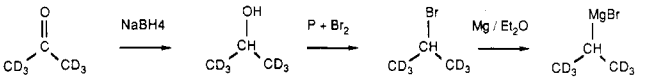
(1) The slow rate of insertion when 1^+ is converted to $[W(\eta\text{-}C_5H_5)_2(PPh_3)(CH_2CH_2CH_3)]^+$ in refluxing acetone implied (assuming a low barrier to association of a donor ligand with a coordinatively unsaturated 16-electron tungstenocene alkyl cation) that insertion/elimination equilibria were unlikely to be rapid.[23]

(2) The observation of distinct resonances from the cyclopentadienyl ligands syn and anti to the methyl substituents in both the exo and endo isomers of 1^+ suggested that alkene rotation, if it occurred, was slow, at least on the NMR time scale.[34]

^{1}H NMR Spectra of $[W(\eta\text{-}C_5H_5)_2(CH_3CH{=}CH_2)H]PF_6$ (1-PF_6). Interpretation of a labeling experiment such as that shown in Scheme II required ^{1}H NMR spectra of 1^+ with significantly better resolution than that available in the previously reported at 100-MHz spectra,[23] but spectra recorded at 500 MHz were amenable to the detailed analysis required for mechanistic studies.

Complex 1^+ (obtained as a 4:3 mixture of isomers) has a low-field spectrum in acetone-d_6 (80 MHz) that contains three singlets in the region characteristic of cyclopentadienyl resonances at δ 5.62, 5.55, and 5.49 which can be assigned to overlapping signals from the two inequivalent cyclopentadienyl resonances of the major isomer and of the minor isomers. In this field a complex and unresolved pattern is observed for the alkene resonances of both isomers between δ 1.5 and 3.5. Two singlets at δ −7.01 and −7.11 with characteristic W satellites (J = 54, 46 Hz)[35] are assigned to the major and minor isomers, respectively.

Scheme III. Preparation of $(CD_3)_2CHMgBr$



At 500 MHz the overlapping C_5H_5 resonances are partially separated and their coupling to the hydrides (J = 0.6 Hz) is observable. At this field strength the alkene region is almost completely resolved and the eight separate resonances can be assigned on the basis of decoupling experiments and computer simulation of all coupling patterns (Figure 1).[26] Identification of 1^+-endo and 1^+-exo as the major and minor isomers was initially based on the assumption that the weak coupling between the hydride and methyne proton (J = 1.1 Hz) in the major isomer and between the hydride and both methylene protons (J = 1.4, 1.6 Hz) in the minor isomer could be assigned to through-space interactions,[36,37] and this interpretation has been subsequently confirmed by the stereospecific preparations of 1^+-endo and 1^+-exo (vide infra). The ^{1}H NMR spectrum of 1^+ in acetone-d_6 was unaffected by temperature changes up to 95 °C or down to −45 °C.

Reaction of $[W(\eta\text{-}C_5H_5)_2Cl_2]$ with $(CD_3)_2CHMgBr$. Monolabeled isopropylmagnesium bromide for the experiment in Scheme II was prepared from acetone-d_6 as shown in Scheme III.

The reaction of $[W(\eta\text{-}C_5H_5)_2Cl_2]$ with the d_6 Grignard reagent was initially carried out in a similar fashion to the preparation of unlabeled 1-PF_6, using EtOH to quench the reaction and H_2O to extract the crude halide salt for counterion exchange. The product obtained contained two protons per molecule (1.9 ± 0.2: ^{1}H NMR of a freshly dissolved sample) in non-cyclopentadienyl ligands, with ca. 90% of these protons evenly distributed between the hydride and methyne positions within the exo and endo isomers[39] and the remaining protons distributed throughout the other alkene resonances of the isomers. Over a period of days the intensities of the resonances assigned to the methylene and methyl peaks of both isomers increased while those of the hydride and methyne resonances decreased. The total integration of alkene and hydride resonances remained unchanged during this period.[40]

It was immediately apparent from these results that the system was more complex than expected. Partial deuteriation of the metal hydride resonance could be accounted for by a combination of the direct and indirect mechanisms for β-elimination (Scheme II), but the presence of two protons per molecule and the formation of material containing protons in *all* of the alkene positions

(32) This scheme is supported, for example, by the isolation of intermediate $[Mo(\eta\text{-}C_5H_5)_2(CH_2CH_3)Cl]$ during formation of $[Mo(\eta\text{-}C_5H_5)_2(C_2H_4)H]^+$ from the reaction of $[Mo(\eta\text{-}C_5H_5)_2Cl_2]$ with $[\{Al(C_2H_5)Cl_2\}_2]$.[23]

(33) There is no obvious steric or electronic reason why a 1,2-hydride shift within a tungstenocene alkylidene hydride should be stereoselective, and we have assumed throughout this paper that tungstenocene alkene hydrides formed by such a reaction would be generated as a mixture of endo and exo isomers.

(34) Together with the initial formation of a mixture of 1^+-endo and 1^+-exo (rather than 1^+-exo alone), this suggested that β-elimination within the isopropyl cation *did* involve a 1,2-hydride shift within an intermediate isopropylidene complex, since simple β-elimination within the isopropyl cation must lead to initial formation of 1^+-exo (Scheme II).

(35) ^{183}W has a natural abundance of 14% and a nuclear spin of $^1/_2$.

(36) This coupling can be partially resolved in the hydride resonances by use of enhanced resolution techniques such as Gaussian multiplication of the FID before transformation.

(37) The small values of these coupling constants, together with the very weak or unobserved coupling of the propene carbons to the hydride (see Experimental Section for ^{13}C NMR data), preclude the possibility of an agostic[38] ground state for 1^+. A similar conclusion was drawn by Bercaw and Doherty in their study of $[Nb(\eta\text{-}C_5H_5)_2(CH_3CHCH_2)H]$.[18]

(38) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395–408.

(39) There was no observable difference in the label levels in the two isomers.

(40) No indication of deuterium incorporation into the cyclopentadienyl positions was found in ^{1}H NMR spectra of partially deuteriated samples of 1^+ or the neutral propene complex. The isotopic envelope of the $[W(\eta\text{-}C_5H_5)_2]$ fragment in mass spectra of the partially deuteriated neutral complex also showed no evidence for deuterium incorporation in any of the experiments described in these studies.

suggested that several low-energy scrambling processes were occurring and that a more detailed study was required.

