UNIVERSITY OF SOUTHERN CALIFORNIA

DEPARTMENT OF CHEMISTRY

Organic / Materials Chemistry Seminar

"From Chemistry with Weakly Coordinating Anions to Absolute Acidity and Protoelectric Potential Map"

Professor Ingo Krossing
Institut für Anorganische und Analytische Chemie
Albert-Ludwigs- Universitat Freiburg

Wednesday, June 13, 2018
12:00 PM
Olah Library

Hosted by Prof. Karl Christe

Scientific Community is Invited

From Chemistry with Weakly Coordinating Anions to Absolute Acidity and the Protoelectric Potential Map

Ingo Krossing

Institute of Inorganic and Analytical Chemistry, and Freiburg Materials Research Center; Albert St. 21, 79104 Freiburg, Germany, E-mail: krossing@uni-freiburg.de; Website: http://portal.uni-freiburg.de/molchem.

Weakly Coordinating Anions (WCAs): If the surface of a larger, chemically robust anion is terminated by fluorine, its performance as a WCA usually gets better. This is mainly due to the low polarizability of element-fluorine bonds and the capability of fluorine to effectively delocalize the negative charges. The lecture will give an overview to the unusual chemistry enabled by the $[Al(OR^F)_4]^-$ (R^F = fluorinated alkoxide) or related types of WCAs.[1,2]

Coordination Chemistry with X_2 as Ligand: The weakly coordinating nature of the $[Al(OR^F)_4]^-$ WCA allowed for the formation of a larger series of unique silver-dihalogen complex $Ag_m(X_2)_n^{y+}$ salts (six examples out of: m = 1, 2; n = 1-6, y = 1, 2; X = Cl, Br, I).

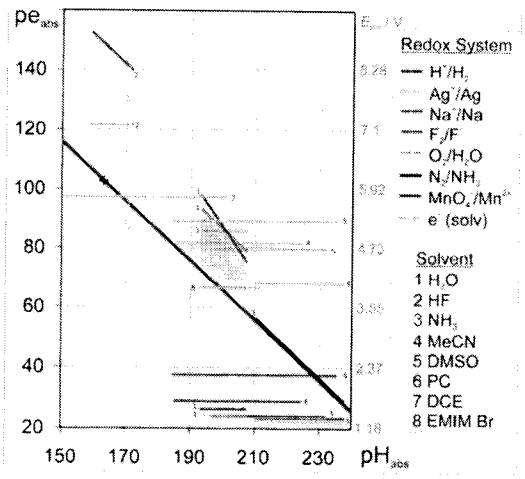
TMCCs, a Starting Point: TMCCs (Transition Metal Carbonyl Cations) are homoleptic carbonyl complexes with strongly blue-shifted "non-classical" CO-stretching frequencies that were almost exclusively prepared in superacids. Using the $[Al(OR^F)_4]^-$ anion, TMCC chemistry could be transferred to solvents like DCM or *o*-$F_2C_6H_4$ and novel species like the open shell $[Cr(CO)_6]^+$ or the first heptacarbonyls $[M(CO)_7]^+$ (M = Nb, Ta) were accessible. The TMCCs and related cations like $[Ni(cod)_2]^+$ are good sources for almost "naked" singly charged TM cations that offer a rich follow up chemistry, i.e. to low-coordinate phosphine-complexes like $[M(P^tBu_3)_2]^+$ (M = Co, Ni).

Cationic Brønsted Acids: With the same WCAs, a series of weakly basic, protonated molecules may be prepared including protonated benzene or 2-norbornyl-cation in organic solvents. However, how can one compare quantitatively the acidity levels vs. classical superacid systems?

Absolute Acidity: We show that the chemical potential changes of the solvated proton with respect to a reference state of maximum acidity – the proton gas – represents a suitable and thermodynamically accurate way to compare acidity over solvent and even phase boundaries on an absolute level.

Absolute Redox Potentials: Similarly, the redox potential of a medium may be set absolute by tying it to the chemical potential of the electron gas as a reference state of maximum reducity.

The Protoelectric Potential Map: The 2D-plot of *absolute acidity* and *reducity* leads to the protoelectric potential map PPM shown below.



The lecture will introduce the individual scales with a strong focus on acidity, and the 2D-plot, give a short overview and show selected applications of the PPM.

Selected References

1.) **Review:** *"Non coordinating anions: fact or fiction? A survey of likely candidates."* I. Krossing*, I. Raabe, *Angew. Chem.* **2004**, *116*, 2116-2142.

2.) **Review:** *„Reactive p-Block Cations Stabilized by Weakly Coordinating Anions."* Tobias A. Engesser, Martin R. Lichtenthaler, Mario Schleep and Ingo Krossing*, *Chem. Soc. Rev.* **2016**, *45*, 789 - 899.

3.) **Review:** *"Basic Remarks on Acidity."* Valentin Radtke, Daniel Himmel, Burkhard Butschke, Ingo Krossing*, *Angew. Chem., Int. Ed.* **2018**, online. http://dx.doi.org/10.1002/anie.201709057