The Search for Larger and More Weakly Coordinating Anions

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Contents

I. Scope of This Review

It is now widely recognized that under certain circumstances the classical "noncoordinating" anions ClO_4^-,[1,2] $SO_3CF_3^-$,[3] SO_3F^-,[3] BF_4^-,[1,4] PF_6^-,[5] AsF_6^-,[6] and SbF_6^- [5a,7] coordinate to metal ions from all regions of the periodic table. This chemistry has been the subject of a number of reviews,[2,3,8,9] one of which appeared recently in this journal.[8] Accordingly, the coordination of these anions to metals will not be afforded comprehensive coverage in this review. Instead, we will focus on anions that are larger and even more weakly coordinating than those mentioned above. These include BPh_4^- and its derivatives, $CB_{11}H_{12}^-$ and related carborane anions, $OTeF_5^-$ and its derivatives, polyoxoanions such as $PW_{12}O_{40}^{3-}$, $HC(SO_2CF_3)_2^-$ and related anions, C_{60}^-, $B(o\text{-}C_6H_4O_2)_2^-$, anionic methylalumoxanes (MAO), and $H(1,8\text{-}C_{10}H_6(BMe_2)_2)^-$ (hydride sponge). We will discuss the well-known group of smaller anions only when direct comparisons to the second group can be made. While the larger, more weakly coordinating anions have fostered unusual, fascinating chemistry, an important part of our focus will be on their limitations, including their coordinating ability and the conditions under which they are not stable. An understanding of their limitations, as well as their strengths, is, after all, what one needs to know when considering a new application for one of these anions.

Steve Strauss (b 1952) was raised in New York City. After graduating from Franklin and Marshall College (A.B., chemistry, 1973), he spent a year as the Director of an after-school education center on the Blackfeet Indian Reservation near Browning, MT. After earning his Ph.D. in inorganic chemistry with D. F. Shriver at Northwestern University (1978), he was a postdoctoral fellow with R. H. Holm at Stanford (1978–1980) and Harvard Universities (1980–1981). He began his academic career at Colorado State University in 1981 and is now Professor of Chemistry. He has been awarded research fellowships by the NIH (postdoctoral) and the Alfred P. Sloan and Alexander von Humboldt Foundations and has received an Excellence in Teaching award from the College of Natural Sciences at CSU. His professional interests include fundamental aspects of transition metal coordination chemistry. His other interests include motorcycling, mountaineering, and rehabilitating injured birds of prey for release to the wild.

II. Introduction

A. Noncoordinating Anions: Fact or Fiction?

It has been 20 years since Rosenthal published his brief paper titled "The Myth of the Non-Coordinating Anion".[1] In this seminal work, he reviewed structural and spectroscopic data that proved unequivocally that anions which are noncoordinating in aqueous solution, such as ClO_4^-, NO_3^-, and BF_4^-, "are found to be coordinating where water has been excluded". He

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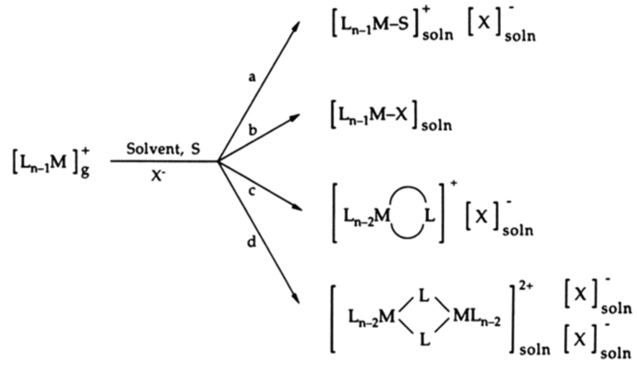

Figure 1. Scheme showing the four ways that vacant coordination sites in cationic complexes can be filled.

concluded by stating, "It is clear that the notion of the non-coordinating anion should be put to rest alongside the notion of the non-coordinating solvent."

