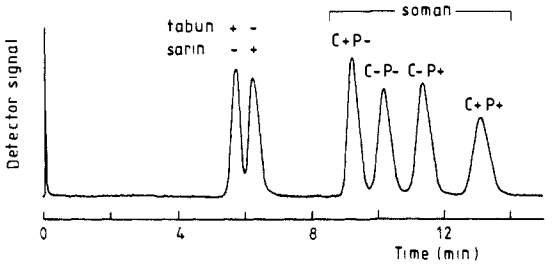

Figure 1. Gas chromatogram (NP detection) after direct injection of a 0.5-μL sample in *i*-PrOH, containing 0.1 mM each of C(±)P(±)-soman, (±)-sarin, or (±)-tabun on a glass column (l = 2 m, i.d. = 0.44 mm) coated with bis[(1*R*)-3-(heptafluorobutyryl)camphorate]nickel(II) in OV 101, operated at 120 °C. Helium (5×10^{-1} m/s) was used as carrier gas. Static coating of the Duran 50 glass column was performed with a solution of the nickel(II) derivative (0.024%, w/v) and OV 101 (0.4%, w/v) in *n*-pentane.[10,11] The enantiomeric peaks of sarin and tabun coincide.

ation gas chromatography[9-12] might be suitable for resolution of nerve agent stereoisomers. We found (Figure 1) that a 2-m capillary column, coated with bis[(1*R*)-3-(heptafluorobutyryl)-camphorate]nickel(II) in OV-101, separates the four stereoisomers of soman and the enantiomers of sarin and tabun almost completely. The stereoisomers of soman were identified by addition of single isomers to C(±)P(±)-soman,[5] whereas (+)- and (-)-sarin were identified in samples enriched with these isomers by synthesis.[7] Since the gas chromatographic resolution of enantiomers increased sharply with a decrease in the amount of analyte, an NP detector was used, which allows detection in the pg range.[4] GC/MS detection confirmed that the peaks, which are within experimental error of equal size for enantiomeric pairs, correspond with unchanged nerve agent. As expected, the elution order of the enantiomers inverted when the complexation phase was synthesized from (1*S*)-3-(heptafluorobutyryl)camphor instead of the 1*R* isomer.[9]

Hoskin and Trick[13] reported that phosphorylphosphatases in rat serum hydrolyze preferentially the enantiomer of tabun which is presumably more toxic in mice than (±)-tabun. Polarimetry in rat serum suggested that the remaining enantiomer was levorotatory. Augustinsson[14] confirmed the stereospecificity of tabun breakdown in rat plasma and suggested that phosphorylphosphatases in human and rabbit plasma are not stereospecific for hydrolysis of (±)-tabun. We identified, isolated, and studied the anticholinesterase properties of the two enantiomers of tabun.

Analogous to the procedure for isolation of P(+)-soman epimers,[5,6] we incubated a 2.3 mM solution of bovine pancreas chymotrypsin (Sigma, type II, dialyzed at pH 3.0) in phosphate buffer (pH 7.5, 25 °C) with a 15% molar excess of (±)-tabun for 5 min. Extraction on Extrelut (Merck) with CCl_4 gave a single tabun enantiomer in 25% yield, which corresponded with the second peak in the gas chromatogram (Figure 1). ^{1}H NMR analysis[7,15] of such a solution in CCl_4, α_{578}^{25} -0.0770° (l = 1; c = 3.35 mg/mL), i.e., $[\alpha]_{578}^{25}$ -23°, confirmed that the levorotatory isomer of tabun was obtained with ≥98% ee. Dilute (≤10 mM) solutions of (-)-tabun in CCl_4 and in *i*-PrOH are optically stable for several months at -25 °C.

To obtain the (+)-enantiomer of tabun by means of stereospecific hydrolysis by phosphorylphosphatases,[5] (±)-tabun (4 mM) was incubated at 25 °C for 30 min in plasma of various species. Plasma from horses and cows gave (+)-tabun with 20% and 28% ee, respectively, whereas incubation in plasma from mice, sheep, rabbits, pigs, guinea pigs, and men gave a slight (≤30% ee) enrichment of residual tabun with the (-)-enantiomer. Only by incubation in rat plasma for 45 min was (+)-tabun[16] obtained with 92-100% ee, albeit in low yields (5-10%). Our results confirm the stereospecific hydrolysis of (±)-tabun by phosphorylphosphatases from rat plasma.[13,14] However, the residual isomer is dextrorotatory instead of levorotatory, as suggested by Hoskin and Trick.[13]