Proton Exchange during the Preparation of 1-PF_6. The incorporation of two protons during the formation of 1-PF_6 from $(CD_3)_2CHMgBr$ implied intermolecular exchange with a proton source such as the EtOH used to quench excess Grignard or the H_2O used in the extraction. When D_2O was used for both steps, the partially deuteriated product only contained 1.1 ± 0.2 protons, predominantly in the methyne and hydride positions of both isomers. The origin of this proton in the Grignard was confirmed by the preparation of pure 1-d_7-PF_6 from [W(η-C_5H_5)$_2$$Cl_2$] and $(CD_3)_2CDMgBr$ when D_2O was used to quench the reaction and extract the halide salt.

Reversible deprotonation of 1-PF_6 to [W(η-C_5H_5)$_2$(CH_2=$CHCH_3$)] (**2**) is well-established,[41] and H for D exchange can be accounted for by a deprotonation–reprotonation cycle under the basic conditions of the workup of 1-d_n-PF_6. Consistent with this, treatment of an NMR sample of 1-PF_6 with D_2O in acetone-d_6 resulted in a gradual loss of the proton resonances (first in the hydride positions and then throughout the alkene) over a period of months, but addition of several milligrams of NaOD to a similar sample resulted in almost complete disappearance of the tungsten hydride resonances before the ^1H NMR spectrum could be taken (<10 min). Proton signals in the alkene region assigned to both isomers disappeared over a period of several days.

The observation of approximately two protons in the alkene and hydride resonances of 1^+ formed from $(CD_3)_2CHMgBr$ by using an EtOH/H_2O workup, and the predominant formation of 1-d_6-PF_6 upon D_2O workup, suggests that the proton in the d_6 Grignard was retained primarily in the alkene ligand, consistent with direct β-elimination as the primary process of collapse of an intermediate isopropyl complex of tungstenocene.

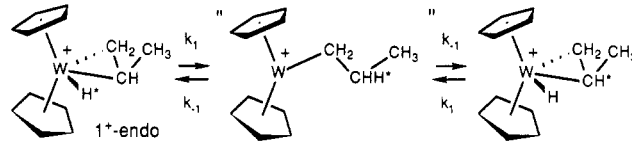
Protonation of [W(η-C_5H_5)$_2$(CD_2=$CDCD_3$)] (2-d_6) and Subsequent Scrambling Processes. Preliminary studies of scrambling within 1^+ were carried out by protonation of 2-d_6 with HPF_6 or CF_3COOH to give [W(η-C_5H_5)$_2$(CD_2=$CDCD_3$)H]$^+$ and monitoring the subsequent reaction by ^1H NMR.[42] Although not amenable to quantitative analysis, these experiments indicated the following.

(1) Protonation of 2-d_6 gave 1-d_6-PF_6 as the same 4:3 mixture of endo and exo isomers obtained from the Grignard reaction.

(2) The ^1H NMR spectrum of the complex 5 min after it was formed by addition of 1 equiv of CF_3COOH to 2-d_6 in acetone-d_6 showed that protonation occurs primarily at the metal center, with ca. 90% of the non-cyclopentadienyl proton integration distributed statistically between the two hydride resonances.

(3) The endo methyne resonance increased, with a concomitant decrease in the endo hydride resonance, over a period of 30 min at room temperature, until the resonances had relative integrated intensities of 1:2.

Scheme IV. Insertion Process Required To Account for Magnetization Transfer within 1^+-Endo



(4) All the alkene resonances gradually increased over the next several hours at the expense of the hydride resonances. The exo methylene peaks grew in most rapidly and had over twice the integrated intensity of any other observable alkene resonance (except the endo methyne) after 3.5 h.

(5) After 2 days the proton was evenly distributed among the vinyl positions in the alkenes of both isomers, but the proton intensity in the methyl resonances was still significantly less than anticipated statistically (for each isomer the methyl resonance integral is approximately twice any one vinyl resonance integral).

(6) After 6 days, the integrated intensity of the methyl resonances had become close to that anticipated statistically (methyl resonance integral/any one vinyl resonance integral = 2.8 ± 0.2 for 1^+-exo and 2.9 ± 0.2 for 1^+-endo).

(7) No further changes were noted after 6 days, and the total integration of the alkene and hydride resonances corresponded to 1.1 ± 0.2 protons.

The final integrated proton distribution for a sample of 1^+-d_6 had nearly twice the statistically anticipated proton intensity in the hydride resonances (relative to the alkene resonances). This is readily interpreted in terms of a thermodynamic preference for the proton to be located at the site of lower zero point energy.[43] Thermodynamic deuterium isotope effects can be calculated for each isomer (eq 3 and 4) as K = 0.48 ± 0.09 for the endo isomer and

$$endo\text{-}[W(\eta\text{-}C_5H_5)_2(CD_2{=}CDCD_3)H]^+ \rightarrow endo\text{-}[W(\eta\text{-}C_5H_5)_2(CD_2{=}CHCD_3)D]^+ \quad (3)$$

$$exo\text{-}[W(\eta\text{-}C_5H_5)_2(CD_2{=}CDCD_3)H]^+ \rightarrow exo\text{-}[W(\eta\text{-}C_5H_5)_2(CDH{=}CDCD_3)D]^+ \quad (4)$$

K = 0.47 ± 0.09 for the exo isomer.[44] This corresponds to $\Delta G°$ = 0.43 ± 0.12 and 0.45 ± 0.11 kcal mol^{-1} at 25 °C for exchange of H from the metal with D from the alkene in 1^+-endo-d_6 and 1^+-exo-d_6, respectively—values which are similar to those found for the isoelectronic niobium complex [Nb(η-C_5Me_5)$_2$(CH_2=CH_2)H]-d_n.[18]

Insertion-Induced Exchanges within 1^+ Observed by Spin Population Transfer. The observed facile scrambling of the metal hydride into the alkene ligand implied that the propene must be reversibly inserting into the W–H bond, a result which was initially surprising given the established propensity of tungstenocene alkene hydrides to undergo only slow, irreversible insertion reactions with nucleophiles such as PPh_3,[23] PMe_2Ph,[24] and halides.[45] This led us to conduct magnetization transfer experiments that might allow observation of the insertion reactions.

