spatial separation of Ru^{3+} and BV^{+} and may be limited by the fact that the potentials of the $2DQ^{2+/+}$ and $BV^{2+/+}$ couples are separated by only 160 mV, so that back electron transfer from BV^{+} to Ru^{3+} via $2DQ^{2+/+}$ is possible. It is likely that isoenergetic electron exchange along the BV^{2+} chain depicted in Scheme I significantly enhances the charge-separated state lifetime; in zeolite Y this electron-hopping rate, measured electrochemically,[10a] is on the order of 10^5 s^{-1}. We note finally that this self-assembling zeolite-based triad resembles the membrane-bound special pair–pheophytin–quinone triad in the reaction center of photosynthetic bacteria;[16] there, a similar spatial arrangement and ordering of redox potentials contribute to two extremely fast forward electron-transfer steps and to a long-lived charge-separated state.[17]

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Organometallic Dioxygen Activation: Formation of (Pentamethylcyclopentadienyl)chromyl Dibromide

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We wish to describe an unusual example of an organometallic process for the activation of dioxygen as oxide. In our search for organometallic oxidants,[1] we had found that the $CpMCl_3^{0/-}$ electrochemical couple increases 750 mV by changing from M = Ti to M = V. This observation prompted an examination of (cyclopentadienyl)chromium halides and oxohalides. Complexes of the type $[CpCrX_2]_2$ (Cp = η^5-C_5H_5) are well known, but their redox properties have not been reported.

Reaction of $[Cp^*Cr(CO)_2]_2$[3] (Cp^* = η^5-C_5Me_5) with excess Br_2 in CH_2Cl_2 produces a green microcrystalline solid after filtration and solvent removal.[4] Extraction of the solid with THF yields blue $[Cp^*CrBr_2]_2$ (**1**) isolated in 97% yield.[5] Analogous to the known $[CpCrCl_2]_2$,[6] **1** can be described as *trans*-$[Cp^*CrBr(\mu\text{-}Br)]_2$ with Cr–Br distances of 2.521 (5) Å (av, bridging) and 2.437 (3) Å (terminal).[4]

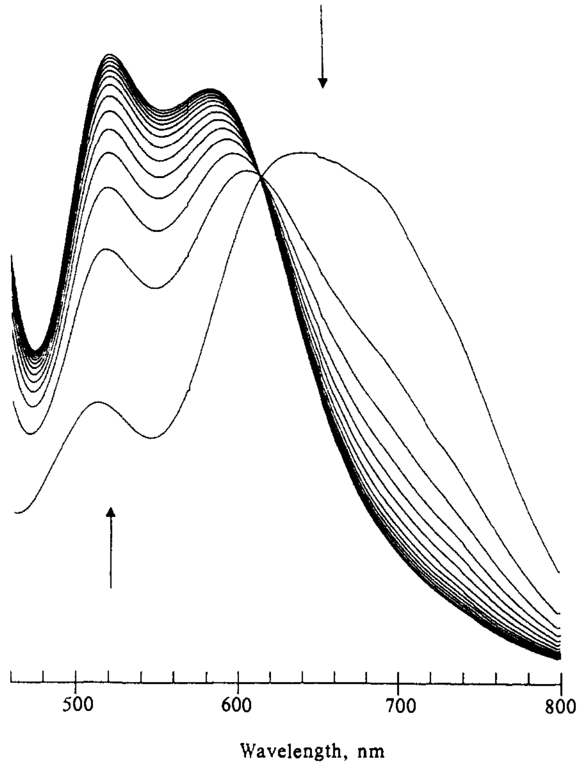

Figure 1. Sequential UV–vis spectra for the oxygenation of $[Cp^*CrBr_2]_2$ (**1**) in CH_2Cl_2 (0.001 M [**1**], 0.34 M [THF], ca. 3 atm P[O_2], Δt = 5 min). The first scan is that *after* addition of O_2, and the arrows indicate positions of initial and final maxima.

The instability of monomeric Cp^*CrBr_x ($x > 2$) from **1** and Br_2 led us to next attempt the synthesis of a mixed oxo–halo chromium complex. The π-donating ability of the oxo group has a decidedly strong influence on the redox properties of organometallic compounds. For example, the recently reported $[Cp^*CrO_2]_2$,[7] despite its label as a high oxidation state complex, is not oxidizing. This species is electrochemically reduced only at quite negative potentials ($E_{1/2}$ = −1360 mV vs Ag/AgCl).

