

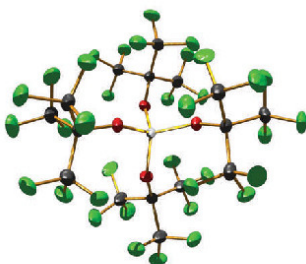


Marcin Gonsior (Autor)  
**From Cationic Silver Complexes to Reactive  
Phosphenium- and Arsenium-Intermediates  
Stabilized by Weakly Coordinating Anions**

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## Chapter A. Introduction to Chemistry with Weakly Coordinating Anions

### A.1 Definition of the Term “Weakly Coordinating Anion” (WCA)

Already in the early 70's it became obvious that commonly used anions like  $[\text{BF}_4]^-$ ,  $[\text{ClO}_4]^-$  and  $[\text{NO}_3]^-$ , considered to be non-coordinating in aqueous solution, coordinate metal cations if only water is excluded.<sup>1, 2</sup> With the advances in structure determination methods by means of spectroscopy and, in particular, by X-ray crystallography, it became evident that in many cases classical “non-coordinating” anions such as  $[\text{CF}_3\text{SO}_3]^-$ ,  $[\text{BF}_4]^-$ ,  $[\text{ClO}_4]^-$ ,  $[\text{AlX}_4]^-$  or  $[\text{MF}_6]^-$  ( $X = \text{Cl} - \text{I}$ ;  $M = \text{P}, \text{As}, \text{Sb}$  etc.) can be coordinated given the suitable counterion.<sup>2</sup> The term “non-coordinating” used with respect to these anions evidently became inadequate. The expression “Weakly Coordinating Anions” that appeared in the literature in the early 90's, more accurately describes the interaction between those anions and their counterions.<sup>3</sup> Since in the last two decades the demand on weakly coordinating anions in terms of their application in catalysis, electrochemistry etc., was growing (and still is), many synthetic efforts have been made in this field so that nowadays the term “Weakly Coordinating Anions” (WCAs) in the literature focuses on the new generation of rather large and chemically robust anions like  $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ ,  $[\text{Sb}(\text{OTeF}_5)_6]^-$ ,  $[\text{CB}_{11}(\text{CF}_3)_{12}]^-$  or  $[\text{Al}(\text{OC}(\text{CF}_3)_3)_4]^-$  (those and other WCAs will be discussed in more detail in chapter A.3).<sup>4, 5</sup>

Which properties transform an anion into a WCA? One criterion is certainly, its coordinating ability, determined by the existence (or accessibility) of the remaining most basic coordinating sites of the anion. In addition the surface charge density of such anions should be minimized with respect to the attraction of electron deficient species. Thus, it follows that the ideal WCA should possess a low negative charge, at best  $-1$ , and should be substituted by many electron withdrawing groups over which the univalent charge is dispersed. In most cases this is achieved by using F containing substituents that build a periphery, which is hardly polarizable. If a basic site, like the O atoms in the  $[\text{Al}(\text{OR}^{\text{F}})_4]^-$  anions ( $\text{R}^{\text{F}}$  = fluorinated alkyl group), is left in the anion, its accessibility can be substantially reduced by using bulky groups, which provide a very important additional kinetic stabilization. Since WCAs are frequently used to stabilize very reactive electrophiles they should only be constructed from chemically inert moieties. Thus, a very weakly coordinating anion is of only little use, if it is unable to survive the attack of its reactive partner! Apparently, this goal can be achieved with various chemically robust

ligands; however, the perfluorinated alkyl groups with strong covalent C–F bonds used throughout this work gave excellent results in this type of chemistry.

