Stereochemistry at Carbon for Alkyl Migration to Oxygen in the Rearrangement of a *tert*-Butylperoxy Alkyl Derivative of Permethylhafnocene†

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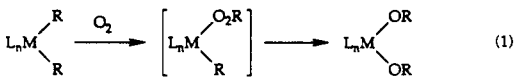
Summary: Neohexyl migration from hafnium to oxygen for *threo*- and *erythro*-(η^5-C_5Me_5)$_2$Hf(CHDCHDCMe$_3$)(OOCMe$_3$) to form *threo*- and *erythro*-(η^5-C_5Me_5)$_2$Hf(OCHDCHDCMe$_3$)(OCMe$_3$) has been found to occur with retention of configuration at the migrating carbon center.

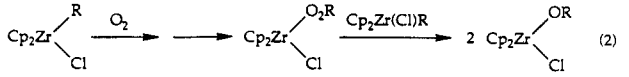
The controlled transfer of oxygen to organic molecules is of fundamental importance in biological systems as well as in the industrial preparation of commodity chemicals. Metal centers with the ability to coordinate both substrate and oxidant may facilitate more controlled and selective transfer of oxygen to substrate. Group 4 transition-metal peroxy alkyls have been proposed as intermediates in several systems: the titanium-catalyzed epoxidation of allylic alcohols[1] and the Shell propylene oxide synthesis,[2] as well as the direct reaction of molecular oxygen with group 4 transition-metal alkyls.[3] Although very few stable alkylperoxy alkyl derivatives have been isolated, these have been implicated in the autoxidation of polyalkyl derivatives of titanium, zirconium, and hafnium (eq 1).[3b,c]



(1)

(L_nM = Cp_2M, R_2M (M = Zr, Hf); [$(Me_3C_3CO)_2$]$_2$M (M = Ti, Zr))

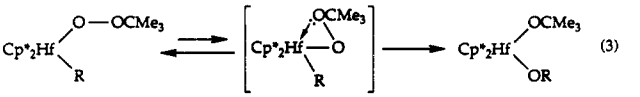
Blackburn, Labinger, and Schwartz[3a] demonstrated that the autoxidation of monoalkyls, $Cp_2Zr(Cl)R$ (Cp = η^5-C_5H_5), proceeds intermolecularly as shown in eq 2. With



(2)

R = *threo*- or *erythro*-CHDCHDCMe$_3$, 50% retention and 50% racemization were observed. This stereochemical outcome was interpreted as the net result of (complete) racemization occurring in the formation of Cp_2Zr(Cl)(O$_2$CHDCHDCMe$_3$) and (complete) retention in the bimolecular, second step.

We have previously reported a series of isolable *tert*-butylperoxy alkyl complexes of permethylhafnocene, Cp*$_2$Hf(R)(OOCMe$_3$) (Cp* = η^5-C_5Me_5; R = CH_3, CH_2CH_3, $CH_2CH_2CH_3$, $CH_2CH_2CH_2CH_2CH_3$, $CH_2CH(CH_3)_2$).[4] An X-ray crystal structure for Cp*$_2$Hf(CH_2CH_3)(OOCMe$_3$) revealed that the *tert*-butylperoxy group is coordinated in an η^1-fashion. The more common bidentate coordination, e.g., as for (dipic)V(O)(η^2-OOCMe$_3$)(H_2O) (dipic = 2,6-pyridinedicarboxylate),[5] is apparently precluded due to unfavorable steric interactions between the bulky Cp* ligand and the *tert*-butyl group. This crowded ligand environment about the less reactive third-row metal, hafnium, allows isolation of these alkylperoxy alkyl derivatives, which upon mild heating undergo rearrangement to the very stable bisalkoxides Cp*$_2$Hf(OCMe$_3$)(OR). The proposed rearrangement pathway involves an $\eta^1 \rightarrow \eta^2$ coordination of the *tert*-butylperoxy ligand, followed by alkyl transfer to the syn oxygen simultaneously with cleavage of the O–O bond (eq 3).