Dilute solutions of **1** (≤2 mM) in CH_2Cl_2 react within minutes with dry O_2 to form red Cp^*CrOBr_2 (**2**), isolated in 97% yield.[8] The rate of this oxidation is slowed by coordinating solvents such as THF or CH_3CN. When this transformation (with added THF) is monitored by optical spectroscopy, we observe a clean isosbestic point at 612 nm (Figure 1). Interestingly, concentrated solutions of **1** (≥100 mM) are not noticeably O_2 sensitive. Furthermore, the μ-oxo compound $[Cp^*CrBr_2]_2O$ is not observed when solutions of **1** and **2** are combined. Compound **1** represents one of the few isolable complexes which cleanly *adds* oxygen to give an oxide.[9,10] Further mechanistic and thermodynamic studies of the relationship

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(4) We have fully characterized the *adduct* $[Cp^*CrBr_2]_2\cdot Br_2$. This species will be described separately, as will the structure of $[Cp^*CrBr_2]_2$.

(5) Anal. Calcd for $C_{10}H_{15}CrBr_2$: C, 34.61; H, 4.36; Cr, 14.98. Found: C, 34.64; H, 4.39; Cr, 14.92. ^1H NMR ($CDCl_3$/TMS, 293 K) δ −58.

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(8) Anal. Calcd for $C_{10}H_{15}CrOBr_2$: C, 33.09; H, 4.16; Cr, 14.32. Found: C, 33.18; H, 4.08; Cr, 14.23. ^1H NMR ($CDCl_3$, 293 K) δ −12.

(9) Oxygen addition: (a) Ru(porphyrin): Groves, J. T.; Ahn, K.-H. *Inorg. Chem.* **1987**, *26*, 3831. (b) $[Cp^*ReO_2]_2$: Herrmann, W. A.; Serrano, R.; Bock, H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 383. (c) $MoO(dtc)_2$: Watt, G. D.; McDonald, J. W.; Newton, W. E. *J. Less-Common Metals* **1977**, *54*, 415. (d) $(Cp)_2NbCl$: Lemenovskii, D. A.; Baukova, T. V.; Fedin, V. P. *J. Organomet. Chem.* **1977**, *132*, C14.

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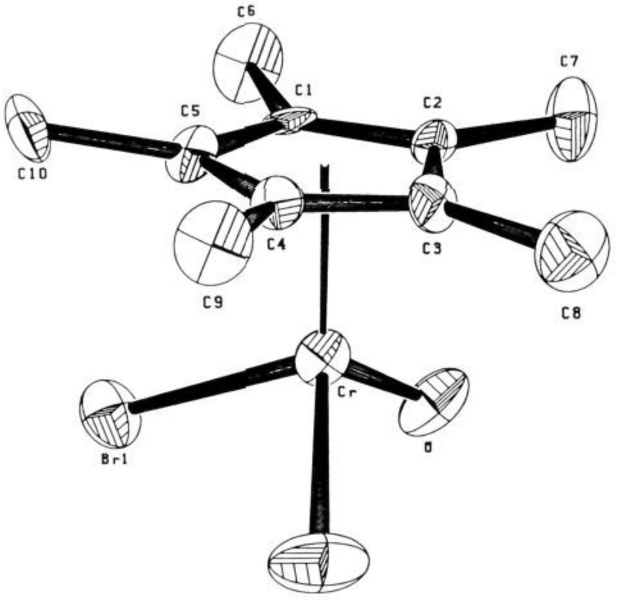

Figure 2. ORTEP view of Cp*CrOBr$_2$ (**2**) with ellipsoids drawn at the 35% probability level.

between **1**, **2**, and O$_2$ are planned.

Magnetic susceptibility measurements (SQUID) on microcrystalline samples of **2** (μ_{eff} (300 K) = 2.02 μ_B, μ_{eff} (5 K) = 1.73 μ_B) indicate that **2** has a larger ground-state orbital contribution than vanadyl (VO^{2+}) complexes.[1,11] The IR spectrum of **2** shows a band at 934 cm^{-1} ($\nu_{Cr=O}$); isotopic labeling[12] using $^{17,18}O_2$ resulted in additional absorptions at 917 and 900 cm^{-1}. A crystallographic study shows that **2** adopts a typical piano-stool geometry with very short Cr–O[7,12a] (1.58 (2) Å) and Cr–Br (2.393 (4) and 2.375 (5) Å) distances (Figure 2).[13] The substantial contraction of the Cr–Br bonds upon conversion to the oxide indicates Cr–Br π-bonding in **2**.

