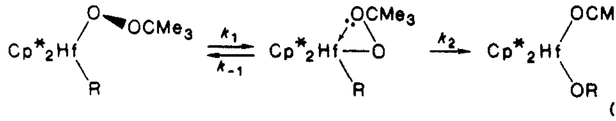

(8)

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.

Acknowledgment. This work was supported by the National Science Foundation (Grant CHE-8303735), by the USDOE Office of Energy Research, Office of Basic Energy Sciences (Grant DE-FG03-85ER13431), by Du Pont, and by Shell Companies Foundation, which are gratefully acknowledged. National Science Foundation Grant CHE-8219039 to the divisional X-ray diffraction facilities is also gratefully acknowledged.

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.

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(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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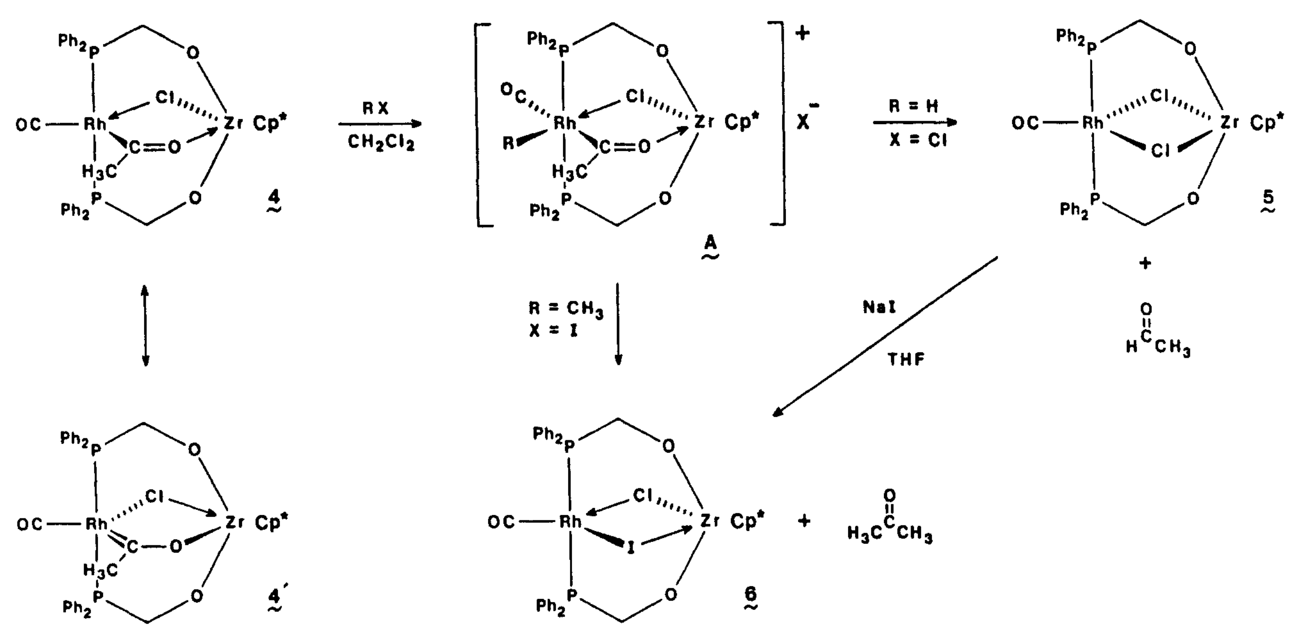
Scheme I



of $[(OC)_2RhCl]_2$ (**3**) provided the $\mu_2{:}\eta^2$-acetyl[18,19] "A-frame" $Cp^*Zr(\mu\text{-}OCH_2Ph_2P)_2(\mu_2{:}\eta^2\text{-}O{=}C(CH_3))(\mu\text{-}Cl)RhCO$ (**4**), as yellow crystals (75%, eq 2). NMR and IR spectra[27] are consistent