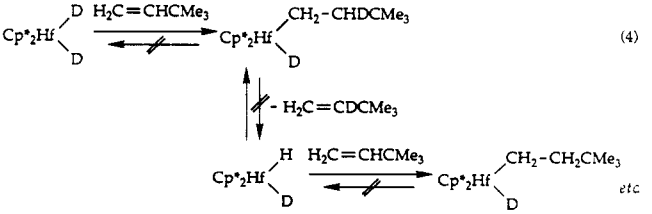
(3)

The clean nature of these reactions provides a rare opportunity to study some of the mechanistic features of the second step of the general process shown in eq 1, particularly the stereochemistry at carbon for the alkyl migration to oxygen in the key carbon–oxygen bond forming step. We report herein the results of a study to address that issue.

Results and Discussion

The use of ^{1}H NMR spectrometry to investigate the stereochemistry for alkyl migrations occurring at metal centers has been previously described.[3a,6] The specific removal of H–H couplings by double deuteration affords an isolated AA′XX′ spin system (e.g., L_nM–CHDCHDCMe$_3$) and two possible isomers, threo and erythro. The observed $^3J_{HH}$ coupling is the weighted average of the couplings of one trans and two gauche conformers. Typical erythro couplings for L_nM–CHDCHDCMe$_3$ are greater than 9 Hz, whereas for the threo isomer couplings are usually less than 6 Hz.

Both *threo*-Cp*$_2$Hf(CHDCHDCMe$_3$)(OOCMe$_3$) (**2a**) and *erythro*-Cp*$_2$Hf(CHDCHDCMe$_3$)(OOCMe$_3$) (**2b**) were prepared according to Scheme I (only a single enantiomer of the two formed is shown in each case). These reactions proceed straightforwardly, and a number of feared complications in the cis addition of [Hf–H] or [Hf–D] to *cis*-neohexene-d_2 or *trans*-neohexene-d_1 do not interfere. For example, if the hafnium–hydride addition occurs reversibly (eq 4), scrambling of labels would result. Moreover, a



(4)

bimolecular interchange of β-hydrogens, analogous to that

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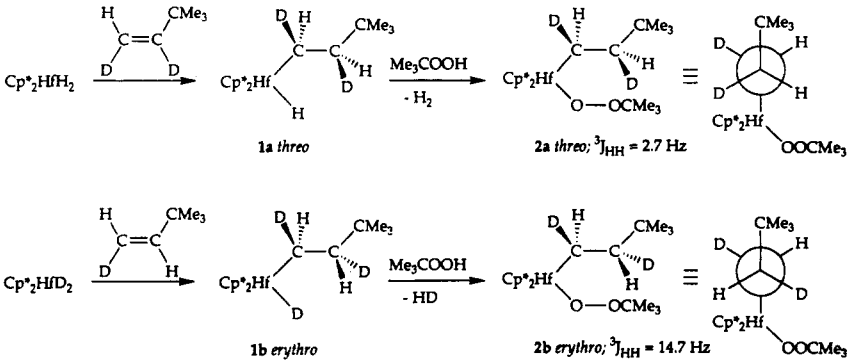
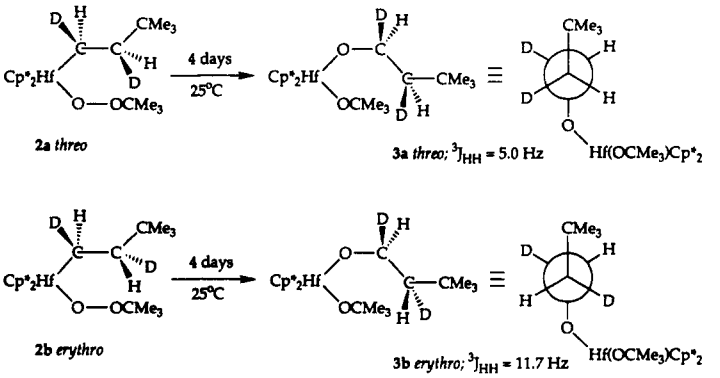
Scheme I