Spin population transfer (spt) involves selectively inverting one resonance of the molecule and then, after a specific interval τ, applying a nonselective $\pi/2$ pulse to

(41) Benfield, F. W. S.; Francis, B. R.; Green, M. L. H. *J. Organomet. Chem.* **1972**, *44*, C13–C14.

(42) CF_3COOH protonation was preferred for monitoring the early stages of the exchange since NMR samples could be prepared and observed immediately. Unfortunately, however, conversion of 1^+-d_6 into a new complex characterized by an (η-C_5H_5) singlet at δ 5.12 (most likely [W(η-C_5H_5)$_2$(CH_2CH_3)($OCOCF_3$)]) became significant after 24 h and impaired further study. HPF_6 protonation, although inconvenient for observing exchange within the first 30 min (see Experimental Section), was ideal for studying later stages of the scrambling processes and provided information complementary to the CF_3COOH experiments. ^1H NMR resonances of the alkene hydride are unaffected by the counterion, and exchange rates with both were qualitatively similar.

(43) Lowry, T. H.; Richardson, K. H. *Mechanisms and Theory in Organic Chemistry*, 2nd ed.; Harper & Row: New York, 1981; Chapter 2.

(44) The experimentally determined K value was independent of the methylene hydrogen of the exo isomer chosen as the basis for the calculation.

(45) Miller, G. M.; Cooper, N. J., manuscript in preparation.

Table I. Rates of Exchange Processes Involving the Hydride Ligands in 1^+-Exo and 1^+-Endo As Determined by spt in Acetone-d_6

resonance inverted (A)	resonance exchanging with A (B)	T (°C ± 1.0)	T_{1A} (s)	T_{1B} (s)	$k_{exchange}$ (s^{-1})	k_1 (s^{-1})
1^+-endo hydride	1^+-endo methyne	64.0	10.11	10.11	0.0723 (45)	0.145 (9)
1^+-endo hydride	1^+-endo methyne	68.0	10.13	10.13	0.111 (5)	0.222 (10)
1^+-endo methyne	1^+-endo hydride	68.0	9.98	9.98	0.119 (5)	0.238 (10)
1^+-endo hydride	1^+-endo methyne	73.5	9.59	9.59	0.203 (7)	0.406 (14)
1^+-endo hydride	1^+-endo methyne	79.0	9.13	9.13	0.347 (9)	0.694 (18)
1^+-endo hydride	1^+-endo methyne	84.5	7.69	7.69	0.523 (12)	1.05 (3)
1^+-endo hydride	1^+-endo methyne	90.5	5.13	5.13	1.07 (3)	2.14 (6)
1^+-exo hydride	1^+-exo methylene[a]	79.0	5.09	4.29[b]	0.0744 (170)	0.112 (25)

[a] The two methylene positions are treated as one site with two hydrogens (see text). [b] The T_1 values for the two methylene positions are assumed to be equal (see text).

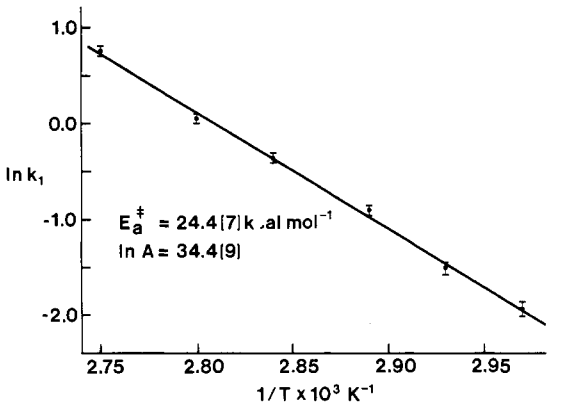


Figure 2. Arrhenius plot for the rate of insertion of the propene into the metal–hydride bond within 1^+-endo as determined by spt.

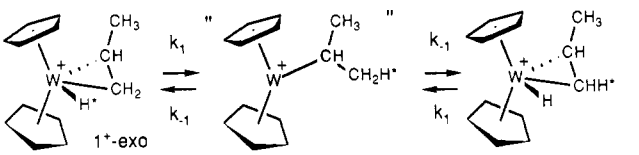
observe the spectrum. Exchange between the irradiated proton (H*) and any other proton (H′) in the molecule will result in a decrease in the observed signal from H′ as its spin population is perturbed by the exchange. This loss of signal can be quantified by integration and can be fitted to the magnetization equations as a function of delay time τ to yield the exchange rate (see Experimental Section).

Irradiation of the hydride resonances of 1^+ resulted in observation of a single exchange process (on the spt time scale of 5–10 s for 1^+) involving the hydride ligands of each isomer of 1^+. The faster of these, which involved exchange between the hydride and the methyne H in 1^+-endo, was most reasonably interpreted in terms of insertion of the propene into the W–H bond to generate an intermediate through which the β-carbon hydrogens become equivalent (Scheme IV). Since magnetization transfer will occur only half of the time, $k_1 = 2k_{exchange}$. The absence of observable insertion products by ^{1}H NMR indicates that $k_{-1} > 100k_1$ in acetone-d_6.

Table I shows the rate constants for this exchange as derived from a nonlinear least-squares fit of the spt data to the magnetization equations over a temperature range of 64–91 °C. Since the hydride resonance is much narrower than the methyne multiplet and is conveniently distant from all other endo peaks, most experiments were conducted by inverting this peak and monitoring the integral of both resonances as a function of the delay interval τ. Inversion of the methyne resonance was found to give equivalent values for T_{1A}, T_{1B}, and $k_{exchange}$ at T = 68 °C. Exchange rates were unaffected over a fivefold change in concentration as anticipated for a unimolecular process.

An Arrhenius plot of the rate data (Figure 2) establishes E_a for this process as 24.4 (7) kcal mol^{-1} with $\Delta H^‡$ = 23.7 (7) kcal mol^{-1} and $\Delta S^‡$ = 11.5 (1.8) eu. Extrapolation using these parameters gives a rate constant of ca. 0.1 min^{-1} at room temperature, consistent with the observation of essentially complete scrambling of H from the metal into the endo methyne position in ca. 30 min upon protonation of **2**-d_6 with CF_3COOH.