This has not happened yet. One continues to find the dogmatic terms "noncoordinating solvent" and "noncoordinating anion" in the recent literature. It would be more meaningful as well as more precise to use the relative terms *weakly coordinating solvent* and *weakly coordinating anion.* In recent years chemists have been able to measure or estimate the strengths of bonds between metals and such weak donors as noble gas atoms[10] and aliphatic hydrocarbons.[11] If liquid xenon and hexane are coordinating solvents, why should one persist in referring to benzene and dichloromethane as noncoordinating? Inorganic chemists have learned that it is meaningless (not to mention risky) to refer to a compound that has not yet been prepared as *nonexistent*, a term that has been used to imply that it cannot be prepared.[12] In much the same way, it is simplistic to refer to a solvent or an anion as noncoordinating simply because a complex containing it bonded to a metal ion has not yet been isolated and structurally characterized *or* because it does not coordinate to some metal ions under some circumstances.

B. Cationic Complexes and Coordinative Unsaturation

Many coordination chemists are concerned with enhancing the chemical reactivity of metal complexes, whether for catalysis, for the synthesis of new complexes, or for examining the binding of extremely weak donors. One measure of reactivity is Lewis acidity. In what ways can it be enhanced using larger and more weakly coordinating anions? Consider an isolated, coordinatively unsaturated cationic complex, $L_{n-1}M^+$. In solution, the vacant coordination site would behave like the Coulombic version of a vacuum, i.e., its potential to attract a pair of electrons would be extremely large. What can fill the void? The scheme shown in Figure 1 shows the four most important possibilities: in a, the solvent (S) coordinates to the metal ion and fills the vacant site; in b the counterion (X^-) fills the site; in c one of the ancillary ligands becomes bidentate; and in d bridges are formed by two ancillary ligands. This is why a truly vacant coordination site may be impossible to achieve at a cationic center in solution, even if the solvent and the counterion are very weakly coordinating. As long as the ancillary ligands are flexible enough, c and possibly d would also preclude the existence of a genuine vacant site even in the gas phase.

Table I. Donor Numbers and Dielectric Constants of Some Common Solvents

solvent	donor number[a]	dielectric constant (T, °C)[b]
C_5H_5N	33	12.3(25)
C_4H_8O	20	7.6(20)
CH_3COCH_3	17	20.7(25)
CH_3CN	14	37.5(20)
$C_6H_5NO_2$	4.4	34.8(25)
C_6H_6	0.1	2.3(20)
1,2-$C_2H_4Cl_2$	0[c]	10.2(25)
CH_2Cl_2	<0 (?)	9.1(20)
C_6H_{14}	<0 (?)	1.9(20)
1,1,2-$C_2Cl_3F_3$	<0 (?)	2.4(25)

[a] Data from ref 15. [b] Data from ref 16. [c] By definition.

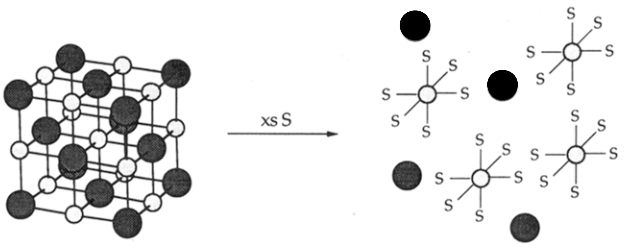

Figure 2. The complete solvation of metal ions contained in a simple MX salt.

This line of reasoning leads to the conclusion that what is normally referred to as a vacant coordination site in a cationic complex is, in perhaps most cases, an extremely weak, extremely labile metal–ligand bond.[13] Perhaps the term *vacant coordination site* should be replaced with *virtual coordination site.* It follows from Figure 1 that the weakest cation–ligand interaction possible in a given solvent is a cation–solvent bond.[14] However, solvents that possess the lowest donor numbers[15] also have the lowest dielectric constants,[16] as shown in Table I. If all other things are kept constant, b is favored over a as the dielectric constant decreases. In the case of $W(SbF_6)(CO)_3(NO)(PR_3)$, for example, the SbF_6^- anion is displaced from the $W(CO)_3(NO)(PR_3)^+$ cation by acetonitrile and acetone but not by dichloromethane or hexane.[17] Quite obviously then, weakening the M–X bond becomes the primary goal of those seeking the closest thing to coordinative unsaturation for a cationic center in a given solvent. Whether one can ever achieve a in weakly coordinating, low dielectric solvents will depend in large part on the availability of new anions that are larger and more weakly coordinating than those in common use.[18]

