Novel Properties of Several High Oxidation State
Organometallic Materials

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The term "high oxidation state" is often interpreted to mean electron defi-
cient. A decisive measure of electron deficiency is the electrochemical reduction
potential of a complex, and by this gauge most organometallic complexes are not
oxidants. This is generally true because many high oxidation state complexes are
of the second and third transition rows, often with strongly π-donating ligands.
A clear example of this is the popular $Cp*ReO_3$ ($Cp* = \eta^5-C_5Me_5$),[1] which is reduced
only at a very negative potential of -1430 mV[3] (vs. Ag/AgCl). Recent work has
begun determining the characteristics of highly oxidizing organometallics, and how
to systematically synthesize them.

Our studies have focused on the class of first transition row compounds $CpMX_3$
($Cp = \eta^5-C_5R_5$, R = H, Me; X = halide or oxide) as stable organometallic analogues[3]
of VCl_4, $VOCl_3$, and $CrOCl_3$. The synthetic rationale developed involves control of
ligand π-donor character such that the metal remains truly electron deficient.
Thus, the vanadium(IV) complex $CpVCl_3$[2] is some 150 mV more oxidizing[3] than the
vanadium(V) complex $CpVOCl_2$. This lecture will discuss several unique systems
discovered during the investigation of high oxidation state/highly oxidizing
organometallics.

One example concerns the limitations in use of oxide to stabilize high valent
metals. For instance, the chromium(V) complex $[Cp*CrO_2]_2$[4] is reduced only at
-1360 mV (vs. Ag/AgCl). This knowledge, combined with the inability to synthesize
(monomeric) $Cp*CrBr_3$, led us to pursue a mixed oxo-halo complex of $Cp*Cr$. To our
surprise, the high-spin complex $[Cp*CrBr_2]$ cleanly activates molecular oxygen to
produce $Cp*CrOBr_2$.[5] This process is uniquely dependent upon concentrations: only
at low chromium concentration does the reaction noticeably proceed.

The oxide in $Cp*CrOBr_2$ is loosely bound and the complex will oxidize phos-
phines, while its analog $CpCrOBr_2$ will oxidize organic sulfides. Oxide loss can
also be promoted by thermolysis or photolysis, resulting in ca. 75% conversion
back to $[Cp*CrBr_2]_2$. In the absence of electrophilic substrates, the loss of
oxide begins with oxygen attack on a $Cp*$ ligand. Once decomposition products are
formed, they become the primary oxygen trap in the system. Reversion of oxide to
dioxygen is not a favorable process.

$$[Cp*CrBr_2]_2 + O_2 \longrightarrow 2\ Cp*CrOBr_2 \xrightarrow{+R} OR$$
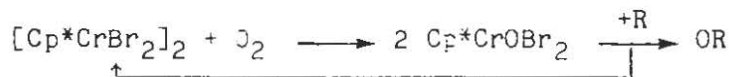
An additional success found during the development of highly oxidizing organ-
ometallics was in the area of charge transfer salt syntheses. Such materials
have received considerable attention with the synthesis of the molecular ferromag-
net $[(Cp*)_2Fe][tetracyanoethylene]$.[6] Complexes such as $CpVX_3$ can be used as
stable electron acceptors in the preparation of charge transfer salts.[7] Combina-
tion of $(MeCp)VCl_3$ with the organic donor tetramethyltetrathiofulvalene (TmTTF)
produces a series of novel salts of the composition $[TmTTF]_n[(MeCp)VCl_3]$ (n = 1,
2). By "advantageous" oxidation of $[TmTTF]_2[(MeCp)VCl_3]$, the mixed-valence cation
and anion salt $[TmTTF]_3[\{(MeCp)VCl_2\}_2O]_2$ was produced.

This 1-dimensional material is comprised of TmTTF stacks separated by μ-oxo vanadium dimers. Single crystals display highly cooperative and field dependent magnetic behavior. At low fields, a ferromagnetic state is present between ca. 50K and 3.5K, with principle interactions perpendicular to the stacking axis. This classifies the materials as an XY ferromagnet, apparently the first such established. At high applied fields, an antiferromagnetic state is present. This low to high field transition is opposite that observed for classical metamagnets: low field antiferromagnetism and high field ferromagnetism. The associative properties of this material are derived from the limited orbital interactions between cation and anion stacks, as well as long range ordering within the spin centers.