$$\mathbf{2} + {}^1/_2\underset{\mathbf{3}}{[(OC)_2RhCl]_2} \xrightarrow[\text{toluene, 25°C}]{} \underset{\mathbf{4}}{Cp^*Zr(\mu\text{-}OCH_2Ph_2P)_2(\mu_2{:}\eta^2\text{-}O{=}C(CH_3))(\mu\text{-}Cl)RhCO} \quad (2)$$

with the structure indicated in Scheme I. Inequivalent methylene protons and a clean $^{31}P\{^1H\}$ doublet (δ 22.92, J_{RhP} = 149 Hz) characterized the *trans*-PPh_2CH_2O bridges. Coupling constants [$^{13}C\{^1H\}$ δ 195.18 (RhCO, J_{CP} = 15, J_{CRh} = 52, J_{CC} = 29 Hz), 309.22 ($(CH_3)C{=}O$, J_{CP} = 11, J_{CRh} = 30, J_{CC} = 29 Hz)] consistent with a tbp Rh core were obtained through ^{13}CO exchange of the terminal CO to give **4**-^{13}C and use of 50% ^{13}CO-enriched **3** to yield **4**-$^{13}C_2$ (statistically 25%). The weak IR band at 1490 cm^{-1} ($\nu(^{13}C{=}O)$ = 1460 cm^{-1}) and the δ 309.22 ^{13}C chemical shift are in accord with a $\mu_2{:}\eta^2$-acetyl that incorporates a strong contribution from the alternate $\mu_2{:}\eta^2$-oxycarbene resonance form (**4′**).[8,18,19,28] Inspection of molecular models indicated that the Cl is likely to be proximate to Rh. A-frame **4** was presumably produced via cleavage of **3** by **2**, chelate formation, and subsequent insertion of free or bound CO into a ZrMe or RhMe (via chloride for Me binuclear exchange)[29] bond accompanied by acyl rearrangement. The Rh(I) center linked to the alkoxyzirconium moiety appropriately models a heterogeneous Rh/ZrO_2 interface while avoiding intimate Rh/Zr contact.

The reactivity of **4** with electrophiles is illustrated in Scheme I. Exposure of **4** to 1 equiv of HCl resulted in the formation of acetaldehyde (61% by GC/MS, ^1H NMR),[19] concomitant with $Cp^*Zr(\mu\text{-}OCH_2Ph_2P)_2(\mu\text{-}Cl)_2RhCO$ (**5**, 68%).[30] A convenient synthesis of **5** was accomplished through reflux of a $CHCl_3$ solution of **4**.[31] Treatment of **4** with methyl iodide (1 equiv) provided acetone (89%) in addition to $Cp^*Zr(\mu\text{-}OCH_2Ph_2P)_2(\mu\text{-}Cl)(\mu\text{-}I)RhCO$ (**6**, 85%),[32] which could also be prepared from NaI and **5**. When **4**-^{13}C was subjected to HCl and CH_3I, the respective CH_3CHO and $(CH_3)_2CO$[33] products contained >98% ^{12}CO (^1H NMR, IR) in accord with direct cleavage of the bridge. The similarity in reaction conditions and products suggested that both electrophilic cleavages arise from attack at Rh (A). Tentative spectroscopic evidence for the putative intermediate resulting from HCl attack was obtained. A rhodium hydride [δ −15.21 (dt, J_{RhH} = 28, J_{PH} = 9 Hz)], inequivalent methylene protons, a new acetyl (δ 1.05), and *t*-PPh_2CH_2O bridges [$^{31}P\{^1H\}$ NMR δ 14.26 (J_{RhP} = 98 Hz)] implicated a structure such as $[Cp^*Zr(\mu\text{-}OCH_2Ph_2P)_2(\mu_2{:}\eta^2\text{-}O{=}C(CH_3))(\mu\text{-}Cl)Rh(CO)H]Cl$ (A)[34] or a similar nonionic formulation. Corresponding CO stretches at 2097 and 1542 cm^{-1} intimated that the intermediate contains a Rh(III) center[35] with an intact $\mu_2{:}\eta^2$-acetyl bridge.