## A.2 Applications of Weakly Coordinating Anions in Fundamental and Applied Science

### A.2.1 Stabilization of Reactive Cations and Complexes of Weak Lewis Bases

The existence of charged and in condensed phase hitherto unknown simple species was often detected in experiments within a mass spectrometer.<sup>6-10</sup> In condensed phases those electrophilic and highly reactive “gas phase” cations have to be partnered by a suitable counterion. Some of them can be stabilized with weakly coordinating anions in condensed phases. Thus, they may now be characterized by classical physical methods (X-Ray, NMR, etc). Accordingly, it was possible to prepare salts of  $[\text{O}_2]^+$ <sup>11</sup> and dihalogen  $[\text{X}_2]^+$  cations ( $\text{X} = \text{Br}, \text{I}$ )<sup>12</sup> as well as the  $[\text{Xe}_2]^+$  cation.<sup>13</sup> Only recently also the salts of  $[\text{HC}_{60}]^+$  and  $[\text{C}_{60}]^+$  were fully characterized in the solid state.<sup>14</sup> There are numerous structures of carbocations that were isolated with WCAs, among them also the simple  $[\text{CX}_3]^+$  carbenium ions ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) that earlier on were extensively investigated at low temperature in solution by Olah et al.,<sup>15, 16</sup> but only recently have been characterized by their crystal structure.<sup>17-19</sup>

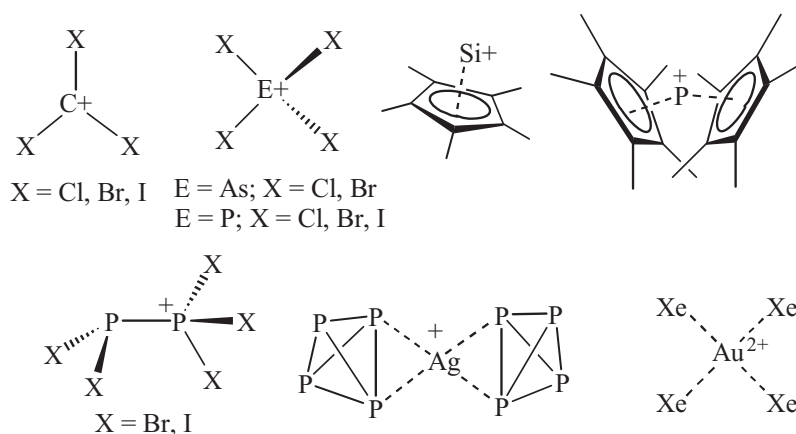


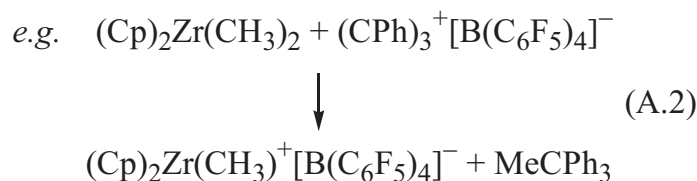
Figure A-1. Exemplary structures of “gas phase cations” and Lewis Acid-Base complexes that were stabilized by WCAs.

WCAs helped to prepare the entire series of  $[\text{PX}_4]^+$  cations ( $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ )<sup>20-25</sup> and two of their arsonium homologues  $[\text{AsX}_4]^+$  ( $\text{X} = \text{Cl}, \text{Br}$ ) while<sup>26-28</sup> the  $[\text{AsF}_4]^+$  and  $[\text{AsI}_4]^+$  cations are still unknown.<sup>29</sup> The rather recent reports on  $[\text{P}_2\text{X}_5]^+$ ,<sup>20, 21</sup>  $[\text{P}_5\text{X}_2]^+$ <sup>20, 30</sup>