Scheme V. Insertion Process Required To Account for Magnetization Transfer within 1^+-Exo

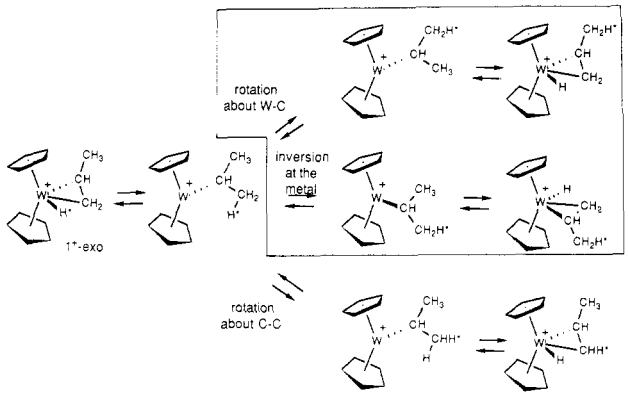


The slower exchange process observed on the spt time scale involved exchange of the hydride resonance of 1^+-exo into both methylene positions. The integrated intensity of the cis and trans methylene resonances of 1^+-exo remained equivalent within experimental error throughout the experiment, and since the T_1 values for the two positions are nearly identical at room temperature (2.2 and 2.3 s for the cis and trans exo methylene resonances, respectively, as measured by standard inversion recovery techniques), it was concluded that exchange was occurring equally into the two sites. This can again be interpreted in terms of an insertion of the propene ligand into the W–H bond to give, in this case, an intermediate isopropyl complex that renders the methylene- and tungsten-bound hydrogens equivalent (Scheme V).

Quantitative analysis of the spt data for 1^+-exo was based on the assumption that the two methylene sites could be treated as one site with two hydrogens; $k_{exchange}$ becomes the observed rate constant for magnetization transfer from the hydride resonance into either methylene resonance and $k_1 = 3/2k_{exchange}$. At 79 °C, k_1 = 0.112 (25) s^{-1} (Table I), ca. $^1/_6$ the rate of the insertion process for the endo isomer at the same temperature. The relatively slow spt exchange in the exo isomer is consistent with the observation in protonation experiments that the hydride in 1^+-d_6 exchanges into the exo methylene positions in several hours at 25 °C, while the hydride exchanges into the endo methyne in ca. 30 min. Activation parameters for exchange in 1^+-exo could not be obtained because of the limited temperature range over which data could be collected without decomposition.

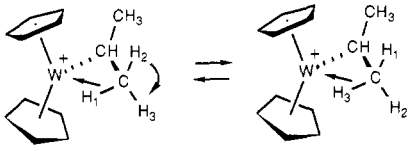
Evidence for Agostic Interactions in Intermediates in the Insertion Reactions. The absence of observable magnetization transfer into the exo methyl resonance upon inversion of the exo hydride is surprising and indicates that the two methyl groups in the isopropyl intermediate *do not exchange* on the spt time scale. The most obvious implications of this (Scheme VI) are that rotation about the W–C bond of the insertion intermediate must be slow and that inversion of the metal center must be slow on the spt time scale. It seems unlikely that the lifetime of the

Scheme VI. Exchange Processes Which Could Follow Insertion within 1^+-Exo[a]



[a] The processes within the box are slow on the spt time scale.

Scheme VII. Turnstyle Rotation within the Agostic Isopropyl Intermediate



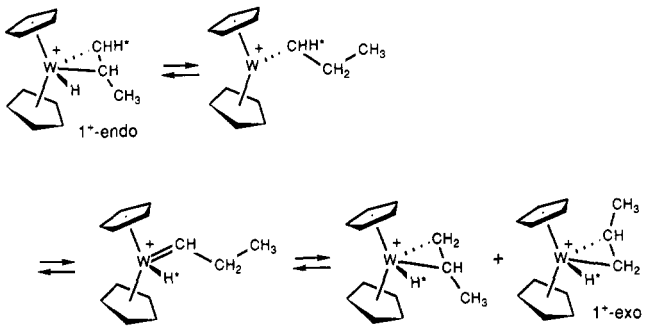
metal alkyl is less than the time necessary for unconstrained rotation about the metal–carbon single bond (ca. 10^{-10} s[46]), since the rotation about the C–C bond which exchanges the hydrogens should be on a similar time scale, and there must therefore be some aspect of the molecular structure that constrains the methyl groups.

It is possible that steric interactions provide the constraining force, but this is unlikely since there is no indication of hindered rotation of the isopropyl group about the metal–carbon bond in $[W(\eta\text{-}C_5H_5)_2\{CH(CH_3)_2\}Cl]$ (**5**), and the cyclopentadienyl resonance of this more congested molecule is a sharp singlet (and the methyl resonance remains a simple doublet) down to −65 °C.[47] A more reasonable explanation is that there is an agostic interaction[38] between the methyl group formed in the insertion reaction and the unsaturated metal center. This would involve coordination of a methyl C–H bond to the metal center and could constrain rotation about the M–C bond and inversion at the metal (an isopropyl "wag" to the enantiomeric structure).

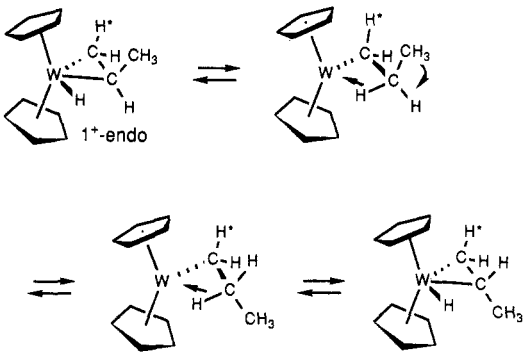
An agostic interaction of this sort would require that turnstyle rotation of the methyl group be facile to account for exchange into the two methylene positions in 1^+-exo (Scheme VII), a process which has been previously established to have a low activation energy in agostic alkyl complexes.[48] The coordinated methyl and free methyl groups must eventually exchange to account for the scrambling into the methyl group observed after protonation of **2**-d_6 (vide supra), but the rate of this process appears to be much slower than the reversible insertion.

If agostic interactions are energetically significant in the isopropyl intermediate in insertion reactions of 1^+-exo, one would also expect significant agostic interactions in the *n*-propyl intermediate in insertion reactions of 1^+-endo. There is, however, no equivalent in 1^+-endo of the marker methyl group in 1^+-exo, although an agostic interaction with the formally unsaturated metal center in an intermediate *n*-propyl complex would provide a steric and electronic rationale for the slow overall insertion reactions of 1^+ with nucleophiles despite what are evidently facile intramolecular insertion processes.