Despite strong binding to the Zr, the $\mu_2{:}\eta^2$-acetyl undergoes facile reductive elimination upon protolysis, implying that a similar pathway is reasonable for heterogeneous H_3CCHO formation.[3] It has been suggested that surface acetates may be penultimate intermediates on the pathway to acetaldehyde.[5,10] Note that the

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(26) Anal. Calcd for **2**, $ZrP_2O_2C_{37}H_{42}$: C, 66.14; H, 6.30. Found: C, 65.86; H, 6.22. ^1H NMR (C_6D_6) δ 0.02 (s, CH_3, 3 H), 1.82 (s, Cp*, 15 H), 4.77 (d, CH_2, 4 H, $^2J_{PH}$ = 7.4 Hz), 7.11 (m, Ph, 8 H), 7.53 (m, Ph, 12 H); $^{31}P\{^1H\}$ NMR δ −11.24; $^{13}C\{^1H\}$ NMR δ 10.59 (Cp*), 27.76 (H_3C), 71.47 (d, CH_2, J_{PC} = 9.9 Hz), 118.64 (Cp*), 128.54 (Ph-C(3)), 128.83 (Ph-C(4)), 133.56 (d, Ph-C(2), $^2J_{PC}$ = 17.6 Hz), 137.68 (dd, Ph-C(1), $^1J_{PC}$ = 14.3, $J_{P'C}$ = 2.2 Hz).

(27) Anal. Calcd for **4**, $RhZrClP_2O_4C_{39}H_{42}$: C, 54.07; H, 4.89; Cl, 4.09. Found: C, 53.86; H, 5.04; Cl, 4.44. ^1H NMR (CD_2Cl_2) δ 1.47 (t, CH_3, 3 H, $^4J_{PH}$ = 1.3 Hz), 2.05 (s, Cp*, 15 H), 4.66 (ddt(v), C*H*H, 2 H, ^2J = 11.4, $^3J_{RhH}$ ~ 1, J_{PH} = 3 Hz), 5.05 (ddt(v), CH*H*, 2 H, ^2J = 11.4, $^3J_{RhH}$ ~ 2, J_{PH} ~ 1 Hz), 7.39 (m, Ph, 12 H), 7.63 (m, Ph, 8 H); $^{31}P\{^1H\}$ NMR δ 22.92 (d, J_{RhP} = 149 Hz); ^{13}C NMR δ 11.44 (Cp*), 40.16 (H_3C), 72.53 (t(v), CH_2, J_{PC} = 18 Hz), 121.58 (Cp*), 128–134 (Ph), 195.18 (CO (**4**-$^{13}C_2$), ddt, J_{RhC} = 52, J_{CC} = 29, $^2J_{CP}$ = 15 Hz), 309.22 (*C*(CH_3)O- (**4**-$^{13}C_2$), ddt, $^2H_{RhC}$ = 30, $^2J_{CC}$ = 29, $^2J_{PC}$ = 11 Hz); IR (**4**/**4**-$^{13}C_2$, CD_2Cl_2) ν(CO) 2014/1969 cm^{-1}, $\nu(H_3CC{=}O)$ 1490/1460 cm^{-1}. Conductivity measurements were consistent with a neutral formulation.

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(30) Anal. Calcd for **5**, $RhZrCl_2P_2O_3C_{37}H_{39}$: C, 51.75; H, 4.58; Cl, 8.26. Found: C, 51.49; H, 4.59; Cl, 8.10. ^1H NMR (CD_2Cl_2) δ 2.02 (s, Cp*, 15 H), 5.15 (s, CH_2, 4 H), 7.45 (br s, Ph, 12 H), 7.68 (m, Ph, 8 H); $^{31}P\{^1H\}$ NMR δ 29.41 (d, J_{RhP} = 122 Hz); IR (Nujol) ν(CO) 1998 cm^{-1}.

(31) In $CDCl_3$, trace H_3CCHO was observed; if DCl is formed, H/D exchange with protic sources (probably the walls of the tube) must be facile.