The rates of inhibition of electric eel acetylcholinesterase (AChE) were measured (pH 7.5, 25 °C) at various concentrations of tabun stereoisomers. In contrast with the extreme P(-)-selectivity of AChE with (±)-sarin and C(±)P(±)-soman, the overall rate constant for inhibition of AChE with (-)-tabun is only 6.3 times larger than with (+)-tabun: 3.9×10^4 and 0.62×10^4 $M^{-1} \cdot s^{-1}$, respectively. The dissociation constants for the complexes of AChE with (+)- and (-)-tabun are 13.1 and 0.62 μM, respectively, with rates of phosphorylation of 8.1×10^{-2} and 2.4×10^{-2} s^{-1} for (+)- and (-)-tabun, respectively. Surprisingly, the overall stereoselectivities of AChE and chymotrypsin (vide supra) for (+)- and (-)-tabun are opposite, whereas both enzymes are preferentially inhibited by the P(-)-isomers of soman and sarin.[5,6]

The LD50's of (-)-, (+)-, and (±)-tabun in mice, after intravenous administration, are 119 (113-130), 837 (771-905),[17] and 208 (193-224) μg/kg, respectively. Hence, in spite of the modest selectivity of AChE for inhibition by (-)-tabun, this isomer is substantially more toxic in mice than (+)-tabun. The species dependence for the stereoselectivity of tabun enantiomer hydrolysis in plasma (vide supra) may influence the relative toxicities of these enantiomers in various species, e.g., in mice and rats.

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(15) In the ^{1}H NMR spectrum of tabun in CCl_4, shifted by tris[(1*R*)-3-(heptafluorobutyryl)camphorate]europium(III), the doublet of the $N(CH_3)_2$ hydrogens of (+)-tabun is at lower field than the corresponding signal of the (-)-enantiomer, cf. ref. 7.
(16) Absolute values of the positive rotations of (+)-tabun in CCl_4 were inconsistent, probably due to coisolated optically active components from rat plasma.
(17) Contained 4% of the (-)-enantiomer.

tert-Butyl Peroxide Complexes of Permethylhafnocene, $(\eta^5\text{-}C_5Me_5)_2Hf(R)(OOCMe_3)$. Stoichiometric Transformation of Alkyl *tert*-Butyl Peroxide Derivatives to Alkoxy *tert*-Butoxides, $(\eta^5\text{-}C_5Me_5)_2Hf(OR)(OCMe_3)$

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Alkyl peroxide complexes of the group 4 transition metals have been invoked as intermediates in titanium-catalyzed epoxidation of allylic alcohols,[1] in the Shell propylene oxide synthesis[2,6] and

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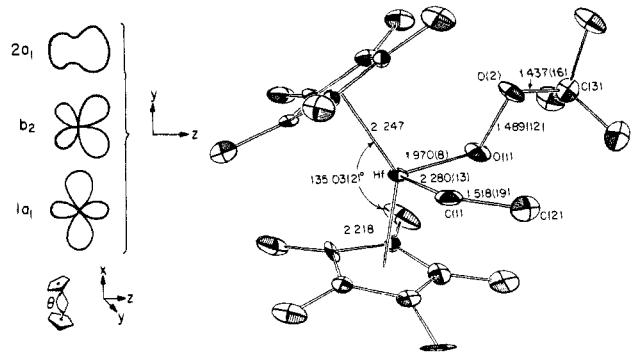

Figure 1. Molecular structure of $(\eta^5\text{-}C_5H_5)_2Hf(CH_2CH_3)(OOCMe_3)$ as determined by X-ray diffraction methods (data collected at 97.5 K). Bond angles: Hf-O(1)-O(2) = 119.6 (6)°, O(1)-Hf-C(1) = 94.1 (4)°, O(1)-O(2)-C(3) = 108.6 (8)°. Torsion angle C(1)-Hf-O(1)-O(2) = −70.9 (7)°. Frontier orbitals for permethylhafnocene moiety are given on the left.

in the direct reaction of dioxygen with group 4 metal alkyls.[3] We report herein the synthesis, structure and reactivity of some of the first well-characterized examples of this class of compounds: $Cp^*_2Hf(R)(OOCMe_3)$ ($Cp^* = (\eta^5\text{-}C_5Me_5)$; R = Cl, H, CH_3, CH_2CH_3, $CH_2CH_2CH_3$, $CH_2CH_2CH_2CH_3$, CH_2CHMe_2, CH=$CHCMe_3$, C_6H_5, $m\text{-}C_6H_3(CH_3)_2$), and $Cp^*(\eta^5,\eta^1\text{-}C_5(CH_3)_4CH_2CH_2CH_2)Hf(OOCMe_3)$.