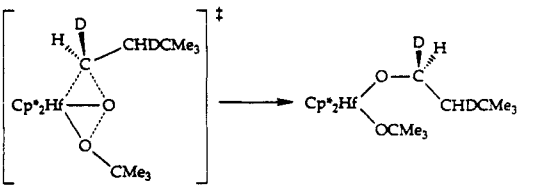


Scheme II



which occurs following hydrozirconation of styrene, also does not appear to interfere.[7] Thus, addition of CH_2=$CHCMe_3$ to $Cp^*_2HfD_2$ results in clean formation of $Cp^*_2Hf(D)(CH_2CHDCMe_3)$ (^1H ^2H NMR), even in the presence of excess 3,3-dimethyl-1-butene. The observation of no $Cp^*_2Hf(D)(CH_2CH_2CMe_3)$, $Cp^*_2Hf(H)(CH_2CHDCMe_3)$, $Cp^*_2Hf(D)(CH_2CD_2CMe_3)$, nor $Cp^*_2Hf(H)(CH_2CD_2CMe_3)$ as coproducts indicates that the rate of β-H or β-D elimination is slow relative to insertion (eq 4). Fortunate too is the selective protonylsis of the hafnium–hydride rather than the hafnium–neohexyl bond on treatment of **1a** or **1b** with *tert*-butyl hydroperoxide (see ref 4).

The coupling constant for the threo *tert*-butylperoxy neohexyl isomer **2a** ($^3J_{HH}$ = 2.7 Hz) is at the low end and the value for the erythro isomer **2b** ($^3J_{HH}$ = 14.7 Hz) at the high end of the ranges normally found for Z–CHDCHDCMe$_3$ compounds. For these cases with Z as the very large [$Cp^*_2Hf(OCMe_3)$] moiety, the trans conformations (shown in Scheme I) are greatly favored, so that the averaged $^3J_{HH}$ consists largely of the coupling constant for those rotamers about the C–C bond. Their rearrangements were found to be quantitative (^1H NMR) after 4 days at room temperature (Scheme II). No intermediates were detected during the course of the reactions, nor did the observed couplings for **2a** or **2b** change during the course of the rearrangement. The neohexoxy *tert*-butoxy products **3a** and **3b** exhibit $^3J_{HH}$ values more nearly alike (5.0 and 11.7 Hz), reflecting reduced effective steric bulk of [$Cp^*_2(OCMe_3)HfO$–] vs [$Cp^*_2(OOCMe_3)Hf$–] brought about by extending the neohexyl group one atom farther away. The large differences in the $^3J_{HH}$ values for **2a** vs **2b** and **3a** vs **3b** permit relatively small amounts of the other isomer to be easily identified. Hence, the results allow us to state that the migration occurs with ≥98% retention of configuration. This result was anticipated, since the most likely mechanism involves Hf–C and O–O bond rupture simultaneous with O–C bond formation:



A reasonable alternative mechanism involving two separate inversion steps is very difficult to envision. The observation of clean retention of configuration rules out mechanisms involving long-lived, geminate radical pairs, i.e., by initial homolysis of the hafnium–carbon bond. Oxygen–oxygen bond homolysis is also unlikely since no products characteristic of *tert*-butoxide radical decomposition were detected during the migration.[8]

Limited solvent studies (in benzene-d_6, acetonitrile-d_3/benzene-d_6 (40/60), or tetrahydrofuran-d_8) have shown that the rate of the overall reaction is insensitive to the solvent employed, suggestive of little charge build up in the transition state.[4a] All of these results, including those of the stereochemical study reported here, are in full accord with a concerted O–O bond cleavage, alkyl migration with retention shown above.

Experimental Section

General Considerations. All manipulations were carried out using either high-vacuum or glovebox techniques as described earlier.[9] Toluene and petroleum ether were distilled from benzophenone ketyl and then vacuum distilled from titanocene[10] prior

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to use. $Cp^*_2HfH_2$ and $Cp^*_2HfD_2$ as well as *trans*-1-deuterio-3,3-dimethyl-1-butene and *cis*-1,2-dideuterio-3,3-dimethyl-1-butene were prepared following literature procedures.[11,12] *tert*-Butyl hydroperoxide (Aldrich, 90%) was dried by azeotropic distillation with benzene and stored as an approximate 4 M solution over 4-Å molecular sieves.[13] All other reagents were either degassed and vacuum distilled from 4-Å molecular sieves or used as received. Alkyl migration reactions of **2a** and **2b** were performed in sealed NMR tubes; spectra were recorded on a JOEL GX-400 spectrometer.