Scheme VIII. Potential α-Elimination/Hydride Shift Mechanism for spt between a Methylene Resonance of 1^+-Endo and Hydride Resonances of 1^+-Endo and 1^+-Exo



Scheme IX. Insertion Mechanism for Magnetization Transfer between Cis and Trans Hydrogens of Methylene Group in 1^+-Endo



The spt Search for α-Elimination Processes within 1^+. The label studies and the spt experiments clearly establish that low-energy insertion/β-elimination sequences account for the predominant exchange processes in this system and imply that an α-elimination/1,2-hydride shift combination does not provide a principal mechanism for the formation of tungstenocene alkene hydrides from the intermediate tungstenocene alkyls. The data do not, however, rule out the possibility that slower α-elimination processes are occurring, and more sensitive spin population transfer experiments utilizing difference spectroscopy were conducted to search for such processes.

In the difference spt experiments, a very small rate of magnetization transfer between two positions in the ligand (which would cause a slight decrease in the nonirradiated peak integral) was progressively enhanced by alternately accumulating the same number of scans with and without peak inversion and subtracting the two FIDs. All resonances that were not involved in an exchange process with the irradiated proton cancelled in the subtraction, while those that were involved in exchanges produced small negative peaks which became more pronounced as the sequence was repeated.

One of the statistically most sensitive difference spt experiments involves selective inversion of a methylene resonance of 1^+-endo. If the intermediate *n*-propyl complex formed upon insertion were ever to collapse through

(46) Lowe, J. P. *Progress in Physical Organic Chemistry*; Streitwieser, A., Jr., Taft, R. W., Eds.; Wiley-Interscience: New York, 1968; Vol. 6, Chapter 1.

(47) Models indicate that the rotational ground state for **5** is unlikely to be a symmetric structure, and the cyclopentadienyl ligands and the methyl groups of the isopropyl moiety should be chemically inequivalent in the absence of rotation.

(48) (a) Cracknell, R. B.; Orpen, A. G.; Spencer, J. L. *J. Chem. Soc., Chem. Commun.* **1984**, 1005–1006. (b) Brookhart, M.; Green, M. L. H.; Pardy, R. B. A. *J. Chem. Soc., Chem. Commun.* **1983**, 691.

an α-elimination/1,2-hydride shift mechanism, selective inversion of one of these resonances would result in magnetization transfer into the hydride region (Scheme VIII).[49] When this experiment was carried out the only observed magnetization transfer was into the trans endo methylene position, consistent with rapid alkene insertion and turnstile rotation (Scheme IX).

Similar difference spt experiments examining the inversion of other alkene resonances indicate that reversible α-elimination/1,2-hydride shift processes, if they occur, must have a rate <2% of the observed insertion/β-elimination process of the endo isomer. It should be noted that these experiments do not, and cannot, rule out the possibility that simple reversible α-elimination is occurring in insertion intermediates of 1^+, as chemically established in closely related systems,[9] since this would not result in any exchange unless it were followed by a 1,2-hydride shift.

Independent Generation of the Intermediate 16-Electron *n*-Propyl and Isopropyl Tungstenocene Alkyls. The experiments above strongly support formation of 1^+ by direct β-elimination from intermediate tungstenocene alkyl cations. If this is the case, 1^+-endo should be specifically and exclusively formed from the *n*-propyl complex $[W(\eta\text{-}C_5H_5)_2(CH_2CH_2CH_3)]^+$, and 1^+-exo should be specifically and exclusively formed from the isopropyl complex $[W(\eta\text{-}C_5H_5)_2\{CH(CH_3)_2\}]^+$.[50] As a final confirmation of the direct β-elimination mechanism in this system, we therefore sought alternate and independent routes to $[W(\eta\text{-}C_5H_5)_2(CH_2CH_2CH_3)]^+$ and $[W(\eta\text{-}C_5H_5)_2\{CH(CH_3)_2\}]^+$.

The exclusive formation of *n*-alkyl derivatives when tungstenocene alkene hydrides react with donor ligands L to give inserted products of the type $[W(\eta\text{-}C_5H_5)_2(n\text{-alkyl})L]^+$ (L = PPh_3,[23] PMe_2Ph,[24] halide[45]) suggested that formation of such a complex with a labile donor ligand could provide an appropriate precursor to $[W(\eta\text{-}C_5H_5)_2(CH_2CH_2CH_3)]^+$. Acetonitrile proved to be a suitable choice for our needs, and $[W(\eta\text{-}C_5H_5)_2(CH_2CH_2CH_3)(NCCH_3)]PF_6$ (**3**-PF_6) was readily prepared by dissolving **1**-PF_6 in CH_3CN and leaving the solution at room temperature for 24 h. Complex **3**-PF_6 could be isolated in high yield (89%) as red-brown needles by recrystallization from CH_3CN/Et_2O and is a particularly convenient precursor to $[W(\eta\text{-}C_5H_5)_2(CH_2CH_2CH_3)]^+$ because the acetonitrile ligand is photolabile.

An NMR tube photolysis of complex $\mathbf{3}^+$ at −40 °C in acetone-d_6 with a medium-pressure mercury arc lamp[51] permitted generation of $[W(\eta\text{-}C_5H_5)_2(CH_2CH_2CH_3)]^+$ which led to exclusive formation of 1^+-endo (>99%) and free CH_3CN as determined by ^1H NMR. This established that transient $[W(\eta\text{-}C_5H_5)_2(CH_2CH_2CH_3)]^+$ does indeed lead specifically to the isomer of 1^+ predicted by the β-elimination mechanism.[52]