(32) Anal. Calcd for **6**, $IRhZrClP_2O_3C_{37}H_{39}$: C, 46.77; H, 4.14; Cl, 3.73; I, 13.36. Found: C, 46.61; H, 4.27; Cl, 3.63; I, 13.21. ^1H NMR (CD_2Cl_2) δ 2.12 (s, Cp*, 15 H), 5.33 (d, C*H*H, 2 H, ^2J = 12 Hz), 5.45 (dt(v), CH*H*, 2 H, ^2J = 12, J_{PH} = 1.6 Hz), 7.29 (m, Ph, 4 H), 7.51 (m, Ph, 12 H), 7.78 (m, Ph, 4 H); $^{31}P\{^1H\}$ NMR δ 23.42 (d, J_{RhP} = 127 Hz); IR (Nujol) ν(CO) 1994 cm^{-1}.

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(34) HCl + **4**; intermediate A: ^1H NMR (CD_2Cl_2) δ −15.21 (dt, RhH, 1 H, J_{RhH} = 28, J_{PH} = 9 Hz), 1.05 (t, CH_3, 3 H, J_{PH} < 1 Hz), 2.10 (s, Cp*, 15 H), 5.10 (dt(v), C*H*H, 2 H, ^2J = 12, J_{PH} = 3 Hz), 5.60 (d, CH*H*, 2 H, ^2J = 12 Hz), 7.45 (m, Ph, 12 H), 7.79 (m, Ph, 4 H), 8.02 (m, Ph, 4 H); $^{31}P\{^1H\}$ NMR δ 14.26 (d, J_{RhP} = 98 Hz); IR (from **4**/**4**-$^{13}C_2$, CD_2Cl_2) ν(CO) 2097/2050 cm^{-1}; $\nu(H_3CC{=}O)$ 1542/1508 cm^{-1}.

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μ_2:η^2-acetyl (4) IR absorption[18,19] falls within the regime of these proposed surface species. The course of oxygenate production may utilize H_{ads} or proton transfers from Rh/support H_2O and ZrOH[22] functionalities in effecting acyl reductive elimination. Compensation for the loss of the Zr-O link in **4** is ultimately provided by the X of the electrophile. The corresponding oxygenate release in a heterogeneous system could be accompanied by the formation of a new Zr-O bond arising from a similar carbonyl-derived intermediate, a neighboring zirconium oxide/hydroxide,[22] or water.

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Circular Dichroism of a Subnanosecond State: (Δ)-Fe(bpy)$_3$$^{2+}$*

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We recently presented the first time-resolved circular dichroism (CD) spectrum of a molecular excited state in a report on the CD of the luminescent (MLCT) state of (Δ)-Ru(bpy)$_3$$^{2+}$.[1] The small CD observed in the bpy$^-$ $\pi\pi^*$ transition at 370 nm ($\Delta\epsilon \approx -3$) is consistent with a single-ligand localized model for the transferred electron in the excited state. We report here the excited-state absorption and CD spectra of (Δ)-Fe(bpy)$_3$$^{2+}$. Like Ru(bpy)$_3$$^{2+}$, the ground state of Fe(bpy)$_3$$^{2+}$ is low-spin d^6. Yet unlike Ru(bpy)$_3$$^{2+}$, its lowest excited state is a metal-centered d-d state.[2-5] Thus, differences are expected in excited-state absorption and CD spectra of these two molecules. We found a large CD in the ligand $\pi\pi^*$ transitions of the excited (Δ)-Fe(bpy)$_3$$^{2+}$, consistent with a metal-centered excited state. Since the excited-state lifetime of Fe(bpy)$_3$$^{2+}$ is 800 ps at room temperature in water,[2,6] this is the first report of a CD spectrum of a state that lives for less than a nanosecond.

Creutz et al. previously obtained the absorption spectrum of excited Fe(bpy)$_3$$^{2+}$ in the visible and near-UV regions down to approximately 310 nm and observed no significant charge-transfer transient absorptions.[2] Figure 1 shows the transient absorption spectrum extended to 280 nm.[7] Because of the short lifetime of the excited state, it was not possible to achieve saturation of the excited state with excitation energies of up to 30 mJ/pulse. We thus used the degree of bleaching observed at 488 nm, a wavelength with no significant excited-state absorption,[2] to correct for ground-state bleaching and produce the true excited-state spectrum. This absorption has slightly lower intensity and exhibits a small red shift relative to the ground-state $\pi\pi^*$ absorption. Clearly, this excited-state absorption can be assigned as primarily ligand $\pi\pi^*$.