The metastability of **2** is indicated by the ease with which it reverts to **1**. Proton NMR studies at 80 °C (hexamethylbenzene as internal standard) indicate that **2** gives **1** in 75% yield over the course of 1.5 h. Upon photolysis in CH$_2$Cl$_2$, **2** reverts to **1** in the same yield. Concentrated solutions of **2** tend especially to revert to **1**, and our attempts to grow crystals of **2** were often frustrated by this instability. Coordinating solvents also tend to convert **2** into Cp*CrBr$_2$·L (L = THF, CH$_3$CN). Careful addition of Br$_2$ to solutions of **2** as well as electrochemical reduction of **2** at −140 mV results in concomitant deoxygenation to give **1**. In the thermal conversions (toluene) of **2** to **1**, ^{18}O-labeling studies in conjunction with GC–MS analyses[14] indicate that the final oxygen-containing species are polychromates (50%), "Cp*OH" (20%), water (10%), and oxidized solvent (e.g., PhCH$_2$OH and PhCHO from toluene). In the photochemical conversion (CH$_2$Cl$_2$), the major oxygen-containing products are polychromates (70%) and water. Notably, O$_2$ is not liberated in these reactions.

The electrophilic character of **2** is indicated by its ability to oxygenate electron-rich substrates. Phosphines (PPh$_3$, P(^{n}Bu)$_3$) readily abstract oxygen from **2**; ^{31}P NMR experiments show that the oxidation of PPh$_3$ is catalytic (CH$_2$Cl$_2$: 0.25 M PPh$_3$, 0.003 M **1**; initial TON ≈ 27 phosphines/20 min at 20 °C). While the metal-catalyzed oxygenation of phosphines is not unusual,[15] our observations do demonstrate the ability of **1** to *repeatedly* activate O$_2$ without decomposition. Compound **2** will not oxygenate Et$_2$S, but CpCrOBr$_2$[16] will. This indicates that the electrophilicity of this class of oxo compounds can be adjusted by substituents on the cyclopentadienyl group.

In conclusion, [Cp*CrBr$_2$]$_2$ is an unusual organometallic complex which activates molecular oxygen. Work is underway to see if this family of organometallic compounds has a future either as oxidants in synthesis or as oxygen carriers.

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Supplementary Material Available: Tables of positional and thermal parameters and bond distances and angles for **2** (2 pages); table of observed and calculated structure factors for **2** (5 pages). Ordering information is given on any current masthead page.

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(13) Cp*CrOBr$_2$: opaque plate 0.2 × 0.3 × 0.6 mm, orthorhombic, $P2_12_12_1$, a = 6.616 (2) Å, b = 14.144 (5) Å, c = 13.664 (6) Å, V = 1278.6 (9) Å^3, and ρ_{calcd} = 1.886 g/cm^3 for Z = 4. Syntex P2$_1$ automated four-circle diffractometer, 26 °C, Mo ($K\bar{\alpha}$ = 0.71073 Å) $3.0 < 2\theta < 46.0°$ ($+h+k+l$) and $3.0 < 2\theta < 15.0°$ ($\mp h \mp k \mp l$), 1402 reflections (1071 unique, R_i = 0.037, 863 observed, $I > 2.58\sigma(I)$); corrected for anomalous dispersion, absorption (maximum and minimum transmission factors, 0.340 and 0.132 for μ = 70.35 cm^{-1}), Lorentz and polarization effects. Direct methods (SHELXS-86) located Br and Cr atoms; difference Fourier synthesis revealed C and O atoms. H atoms were not included in structure factor calculations. Non-H atoms were independently refined with anisotropic thermal coefficients. Variance between observed and calculated structure factors slightly dependent upon amplitude and inverse sin(θ). R = 0.077 and R_w = 0.098.

(14) Reaction solutions were analyzed by GC–MS using a methyl silicone gum column (H$_2$O, PhCH$_2$OH, PhCHO). After evaporation of the solvent, the residue was extracted with CH$_2$Cl$_2$ and analyzed by FD–MS (Cp*OH). The CH$_2$Cl$_2$-insoluble solid contained the majority of the label; it was extracted with methanol and assayed for CH$_3$^{18}OH by GC–MS.

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(16) Prepared from Cp$_2$Cr and Br$_2$ followed by oxygenation to give CpCrOBr$_2$. Anal. Calcd for C$_5$H$_5$CrOBr$_2$: C, 20.50; H, 1.72; Cr, 17.75. Found: C, 21.58; H, 1.78; Cr, 17.86. ^{1}H NMR (CD$_2$Cl$_2$, 295 K) δ 168; E_p (CH$_2$Cl$_2$, TBAHFP, Ag/AgCl) 120 mV.

Synthesis and Structure of a Tungstacyclopentatriene

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Metallacyclic compounds of the transition elements constitute an important class of organometallic species, implicated in a wide range of both stoichiometric and catalytic reactivity.[2-6] Besides

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