(X = Br, I) and  $[\text{P}_3\text{I}_6]^+{}^{21}$  extended the family of the hitherto known only two types of binary phosphorus halogen cations. Other highly reactive species like  $[\text{Mes}_3\text{Si}]^+{}^{31}$ ,  $[\text{N}_5]^+{}^{32}$ , or only very recently synthesized  $[\text{Cp}^*\text{Si}]^+{}^{33}$  and  $[(\text{Cp}^*)_2\text{P}]^+{}^{34}$  were also reported. Unusual or otherwise difficult if at all accessible complexes such as  $[\text{Au}(\text{Xe})_4]^{2+}{}^{35}$ ,  $[\text{Ag}(\text{CO})_2]^+{}^{36}$ ,  $[\text{Ir}(\text{CO})_6]^{3+}{}^{37}$ ,  $[\text{Ag}(\text{L})_2]^+$  (L = P<sub>4</sub>,<sup>38</sup> S<sub>8</sub>,<sup>39</sup> P<sub>4</sub>S<sub>3</sub>,<sup>40</sup>) and  $[\text{Ag}(\text{C}_2\text{H}_4)_3]^+$  could be prepared, when the counterion was a WCA. Thus the chemistry with WCAs is a possibility to stabilize positively charged species that include very special or even unique bonding properties. This principle of stabilizing reactive cationic species with large WCAs of low basicity has to be seen in analogy to the application of large cations to stabilize reactive anions, e.g. complex azide anions such as  $[\text{B}(\text{N}_3)_4]^-{}^{41, 42}$  or  $[\text{As}(\text{N}_3)_6]^-{}^{43}$ , or to large, sterically demanding ligands which are commonly used to stabilize reactive unusual species that otherwise decompose, e.g. metalloidal Al- or Ga-clusters such as  $\text{Al}_{50}\text{Cp}_{12}^*{}^{44}$  or  $[(\text{Ga}_{84}(\text{N}(\text{SiMe}_3)_2)_{20})]^{4-}{}^{45}$ .

### A.2.2 Applications in Catalysis

WCAs are of great importance in homogenous catalysis such as olefin polymerization processes or hydrogenation reactions.<sup>46, 47, 48-51</sup> Metallocenes of the formula  $[(\text{Cp})_2\text{M}(\text{Me})]^+$  that are active catalysts, require a stable and weakly coordinating counterion. The activity and selectivity of the polymerization strongly depends on the counterion. Exemplarily, active Ziegler-Natta polymerization catalysts were generated from  $(\text{Cp})_2\text{M}(\text{Me})_2$  (M = Ti, Zr) and a large excess of the technically used Lewis acid and anion generator methylalumoxane (MAO). Trityl- and tertiary ammonium salts of weakly coordinating anions or simple metallorganic Lewis-acids like  $\text{B}(\text{Ar}^{\text{F}})_3$  ( $\text{Ar}^{\text{F}} = \text{C}_6\text{F}_5$ ) generate very reactive catalysts of a well defined composition (see Equations A.1 and A.2).<sup>46</sup>



It was shown that the activity of a catalyst increases with decreasing coordination ability of the anion:  $[\text{MeB}(\text{Ar}^{\text{F}})_3]^- \ll [\text{B}(\text{Ar}^{\text{F}})_4]^- < [(\text{Ar}^{\text{F}}\text{B})_3\text{-X-B}(\text{Ar}^{\text{F}})_3]^- < [(\text{Ar}^{\text{F}})_3\text{Al-X-Al}(\text{Ar}^{\text{F}})_3]^-$

(X = CN<sup>-</sup>, 1,3-imidazolyl).<sup>52-54</sup> High conversion rates and stereoselectivity in the enantioselective hydrogenation of substituted alkenes with chiral Ir-based catalysts were achieved due to weakly coordinating anions.<sup>55</sup> Other simple but important catalysts are salts of the Li<sup>+</sup> cation and a WCA that catalyze a number of organic reactions such as the Diels-Alder reaction, 1,4-conjugate addition reactions or pericyclic rearrangements, successfully replacing the potentially explosive Li<sup>+</sup>[ClO<sub>4</sub>]<sup>-</sup>.<sup>56-59, 60</sup> Lithium salts of [Al(OR<sup>F</sup>)<sub>4</sub>]<sup>-</sup> (R<sup>F</sup> = C(Ph)(CF<sub>3</sub>)<sub>2</sub>),<sup>61</sup> [B(Ar<sup>F</sup>)<sub>4</sub>]<sup>-</sup> (Ar<sup>F</sup> = C<sub>6</sub>H<sub>3</sub>(CF<sub>3</sub>)<sub>2</sub>),<sup>62</sup> [Nb(OR<sup>F</sup>)<sub>6</sub>]<sup>-</sup> (R<sup>F</sup> = C(H)(CF<sub>3</sub>)<sub>2</sub>),<sup>63</sup> [CB<sub>12</sub>Me<sub>12</sub>]<sup>-</sup>,<sup>64</sup> or [Co(B<sub>9</sub>C<sub>2</sub>H<sub>11</sub>)<sub>2</sub>]<sup>-</sup>.<sup>65, 66</sup> were used even in very non polar solvents such as toluene<sup>64</sup> and hexane<sup>61</sup> with very high efficiency. Ag<sup>+</sup> salts of WCAs were also used as catalysts,<sup>60</sup> e.g. Ag(PPh<sub>3</sub>)<sup>+</sup>[CB<sub>11</sub>H<sub>6</sub>Br<sub>6</sub>]<sup>-</sup> was shown to be the best catalyst for a series of hetero Diels-Alder reactions.<sup>67</sup>