Finding an isopropyl derivative of tungstenocene that could be used as precursor of the 16e species $[W(\eta\text{-}C_5H_5)_2\{CH(CH_3)_2\}]^+$ was considerably more challenging than in the *n*-propyl case. As discussed above, reactions of 1^+ with nucleophiles invariably result in the formation of the less sterically encumbered *n*-propyl derivatives, and approaches based on the addition of nucleophilic isopropyl sources (such as Li(isopropyl), MgBr(isopropyl), and Hg(isopropyl)$_2$) to electrophilic tungstenocene centers were unsuccessful. An appropriate precursor to $[W(\eta\text{-}C_5H_5)_2\{CH(CH_3)_2\}]^+$ was finally prepared from the reaction of the strongly nucleophilic $[\{W(\eta\text{-}C_5H_5)_2HLi\}_4]$ (which behaves as if it contains $[W(\eta\text{-}C_5H_5)_2H]^-$)[25] with isopropyl tosylate in toluene to form $[W(\eta\text{-}C_5H_5)_2\{CH(CH_3)_2\}H]$ (**4**) in low yields (21%). Crude samples of **4** were invariably contaminated with $[W(\eta\text{-}C_5H_5)_2H_2]$ (despite rigorous exclusion of potential proton sources such as traces of water), and could only be purified by complex recrystallization procedures (see Experimental Section). Crude **4** could, however, be converted directly to $[W(\eta\text{-}C_5H_5)_2\{CH(CH_3)_2\}Cl]$ (**5**) in good yields (83%, corrected for $[W(\eta\text{-}C_5H_5)_2H_2]$) by reaction with $CHCl_3$. Complex **5** was readily separated from the insoluble $[W(\eta\text{-}C_5H_5)_2Cl_2]$ formed from the $[W(\eta\text{-}C_5H_5)_2H_2]$ under these conditions, and was obtained as analytically pure dark red needles and plates by slow concentration of a diethyl ether solution at room temperature.

The chloride was removed by stirring a slurry of **5** with $TlPF_6$ in acetone. An NMR tube reaction (see Experimental Section) established that this procedure led to exclusive formation of 1^+ as the exo isomer (>98%), demonstrating that transient $[W(\eta\text{-}C_5H_5)_2\{CH(CH_3)_2\}]^+$ does indeed lead specifically to 1^+-exo as predicted by the β-elimination mechanism.

Interconversion of 1^+-Exo and 1^+-Endo without Base Catalysis—Alkene Rotation. A combination of alkene insertion within 1^+-exo and 1^+-endo and a slow exchange of the methyl groups within the isopropyl intermediate by either of the mechanisms in Scheme VI can account for many of the scrambling reactions seen when **2**-d_6 is protonated, but the final achievement of a statistical distribution of the proton within the propene ligand, in particular the appearance of protons in the methyne position in 1^+-exo and the methylene and methyl positions in 1^+-endo, requires that there be a pathway for the conversion of one isomer to the other under neutral or acidic conditions.

Direct observation of the interconversion of 1^+-exo and 1^+-endo was made possible by the preparations of pure 1^+-exo and 1^+-endo described above. The isomerizations, which were complete within 36 h, were followed by ^1H

Table II. Equilibrium and Kinetic Data for Interconversion of 1^+-Exo and 1^+-Endo

starting isomer	T (°C ± 0.5)	K_{eq}[a]	10^5k_2 (s^{-1})	10^5k_{-2} (s^{-1})
		neutral conditions[b]		
exo	21.0	1.34 (7)	1.49 (6)	2.00 (8)
endo	21.0	1.30 (7)	1.52 (8)	1.98 (10)
endo	25.0	1.34 (7)	2.82 (12)	3.78 (16)
endo	30.5	1.35 (7)	5.45 (13)	7.36 (18)
endo	36.0	1.35 (7)	10.6 (1.1)	14.3 (1.5)
endo	41.0	1.38 (7)	20.8 (1.2)	28.7 (1.7)
endo	49.0	1.36 (7)	50.0 (2.3)	68.0 (2.8)
endo	54.0	1.39 (7)	77.7 (6.5)	108.0 (9.0)
		acidic conditions[c]		
endo	21.0	1.33 (7)	1.87 (12)	2.49 (16)
		basic conditions[d]		
endo	21.0	1.35 (7)	>600	>800

[a] K_{eq} is the equilibrium constant for the conversion of 1^+-exo to 1^+-endo and $K_{eq} = k_{-2}/k_{+2}$. [b] In acetone-d_6. [c] In acetone-d_6 with 7 equiv of CF_3COOH. [d] In acetone-d_6 with 10 equiv of NEt_3.

(49) Magnetization transfer into the other vinyl positions of both isomers of 1^+ would also be anticipated from the reaction sequence in Scheme VIII and its reverse (which must be occurring at an equal rate).

(50) This is not at variance with the formation of a mixture of 1-exo-PF_6 and 1-endo-PF_6 from the reaction of $[W(\eta\text{-}C_5H_5)_2Cl_2]$ with *n*-propyl- or isopropylmagnesium bromide (as observed), since the isomers could be equilibrated by the protonation/deprotonation sequences established by the labeling studies.

(51) Slightly higher yields of 1^+ were obtained by using a 75-W sun lamp, but the slower reaction rate led to significant isomerization (see below) and typically gave 95:5 mixtures of the endo and exo isomers.

(52) 1^+-endo can also be generated selectively in a nonphotolytic sequence by reacting $[W(\eta\text{-}C_5H_5)_2(CH_2CH_2CH_3)Cl]$ (formed by heating solutions of 1-PF_6 with LiCl) with $TlPF_6$.

NMR from both directions, and the data were shown to be consistent with analysis as a first-order reversible reaction (see Experimental Section). At 25 °C the first-order rate constants k_2 and k_{-2} determined from the isomerization of 1^+-endo are 0.102 (4) and 0.139 (5) h^{-1}, respectively.[53] The rate constants determined from the separate isomerizations of 1^+-exo and 1^+-endo to equilibrium mixtures at 21 °C were equal within experimental error, and the rates were unaffected by an eightfold change in concentration, consistent with a unimolecular reaction. The rate of isomerization of 1^+-endo to 1^+-exo was determined at a range of temperatures between 21 and 54 °C (Table II), and an Arrhenius plot yielded activation parameters of E_a = 22.4 (0.4) kcal/mol,[54] $\Delta H^\ddagger$ = 21.8 (0.4) kcal/mol, and $\Delta S^\ddagger$ = −2.4 (1.2) eu.