Preparation of the pseudo-halides $CpMX_3$ can only be extended to a point--that determined by the oxidizing potential of the free halogen. For instance, VCl_4 is stable under ambient conditions, while VBr_4 decomposes to VBr_3 and Br_2.[8] The systematic investigation of the vanadium and chromium iodides has led us to discover how iodine Lewis acid/base behavior can directly reflect metal oxidation states. We have been successful in synthesizing the series $Cp*CrI_x$ (x = 3, 5.5) and $CpVI_3$ which display such behavior.

The chromium iodides exist as polymers, and are related to each other by the influence of excess iodine. The material $\{Cp*CrI_3\}_n$ consists of infinite chains of triiodide linked dimers, $\{[Cp*CrI(I_3)]_2 \cdot [Cp*CrI_2]_2\}_n$. Upon treatment with excess I_2, iodide abstraction occurs forming $[(Cp*)_2Cr_2(\mu-I)_3]^+$ dimers and a poly(iodine-iodide) network based on the novel polyiodide I_{16}^{2-}. The iodide in this anion is coordinated by four I_2 molecules, each bridging to other iodines or to another iodide. This material is apparently formed by the Lewis acid attack of iodine on the electron rich iodides of $Cp*Cr^{2+}$, yielding an "inverted coordination complex" within which the organometallic moieties are encapsulated:

$$[Cp*CrI_2]_2 + 3\ I_2 \longrightarrow [(Cp*)_2Cr_2I_3]^+\ I_2 \leftarrow (I^-) \Rightarrow (I_2)_2.$$
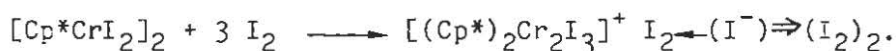
The vanadium iodide $CpVI_3$ forms despite the notion that iodide should not be able to support a vanadium(IV) oxidation state. Solutions of the complex display two ^1H NMR signals and solvent/concentration behavior which suggests a high degree of association. The solid displays magnetic behavior at room temperature which is typical of a d^1 complex, but becomes nearly diamagnetic below ca. 50K. Characterization of the solid state by crystallography indicates that the complex adopts a traditional $CpML_3$ piano-stool configuration, but with significant iodide-iodide contacts. These close contacts between iodides indicates significant Lewis acid behavior, reflecting the unfavorable oxidation state of the vanadium. Contraction of the lattice with decreasing temperature occurs largely along these contacts (as determined by variable temperature crystallography), and in combination with magnetic susceptibility data suggests that the best formulation of the material is $\{CpVI_3\}_n$ or even $\{CpVI(\eta^1-I_2^-)\}_n$:

$$2n\ CpVI_3 \longrightarrow \{"V \leftarrow I \cdots I-V"\}_n.$$

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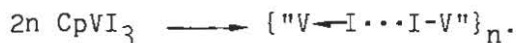
References

1.   Okuda, J.; Herdtweck, E. and Herrmann, W. A. Inorg. Chem. 1988, 27, 1254.

2.   Fischer, E. O.; Vigoureux, S. and Kuzel, P. Chem. Ber. 1960, 93, 701.
     Thiele, von, K.-H. and Oswald, L. Z. Anorg. Allg. Chem. 1976, 423, 231.

3.   Morse, D. B.; Hendrickson, D. N.; Rauchfuss, T. B. and Wilson, S. R.
     Organometallics 1988, 7, 496.

4.   Herberhold, M.; Kremnitz, W.; Razavi, A.; Schöllhorn, H. and Thewalt, U.
     Angew. Chem. Int. Ed. Engl. 1985, 24, 69.

5.   Morse, D. B.; Rauchfuss, T. B. and Wilson, S. R. J. Am. Chem. Soc. 1988, 110,
     8234.

6.   Miller, J. S.; Calabrese, J. C.; Rommelmann, H.; Chittipeddi, S. R.; Zhang,
     J. H.; Reiff, W. M. and Epstein, A. J. J. Am. Chem. Soc. 1987, 109, 769.

7.   Morse, D. B.; Rauchfuss, T. B. and Wilson, S. R. J. Am. Chem. Soc. 1988, 110,
     2646.

8.   Greenwood, N. N. and Earnshaw, A. "Chemistry of the Elements," Pergamon
     Press, Oxford, 1984, Chapter 22.