### A.2.3 Applications in Electrochemistry and Li Ion Batteries

The tetraalkylammonium salts NR<sub>4</sub><sup>+</sup>[X]<sup>-</sup> (R = Me, Et, Pr, Bu; X = ClO<sub>4</sub>, BF<sub>4</sub>, PF<sub>6</sub>, CF<sub>3</sub>SO<sub>3</sub>) are frequently used as supporting electrolytes in electrochemical non-aqueous analytical methods like cyclic voltamperometry (CVA) or cyclic voltammetry (CV).<sup>68-70</sup> The general requirement for those salts is to be stable towards reduction and oxidation,<sup>71, 72</sup> i.e. to have a large “electrochemical window”. Moreover, they should be soluble in non-polar solvents to introduce a less reactive solvent than the usually employed polar media like acetonitrile.<sup>73, 74</sup> Supporting electrolytes with WCAs like N(Bu)<sub>4</sub><sup>+</sup>[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup><sup>75-77</sup> and N(Bu)<sub>4</sub><sup>+</sup>[B(C<sub>6</sub>H<sub>3</sub>(CF<sub>3</sub>)<sub>2</sub>)<sub>4</sub>]<sup>-</sup><sup>78-80</sup> were reported to be very robust towards the formed oxidized species and effectively solubilize positively charged species formed in anodic processes. Also the [F<sub>3</sub>P(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub>]<sup>-</sup> anion<sup>81</sup> is now commercially available and its salts are more soluble and more stable than the [PF<sub>6</sub>]<sup>-</sup> parent salts.

It is also of great importance, from a customers point of view, to replace in the currently used of Li<sup>+</sup>[PF<sub>6</sub>]<sup>-</sup> conducting salt the Li Ion Batteries and so to eliminate its disadvantages. To further increase the possible battery current, more stable anions [A]<sup>-</sup> that still generate highly conducting Li<sup>+</sup>[A]<sup>-</sup> solutions are needed. Likely candidates are small anions like [F<sub>4-x</sub>B(CF<sub>3</sub>)<sub>x</sub>]<sup>-</sup> (X = 2, 3, 4), [F<sub>6-x</sub>P(CF<sub>3</sub>)<sub>x</sub>]<sup>-</sup> (x = 3, 4, 5),<sup>82-84</sup> [F<sub>3</sub>P(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub>]<sup>-</sup><sup>81</sup> and [B(R')<sub>2</sub>]<sup>-</sup> (R' = O-C(CF<sub>3</sub>)<sub>2</sub>-C(CF<sub>3</sub>)<sub>2</sub>-O).<sup>85</sup> However, contradicting the expectation, larger WCAs such as [B(Ar<sup>F</sup>)<sub>4</sub>]<sup>-</sup>,<sup>86</sup> [M(OR<sup>F</sup>)<sub>4</sub>]<sup>-</sup> (M = B, Al; R<sup>F</sup> = C(H)(CF<sub>3</sub>)<sub>2</sub> etc.)<sup>87</sup> were shown to give very high conductivities,<sup>88</sup> in particular, if incorporated in the matrix of a poly(ethyleneoxide) polymer.<sup>89</sup>