These data established that 1^+-exo and 1^+-endo do interconvert under neutral conditions as anticipated from the protonation studies on 2-d_6, but do not address the mechanism for interconversion. It was conceivable that 1^+ was so acidic that we were still observing base-catalyzed isomerization. This possibility was, however, eliminated by experiments which established that the rate of isomerization of 1^+-endo to 1^+-exo was only slightly influenced by the presence of 7 equiv of CF_3COOH (Table II).[55]

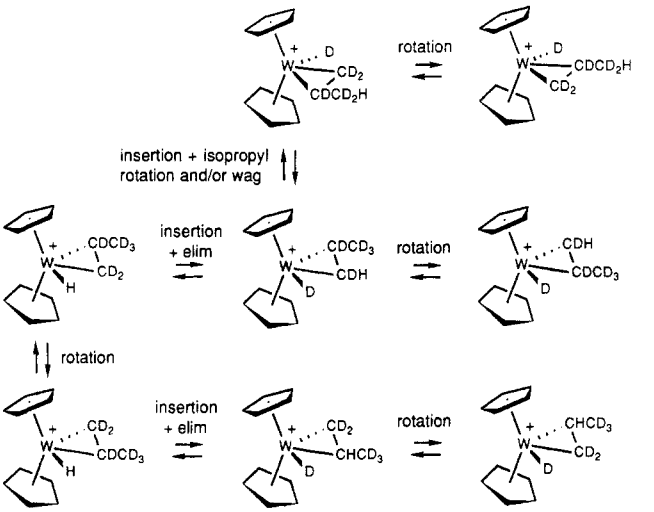
The low value of $\Delta S^\ddagger$ indicates that isomerization is unlikely to involve dissociation of the alkene in the rate-determining step.[43] This conclusion is supported by two further observations: (1) an acetonitrile solution of 1-PF_6 does not form any $[W(\eta\text{-}C_5H_5)_2(NCCH_3)H]PF_6$—a compound known to be stable under these conditions;[56] (2) a solution of 1-PF_6 in acetone under 1 atm of ethylene showed no evidence (^1H NMR) for the formation of $[W(\eta\text{-}C_5H_5)_2(CH_2{=}CH_2)H]PF_6$ after 1 week.

The slow, nondissociative interconversion of 1^+-exo and 1^+-endo under neutral and acidic conditions most reasonably involves slow rotation of the alkene ligand in 1^+, although it is possible to devise schemes involving alkene insertion, α-elimination, and 1,2-hydride shift in a cationic intermediate alkylidene complex that interconvert 1^+-exo and 1^+-endo without alkene rotation.

Interconversion of 1^+-exo and 1^+-endo with Base Catalysis and in the Solid State. Access to pure 1^+-endo and 1^+-exo suggested that it might be feasible to directly determine the rate of the deprotonation–reprotonation process for equilibrating the isomers under basic conditions, and we accordingly added 10 equiv of NEt_3 (which is not a strong enough base to generate observable concentrations of the deprotonated form) to an NMR sample of 1^+-endo. This resulted in complete equilibration of the two isomers before a spectrum could be obtained (<5 min) and established that 10^5k_2 is >600 s^{-1} under these conditions.

There should be relatively little additional barrier to alkene rotation within 1^+ in the solid state, and we have indeed observed that samples of 1-endo-PF_6 and 1-exo-PF_6 stored as a microcrystalline powder under nitrogen at room temperature isomerize to an equilibrium mixture in ca. 1 week, although the pure isomers can be kept indefinitely at −80 °C. Detailed measurements of the rate of this reaction are beyond the scope of this paper, but its occurrence does support the suggestion that isomerization of 1^+ under neutral conditions is an intramolecular process.

Scheme X. Principal Scrambling Reactions Following Protonation of 2-d_6



Conclusions

The combined results of the protonation studies, the spt experiments, and the kinetic studies of the interconversion of 1^+-exo and 1^+-endo provide a detailed and internally consistent interpretation of the reaction of $[W(\eta\text{-}C_5H_5)_2Cl_2]$ with $(CD_3)_2CHMgBr$ described above. This establishes that the surprisingly facile exchange and isomerization processes within 1^+ preclude the straightforward discrimination between direct and indirect β-elimination routes to 1^+ envisaged in Scheme II, but we have obtained a sufficiently detailed understanding to conclude that the indirect mechanism is not an observable pathway to 1^+. This conclusion is supported by the exclusive formation of 1^+-endo and 1^+-exo, respectively, when the 16-electron tungstenocene alkyls $[W(\eta\text{-}C_5H_5)_2(CH_2CH_2CH_3)]^+$ and $[W(\eta\text{-}C_5H_5)_2\{CH(CH_3)_2\}]^+$ are generated independently.

The exchange mechanisms involved in the movement of labels within 1^+ under neutral or acidic conditions are summarized in Scheme X, which shows how four principal processes scramble the hydrogen following protonation of 2-d_6:

(1) Insertion of the propene into the W–H bond in 1^+-endo, with kinetic parameters (as measured by spt studies at higher temperatures) comparable to those observed for insertion in isoelectronic Nb complexes,[18] results in complete exchange between the hydride and methyne positions within 30 min at room temperature.

(2) A slower insertion of the propene into the W–H bond in 1^+-exo, which was also observed in spt studies, exchanges the exo hydride and both exo methylene hydrogens in ca. 2.5 h at room temperature.

(3) 1^+-endo and 1^+-exo interconvert slowly under neutral and acidic conditions by a nondissociative unimolecular process which reaches equilibrium in ca. 1.5 days, and which we propose involves alkene rotation.

(4) Rotation about the W–C bond, or isopropyl "wag", exchanges the methyl groups of the intermediate isopropyl complex and allows the eventual equilibration of protons into the methyl groups of both isomers (ca. 6 days).

It is important to note that there is *not* unconstrained rotation about the W–C bond in the intermediate isopropyl complex, since this would result in scrambling into the methyl group of 1^+-exo on the same time scale as scram-

(53) These rates are consistent with the observation that complete scrambling within the vinyl positions of 1^+-d_n takes about 2 days.

(54) Alkene rotation does not compete with insertion as a mechanism for spt, despite the similarity in activation energies, because the different preexponential terms cause insertion to be much faster than rotation at the temperatures required to observe spt.

(55) The rate is in fact slightly faster under these conditions. This may be a consequence of changes in solvent polarity: Klumpp, G. W. *Reactivity in Organic Chemistry*; Wiley: New York, 1982; Chapters 3 and 4.

(56) Asaro, M. F.; Cooper, N. J., manuscript in preparation.

bling into the methylene. This would be inconsistent with both the spt and labeling data, and we suggest that the absence of unconstrained rotation reflects a significant agostic interaction in the isopropyl intermediate (see Schemes VI and VII).