The synthetic strategy for compounds in this series (eq 1–4)

$$Cp^*_2Hf(R)(H) + HOOCMe_3 \longrightarrow Cp^*_2Hf(R)(OOCMe_3) + H_2 \quad (1)$$

R = Cl, H, CH_3, CH_2CH_3, $CH_2CH_2CH_3$, CH=$CHCMe_3$, C_6H_5, $m\text{-}C_6H_3(CH_3)_2$

$$Cp^*_2Hf\text{—}Me + HOOCMe_3 \longrightarrow Cp^*_2Hf(CH_2CHMe_2)(OOCMe_3) \quad (2)$$

$$Cp^*_2Hf\text{—}\square + HOOCMe_3 \longrightarrow Cp^*_2Hf(CH_2CH_2CH_2CH_3)(OOCMe_3) \quad (3)$$

$$Cp^*(\eta^5,\eta^1\text{-}C_5(CH_3)_4CH_2CH_2CH_2)HfH + HOOCMe_3 \longrightarrow Cp^*(\eta^5,\eta^1\text{-}C_5(CH_3)_4CH_2CH_2CH_2)Hf(OOCMe_3) + H_2 \quad (4)$$

utilizes the high oxophilicity of hafnium for the protiolytic cleavage of Hf–H or Hf–C[4] σ bonds with moderately acidic *tert*-butyl hydroperoxide. The thermal stabilities of members of the series are sufficient for their isolation, except for $Cp^*_2Hf(H)(OOCMe_3)$, which decomposes above −35 °C. Analytical, ^1H NMR, and IR (ν(OO) = 835–850 cm^{-1}) data support the above formulations.

Crystals of $Cp^*_2Hf(CH_2CH_3)(OOCMe_3)$ were grown from acetone solution, and its structure determined by X-ray diffraction.[5] The most significant feature is the (η^1-$OOCMe_3$) coordination (Figure 1), despite the fact that $Cp^*_2Hf(CH_2CH_3)(\eta^2\text{-}OOCMe_3)$ would be formally an 18-electron complex. A bidentate coordination of the *tert*-butyl peroxide ligand, analogous to the related compound, (dipic)V(O)(η^2-$OOCMe_3$)(H_2O)[6] (dipic = 2,6-pyridinedicarboxoxylate), appears to be precluded by unfavorable steric interactions between (η^5-C_5Me_5) and (CMe_3), and, indeed, the ($OCMe_3$) substituent is located in the center of the wedge formed by the two (η^5-C_5Me_5) ligands. The (Hf–O–O–C) dihedral angle of 70.9° suggests substantial π donation from O(1) to the empty $1a_1$ orbital of the $[Cp^*_2Hf(CH_2CH_3)]$ moiety,[7] and the relatively short Hf–O(1) bond length of 1.970 (8) Å is indicative of multiple Hf=O(1) bonding.[8]

The mode of decomposition for these complexes is highly dependent upon the nature of R. For $Cp^*_2Hf(C_6H_5)(OOCMe_3)$ and $Cp^*_2Hf(m\text{-}C_6H_3(CH_3)_2)(OOCMe_3)$ decomposition occurs above room temperature to generate products suggestive of O–O bond homolysis. Thus, in the presence of 5–16 equiv of 9,10-dihydroanthracene, clean first-order decomposition to $Cp^*_2Hf(C_6H_5)(OH)$ and $HOCMe_3$ is observed (eq 5). By measuring

$$Cp^*_2Hf(C_6H_5)(OOCMe_3) \xrightarrow[40\text{–}100\ °C,\ \text{benzene-}d_6]{C_{14}H_{12}} Cp^*_2Hf(C_6H_5)(OH) + HOCMe_3 \quad (5)$$

the activation parameters for the above reaction ($\Delta H^\ddagger$ = 22.6 kcal mol^{-1}, $\Delta S^\ddagger$ = −9.7 eu) a value for the O–O bond strength of 22 kcal mol^{-1} is estimated, considerably lower than that measured for dialkyl peroxides (37 ± 1 kcal mol^{-1}).[9] The decomposition of $Cp^*_2Hf(Cl)(OOCMe_3)$ occurs slowly at room temperature; however, conditions for a clean, stochiometric pathway could not be identified.[10]