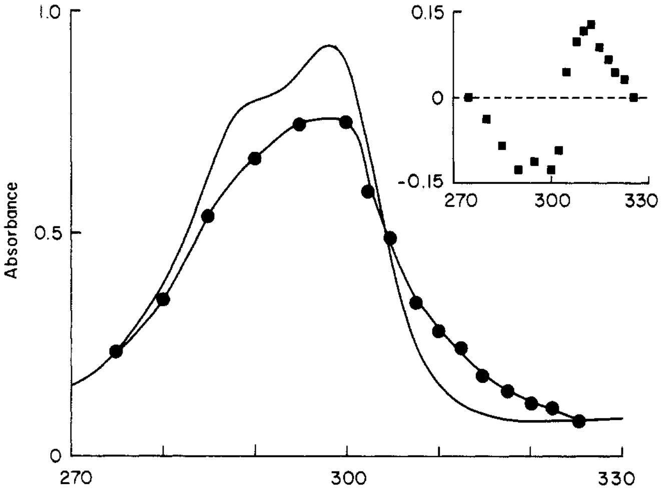

Figure 1. Ground-state absorption spectrum (—) and excited state absorption spectrum (●) of Fe(bpy)$_3$$^{2+}$ in the $\pi\pi^*$ region. Inset: The transient difference spectrum extrapolated to complete ground-state depletion (excited-state production).

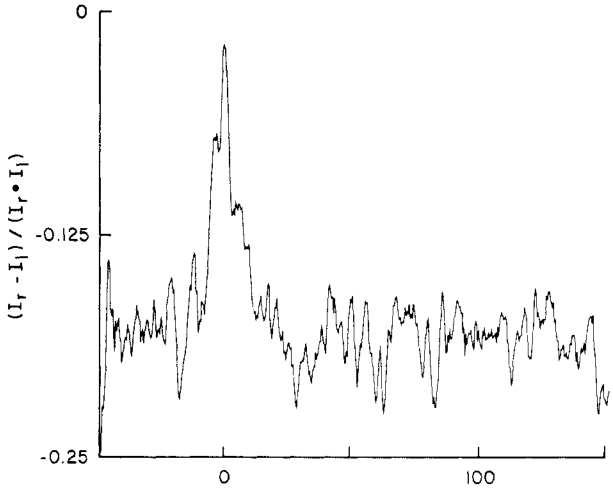

Figure 2. An example of the transient CD signal, representing the average of 256 measurements, seen at 297.5 nm. The signal $(I_r - I_l)/(I_r + I_l)$ is equal to $\Delta\epsilon(2.3cl/\delta)$, where the concentration of (Δ)-Fe(bpy)$_3$$^{2+}$ in water is 4.0×10^{-5} M, the path length is 0.2 cm, and the retardation in the probe beam strain plate, δ, is 0.018 rad (see ref 8). Excitation was with a 532-nm, 30-mJ, 4-ns pulse. A maximum of 0.5 of the chromophores within the probe beam were excited at any time during the laser pulse.

The excited-state CD of (Δ)-Fe(bpy)$_3$$^{2+}$ was obtained by using the laser photolysis apparatus used for transient absorption work with the probe beam optics modified for CD measurements as described in ref 8. Figure 2 shows a typical signal when half of the (Δ)-Fe(bpy)$_3$$^{2+}$ within the probe beam is excited at the maximum of the laser pulse. The width of the transient signal is a function of the excited-state lifetime, the excitation pulse width, and the response time of the detection system.

The actual CD signal of the excited state, rather than the change in CD upon excitation, was determined by applying a correction to the change in the signal obtained at the maximum of the laser excitation. The degree of ground-state depletion (excited-state production) at the maximum of the laser pulse was determined, and the change in the CD signal was divided by this value and then added to the ground-state CD to give the excited-state CD. The ground state racemizes quickly,[9,10] with a

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