The evidence for agostic alkyl intermediates in insertion reactions of 1^+ is one of three ways in which our results complement those of Doherty and Bercaw on olefin insertion in $[Nb(\eta\text{-}C_5Me_5)_2(RCH{=}CH_2)H]$ complexes.[18a] A second difference is that the availability of pure 1^+-exo and 1^+-endo has allowed us to monitor alkene rotation within 1^+ (the Nb complexes are exclusively endo), and a third is that the neutral Nb complexes do not exhibit an equivalent of the deprotonation/protonation sequences observed with 1^+. These are rapid when catalyzed by added base and have an effect on label distributions similar to that of alkene rotation.

The lack of evidence within this study for an indirect α-elimination, 1,2-hydride shift mechanism for overall β-elimination from the tungstenocene alkyls studied does not conflict with the previous evidence for chemically facile α-elimination within this system. A more reasonable interpretation is that the 1,2-hydride shift within an intermediate tungstenocene alkylidene hydride is slow: the β-carbon in the potential alkylidene intermediate must be held at some distance from the metal, and there is unlikely to be good overlap between the p orbital on the carbon that will form the alkene π-bond and the frontier orbital of the metal during the early stages of the 1,2-hydride shift. This would result in considerable unstabilized carbonium ion character in the transition state and disfavor the 1,2-hydride shift.[57] It seems probable that similar problems will arise in other systems, and we conclude that the combination of an α-elimination reaction with a 1,2-hydride shift is unlikely to be a common alternative to direct β-elimination.[58]

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Registry No. *endo*-**1**-PF_6, 114298-83-8; *exo*-**1**-PF_6, 114298-85-0; *endo*-**1**-d_5-PF_6, 114273-28-8; *exo*-**1**-d_5-PF_6, 114375-26-7; *endo*-**1**-d_6-PF_6, 114251-75-1; *exo*-**1**-d_6-PF_6, 114298-87-2; *endo*-**1**-d_7-PF_6, 114251-77-3; *exo*-**1**-d_7-PF_6, 114375-07-4; **2**, 37343-23-0; **2**-d_6, 114251-78-4; **3**-PF_6, 114251-80-8; **4**, 114251-81-9; **5**, 102977-68-4; $(CD_3)_2CHMgBr$, 99727-83-0; $(CD_3)_2CO$, 666-52-4; $(CD_3)_2CHOH$, 3976-29-2; $(CD_3)_2CHBr$, 52809-76-4; $(CD_3)_2CDMgBr$, 114251-82-0; $(CD_3)_2CDOD$, 22739-76-0; $(CD_3)_2CDBr$, 39091-63-9; $(CH_3)_2CHO$-TS, 2307-69-9; TsCl, 98-59-9; $(CH_3)_2CHOH$, 67-63-0; $(CH_3)_2CH$-MgBr, 920-39-8; $[W(\eta\text{-}C_5H_5)_2Cl_2]$, 12184-26-8; $W(\eta\text{-}C_5H_5)_2HLi$, 53322-18-2.

(57) A similar accumulation of charge on the β-carbon has been postulated for the rearrangement of electrophilic iron alkylidene species via a 1,2-hydride shift, and Brookhart has shown that alkyl substituents on the β-carbon of alkylidene complexes of the type $[(\eta\text{-}C_5H_5)(CO)(PPh_3)Fe{=}CHR]^+$ greatly increase the rate of rearrangement to the alkene complex, presumably by stabilizing the incipient carbonium center formed in the transition state.[11c]

(58) Unless there are special factors such as the steric restraints operative in the platinacyclobutanes for which α-elimination routes to alkenes have been established: Parsons, E. J.; Jennings, P. W. *J. Am. Chem. Soc.* **1987**, *109*, 3973–3977 and references therein.

Chromium Tricarbonyl Facilitated Nucleophilic Aromatic Substitution by Metal Carbonyl Anions: The Synthesis and Molecular Structure of a New Class of Bimetallic π-Arene Complexes

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The highly nucleophilic metal carbonyl anions $[CpFe(CO)_2]^-$ and $[(C_5Me_5)Fe(CO)_2]^-$ ($C_5Me_5 \equiv Cp^*$) react with $(\eta\text{-}XRC_6H_4)Cr(CO)_3$ substrates in a previously unknown type of nucleophilic aromatic substitution to form $(\eta^6\text{-}\{CpFe(CO)_2\}RC_6H_4)Cr(CO)_3$ products. A variety of less reactive metal nucleophiles, including $[CpMo(CO)_3]^-$, $[CpNi(CO)]^-$, $[Mn(CO)_5]^-$, and $[Co(CO)_4]^-$, fail to participate in the substitution reactions. The structure of $(\eta\text{-}\{CpFe(CO)_2\}ClC_6H_4)Cr(CO)_3$ has been determined by X-ray crystallography. The compound crystallizes in the space group $P2_1/n$ with four molecules in the unit cell of dimensions a = 7.969 (2) Å, b = 18.982 (4) Å, c = 10.789 (2) Å, and β = 91.45 (3). Full-matrix least-squares refinement yielded R = 0.0353 for 2153 reflections. The structure shows that the conformation of the $Cr(CO)_3$ fragment is determined by a cogging of the carbonyl ligands of the $CpFe(CO)_2$ and $Cr(CO)_3$ units to avoid steric interactions, although ^1H and ^{13}C NMR studies failed to show a perceptible barrier to $Cr(CO)_3$ rotation about the $Cr\text{–}Ph_{centroid}$ vector. Certain haloarene substrates react predominantly through an apparent electron-transfer pathway to produce $[CpFe(CO)_2]_2$ and $(\eta\text{-}RC_6H_5)Cr(CO)_3$. The fraction of reduced products formed is dependent on (1) the reducing power of the anion ($[Cp^*Fe(CO)_2]^- \gg [CpFe(CO)_2]^-$), (2) the electron-donating ability of the R group (electron donor ≫ electron acceptor), (3) the substitution pattern of the arene (in general ortho ≫ meta ≅ para), and (4) the identity of the halogen leaving group (I ≫ Cl > F).

The activation of carbon–hydrogen and carbon–halogen bonds in aromatic hydrocarbons by homogeneous transition-metal catalysts are processes of significant industrial importance.[2] A variety of Pd- and Ni-catalyzed reactions,

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