$Cp^*_2Hf(H)(OOCMe_3)$ decomposes to $Cp^*_2Hf(OH)(OCMe_3)$ smoothly even at −35 °C in toluene-d_8, and the alkyl complexes rearrange cleanly just above room temperature to the alkoxy *tert*-butoxide derivatives as shown in eq 6 and 7.[11] Measurements

$$Cp^*_2Hf(R)(OOCMe_3) \xrightarrow[\text{solvent}]{33\ °C} Cp^*_2Hf(OR)(OCMe_3) \quad (6)$$

R = CH_3,[11] CH_2CH_3, $CH_2CH_2CH_3$, $CH_2CH_2CH_2CH_3$, CH_2CHMe_2; solvent = benzene-d_6, THF-d_8,[12] acetonitrile-d_3/benzene-d_6 (40:60)[12]

$$Cp^*(\eta^5,\eta^1\text{-}C_5(CH_3)_4CH_2CH_2CH_2)Hf(OOCMe_3) \xrightarrow{33\ °C} Cp^*(\eta^5,\eta^1\text{-}C_5(CH_3)_4CH_2CH_2CH_2O)Hf(OCMe_3) \quad (7)$$

of the kinetics reveal first-order rate constants (benzene-d_6, 33 °C): $Cp^*_2Hf(CH_2CH_3)(OOCMe_3)$ (9.5×10^{-5} s^{-1}); $Cp^*_2Hf(CH_2CH_2CH_2CH_3)(OOCMe_3)$ (1.0×10^{-4} s^{-1}), $Cp^*_2Hf(CH_2CH_2CH_3)(OOCMe_3)$ (1.5×10^{-4} s^{-1}); $Cp^*(\eta^5,\eta^1\text{-}C_5(CH_3)_4CH_2CH_2CH_2)Hf(OOCMe_3)$ (4.5×10^{-4} s^{-1}); $Cp^*_2Hf(CH_2CHMe_2)(OOCMe_3)$ (1.8×10^{-3} s^{-1}). These relative rates do not follow a regular pattern and probably reflect a multistep pathway (vide infra). The intramolecular nature of the rearrangement is indicated by the activation parameters ($\Delta H^\ddagger$ = 19.6 (3) kcal mol^{-1}, $\Delta S^\ddagger$ = −13 eu) for $Cp^*_2Hf(CH_2CH_3)(OOCMe_3)$ and, indirectly, by the lack of formation of $Cp^*_2Hf(OH)(H)$[13] (or any other products derived from $Cp^*_2HfH_2$), when the decomposition of $Cp^*_2Hf(CH_2CH_3)(OOCMe_3)$ was carried out in the presence of approximately 1 equiv of $Cp^*_2HfH_2$.

A likely first step in the rearrangement shown in eq 5 would be η^2-coordination of the *tert*-butyl peroxide ligand, as has been previously postulated for oxygen-transfer reactions.[1b,14] The complex rate dependence on the sterics of the alkyl group of $Cp^*_2Hf(R)(OOCMe_3)$ could be taken as consistent with the stepwise process shown in eq 8, since the prequilibrium would be sensitive primarily to steric factors (e.g., the tenfold increase in rate for R = isobutyl vs. R = *n*-butyl) whereas the migration to

(5) X-ray crystallography. $Cp^*_2Hf(OOC(CH_3)_3)CH_2CH_3$ crystallizes from acetone in the monoclinic system, space group $P2_1/c$, with a = 19.890 (7) Å, b = 8.746 (4) Å, c = 17.532 (6) Å, β = 124.987 (24)°, V = 2498 (2) $Å^3$, and Z = 4. From 2349 reflections collected at 97.5 K using Mo Kα radiation out to 2θ = 40°, the structure was solved and refined by standard methods to yield R_F = 0.054 (2222 reflections, $I > 0$). Full structural details are available in the supplementary material.

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(10) The very crowded coordination spheres of these *tert*-butyl peroxide derivatives is illustrated by their lack of reactivity with cyclohexene, ethylene, carbon monoxide, and trimethylphosphine.