$Cp^*_2Hf(H)(CH_2CH_2CMe_3)$ (1). A 2.00-g (4.43-mmol) sample of $Cp^*_2HfH_2$ was dissolved in 25 mL of toluene. 3,3-Dimethyl-1-butene (5 mL, 38.8 mmol) was added by vacuum transfer; the reaction was stirred at ambient temperature for 10 h. The volatiles were removed in vacuo, and the residue was taken up in petroleum ether and filtered. The filtrate was concentrated and cooled to −78 °C, precipitating a white crystalline solid. Yield: 1.29 g (54.4%). ^{1}H NMR (benzene-d_6): δ 12.85 (s, Hf*H*), 1.94 (s, *Cp**), 1.02 (s, $HfCH_2CH_2CMe_3$), 0.86 (AA′XX′, $HfCH_2CH_2CMe_3$), −0.16 (AA′XX′, $HfCH_2CH_2CMe_3$). Anal. Calcd for $C_{26}H_{44}Hf$ (found): C, 58.36 (58.41); H, 8.29 (7.62).

***threo*-$Cp^*_2Hf(H)(CHDCHDCMe_3)$ (1a).** In a procedure analogous to the preparation of 1, a 2.51-g (5.57-mmol) sample of $Cp^*_2HfH_2$ and 0.90 mL (6.98 mmol) of *cis*-1,2-dideuterio-3,3-dimethyl-1-butene gave, after workup, 1.29 g (43%) of a white sample of **1a**. ^{1}H NMR (benzene-d_6): δ 12.85 (s, Hf*H*), 1.95 (s, *Cp**), 1.02 (s, $HfCHDCHDCMe_3$), 0.86 (br, $^3J_{HH}$ < 2.5 Hz, $HfCHDCHDCMe_3$), −0.22 (br, $^3J_{HH}$ < 2.5 Hz, $HfCHDCHDCMe_3$).

***erythro*-$Cp^*_2Hf(D)(CHDCHDCMe_3)$ (1b).** In a procedure analogous to the preparation of 1, a 1.23-g (2.72-mmol) sample of $Cp^*_2HfD_2$ and 0.38 mL (2.95 mmol) of *trans*-1-deuterio-3,3-dimethyl-1-butene gave, after workup, 0.82 g (56%) of **1b** as a white solid. ^{1}H NMR (benzene-d_6): δ 1.96 (s, *Cp**), 1.05 (s, $HfCHDCHDCMe_3$), 0.83 (d, $HfCHDCHDCMe_3$, $^3J_{HH}$ = 14.6 Hz), −0.22 (d, $HfCHDCHDCMe_3$, $^3J_{HH}$ = 14.6 Hz).

$Cp^*_2Hf(CH_2CH_2CMe_3)(OOCMe_3)$ (2). A 0.91-g (1.7-mmol) sample of 1 was dissolved in 40 mL of toluene and the solution cooled to 0 °C. *tert*-Butyl hydroperoxide (0.62 mL, 1.86 mmol) was added via syringe against an argon counterflow. The reaction was stirred for 30 min. The volatiles were removed in vacuo and the residuals taken up in acetone, filtered, concentrated, and cooled to −78 °C. The white crystalline product was collected by filtration and dried in vacuo. Yield: 0.53 g (49.8%). ^{1}H NMR (benzene-d_6): δ 1.90 (s, *Cp**), 1.50 (AA′XX′, $HfCH_2CH_2CMe_3$), 1.21 (s, $HfOOCMe_3$), 1.16 (s, $HfCH_2CH_2CMe_3$), 0.25 (AA′XX′, $HfCH_2CH_2CMe_3$). Anal. Calcd for $C_{30}H_{52}O_2Hf$ (found): C, 57.82 (57.60); H, 8.41 (8.06).

***threo*-$Cp^*_2Hf(CHDCHDCMe_3)(OOCMe_3)$ (2a).** In a procedure analogous to the preparation of **2**, a 0.63-g (1.18-mmol) sample of **1a** and 0.6 mL of *tert*-butyl hydroperoxide (2.4 mmol) gave, after workup, 0.26 g (34%) of **2a** as a white solid. ^{1}H NMR (benzene-d_6): δ 1.90 (s, *Cp**), 1.47 (d, $HfCHDCHDCMe_3$, $^3J_{HH}$ = 2.7 Hz), 1.21 (s, $HfOOCMe_3$), 1.15 (s, $HfCHDCHDCMe_3$), 0.17 (d, $HfCHDCHDCMe_3$, $^3J_{HH}$ = 2.7 Hz).

***erythro*-$Cp^*_2Hf(CHDCHDCMe_3)(OOCMe)$ (2b).** In a procedure analogous to the preparation of **2**, a 0.65-g (1.2-mmol) sample of **1b** and 0.61 mL (2.4 mmol) of *tert*-butyl hydroperoxide gave, after normal workup, 0.34 g (45%) of **2b** as a white microcrystalline solid. ^{1}H NMR (benzene-d_6): δ 1.90 (s, *Cp**), 1.46 (d, $HfCHDCHDCMe_3$, $^3J_{HH}$ = 14.7 Hz), 1.21 (s, $HfOOCMe_3$), 1.15 (s, $HfCHDCHDCMe_3$), 0.18 (d, $HfCHDCHDCMe_3$, $^3J_{HH}$ = 14.7 Hz).

$Cp^*_2Hf(OCH_2CH_2CMe_3)(OCMe_3)$ (3). A 0.30-g (0.48-mmol) sample of **2** was dissolved in 25 mL of toluene; the solution was allowed to stand at ambient temperature for 4 days. Removal of solvent in vacuo and crystallization from acetone gave a white solid. Yield: 0.21 g (70%). ^{1}H NMR (benzene-d_6): δ 4.34 (AA′XX′, $HfOCH_2CH_2CMe_3$), 2.00 (s, *Cp**), 1.76 (AA′XX′, $HfOCH_2CH_2CMe_3$), 1.42 (s, $HfOCMe_3$), 1.00 (s, $HfOCH_2CH_2CMe_3$). Anal. Calcd for $C_{30}H_{52}O_2Hf$ (found): C, 57.82 (57.95); H, 8.41 (8.14).

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Registry No. 1, 137394-32-2; **1a**, 137394-33-3; **1b**, 137394-34-4; **2**, 137394-35-5; **2a**, 137394-36-6; **2b**, 137394-37-7; **3**, 137394-38-8; $Cp^*_2HfH_2$, 81956-87-8; 3,3-dimethyl-1-butene, 558-37-2; *cis*-1,2-dideuterio-3,3-dimethyl-1-butene, 84784-40-7; *trans*-1-deuterio-3,3-dimethyl-1-butene, 57002-05-8.

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Correlation of ^{103}Rh NMR Shielding and Rate Constants of CO Displacement Reactions in $(\eta^5\text{-}C_5H_4X)Rh(CO)_2$ Complexes†

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Summary: ^{103}Rh chemical shifts of $(\eta^5\text{-}C_5H_4X)Rh(CO)_2$ complexes (X = H, CH_3, $N(CH_3)_2$, CF_3, Cl, NO_2) show a linear correlation (R^2 = 0.973) with rate constants log k_{obsd} of the CO/PPh_3 displacement reaction reported by Basolo and Cheong. Increasing reactivity is reflected in lower shielding of the ^{103}Rh nucleus, and substituents with lone-pair electrons ($N(CH_3)_2$, Cl) do not disturb the correlation.

Seven years ago we reported together with Bönnemann et al. a linear relationship between the ^{59}Co chemical shift of several $(\eta^5\text{-}C_5H_4R)Co(COD)$ complexes and their catalytic activity.[2] In 1989 it was shown by DeShong et al. and our group that the ^{55}Mn resonance of a series of manganacycles correlated linearly with the logarithm of the observed rate constants for a demetalation reaction.[3] More recently, ^{59}Co shielding in alkylcobaloximes and related complexes has proven to be very sensitive to steric

† Transition-Metal NMR Spectroscopy. 19. Part 18: Reference 1.

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