(11) $Cp^*_2Hf(CH_3)(OOCMe_3)$ and $Cp^*_2Hf(CH$=$CHCMe_3)(OOCMe_3)$ decompose by more than one pathway, similar to the chloride derivative. The former yields ca. 50% $Cp^*_2Hf(OCH_3)(OCMe_3)$ at 34 °C; the latter ca. 30% $Cp^*_2Hf(CH$=$CHCMe_3)(OH)$. Other products seem to arise from the loss of a Cp^* ligand.

(12) In these coordinating solvents, slower further decomposition of the product bis(alkoxide) to Cp^*H and unknown other products is also observed.

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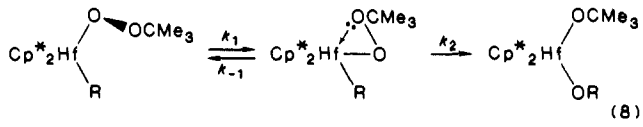

(8)

oxygen (step k_2) should respond to both sterics and electronic changes for R. The higher stability of the phenyl derivative may also be accommodated with this mechanism, since the planar phenyl ring is constrained to lie in the equatorial plane of the bent sandwich structure,[15] thus discouraging formation of reactive $[Cp^*_2Hf(C_6H_5)(\eta^2\text{-}OOCMe_3)]$. Although the range of solvent polarities is severely limited by the high reactivity of these compounds, no significant difference was noted for the rate of rearrangement of $Cp^*_2Hf(CH_2CH_3)(OOCMe_3)$ among the solvents listed (eq 6), suggesting little polar character for the transition state of step k_2.

The crowded ligand environment surrounding a less reactive, third-row transition metal is very likely responsible for the thermal stability exhibited by members of this series of complexes. These same features appear to dictate the mechanism(s) for rearrangement to the very stable bis(alkoxide) derivatives.

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Supplementary Material Available: Tables of analytical, NMR, and IR spectroscopic data for all isolated compounds, atomic coordinates, thermal parameters, bond lengths & angles, least-squares planes, and torsion angles and experimental procedures and crystal structure determination (12 pages); structure factor tables for $Cp^*_2Hf(C_2H_5)(OOC_4H_9)$ (10 pages). Ordering information is given on any current masthead page.

(15) Although the crystal was disordered, a partial X-ray structure determination for $Cp^*_2Hf(C_6H_5)(OOCMe_3)$ revealed this arrangement for the phenyl group. The barrier for aryl rotation is sufficiently large that NMR spectra indicate this static structure in solution at ambient temperature.

Oxygenate Formation from Electrophilic Attack of a Rh/Zr "A-Frame" Containing a μ_2:η^2-Acetyl Bridge

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The current economic climate has shifted the emphasis in Fischer-Tropsch (F-T) research from hydrocarbons to oxygenates, useful precursors to a variety of chemicals. While C_1 chemistry, principally MeOH based, has reached the commercial stage,[1] the selective formation of higher oxygenates remains a challenging problem.[2] Features critical to such selectivity are exhibited by supported-Rh catalysts:[3] (1) CO adsorption and dissociation are suppressed by strong metal support interactions (SMSI);[4-6] (2) Rh engenders facile CO insertions;[7] (3) IR studies are indicative of CO_{ads},[8,9] acyl, and acetate[10,11] species that interact with the support; (4) MeOH and C_2 products are formed from different sites.[5,12,13] Mechanistic interpretations converge on a key migration of surface Me to CO_{ads} occurring at interfacial Rh/support sites.[5,10,12,14-16]

Organometallic species have proven valuable in modeling[17-19] spectroscopic and reactivity properties of hydrocarbon F-T catalysts.[20] Considering highly C_2-oxygenate-selective Rh/ZrO_2 as representative[21,22] of heterogeneous oxygenate catalysts, the synthesis of a "homogenous Rh/Zr interface" was deemed appropriate. Herein is described the preparation of an "A-frame"[23] complex which produces oxygenates when subjected to electrophiles.

The addition of 2 equiv of $HOCH_2Ph_2P$[24] to Cp^*ZrMe_3 (**1**, $Cp^* = \eta^5\text{-}C_5Me_5$)[25] afforded white crystalline $Cp^*MeZr(OCH_2Ph_2P)_2$ (**2**)[26] in good yield (89%, eq 1). Treatment of **1** with 0.5 equiv

$$\underset{\mathbf{1}}{Cp^*ZrMe_3} + 2HOCH_2Ph_2P \xrightarrow[\text{hexane, 25 °C}]{-2CH_4} \underset{\mathbf{2}}{Cp^*MeZr(OCH_2Ph_2P)_2} \quad (1)$$

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