Let us next consider situations in which there are no ancillary ligands, such as simple M^+X^- salts. In most cases, specific metal–solvent bonds are formed when these salts are dissolved. An ideal situation, the generation of completely solvated metal ions, is shown in Figure 2. For a given solvent system, this would be the ultimate starting material for metal complex synthesis. In principle, if one wants to solubilize a metal ion in a weakly coordinating solvent, one simply has to use a larger anion, since lattice energies for many M^+X^- salts vary linearly with the inverse cube root of the formula unit volume.[19] However, if one tries to achieve this with an even more weakly coordinating solvent,

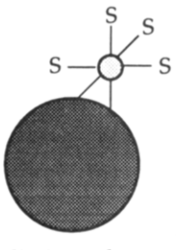

Figure 3. A more realistic goal: a partially solvated metal ion (small sphere) ion paired to a very large counterion.

the concomitant low dielectric constant will likely produce a species such as the one depicted in Figure 3. Here, a cation–anion pair is dissolved intact, producing a polar solute instead of charged species but importantly allowing for the presence of some weak, labile metal–solvent bonds. The anion requirements for the latter situation are less severe than those needed to produce completely solvated metal ions: the cation–anion interactions in the lattice must only be weak enough to allow the solvent to electronically decouple the cation from all but one anion.

C. Ideal Properties for Weakly Coordinating Anions

Next, let us consider the optimal set of properties for weakly coordinating anions. The first two properties are low overall charge and a high degree of charge delocalization. Ideally, all new weakly coordinating anions should have a −1 charge, but in some cases a species with a −2 charge may have certain advantages and can be tolerated (one advantage, for example, is a lower equivalent mass). The charge should be delocalized over the entire anion, so that no individual atom or group of atoms bears a high concentration of charge. Obviously, this suggests that the larger the anion (the more atoms it contains), the more delocalized the charge and the more weakly coordinating it will be. An equally important property is the presence of only very weakly basic sites on the periphery of the anion. Thus, anions with only hydrogen atoms or fluorine atoms available for binding to the cation should be more weakly coordinating than anions with accessible oxygen atoms or chlorine atoms: several studies have shown that BF_4^- and PF_6^- are more weakly coordinating than, for example, ClO_4^- or $SO_3CF_3^-$.[20]

Charge, charge delocalization, size, and the absence of basic sites notwithstanding, perhaps the most important property is the kinetic stability, if not the thermodynamic stability, of the anion. There are two potential problems to be avoided. First, some very large weakly coordinating anions could dissociate into smaller, more strongly coordinating fragments. For example, rapid fluoride ion abstraction by electrophiles is well known[21a,b,d–g] to be a problem even with small anions such as BF_4^- and PF_6^-. (There are even a few reported cases of fluoride abstraction from SbF_6^-.[21c,h]) Second, the stability of a weakly coordinating anion with respect to oxidation will determine whether it can be used as a counterion for the most electrophilic cations, many of which will also be strong oxidants. The well-known tendency of BPh_4^- to undergo chemical and electrochemical oxidation,[22] which will be discussed below, is a case in point.

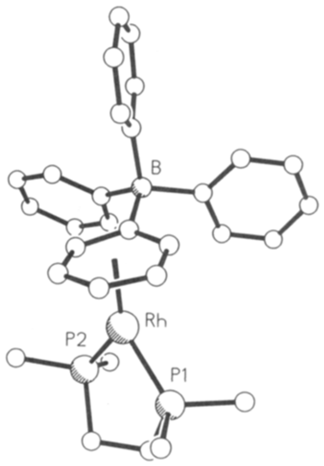

Figure 4. Structure of $Rh(BPh_4)(diphos)$. The unlabeled open spheres are carbon atoms. For clarity, hydrogen atoms have been omitted and only the ipso carbon atoms on the diphosphine phenyl rings are shown.

III. Tetraphenylborate and Related Anions

A. BPh_4^-

1. Coordination to Metal Ions

The tetraphenylborate anion has found extensive use as, among other things, a phase-transfer catalyst and a weakly coordinating anion.[23] Its most recent and perhaps most important application is as the counterion in one-component, soluble Ziegler–Natta olefin polymerization catalysts, in which the catalytically active species is a cationic group 4 metallocene complex of the general type $M(Cp)_2(R)^+$ (M = Ti, Zr, Hf, Th).[24]

It has been known for some time that BPh_4^- can coordinate to metal ions. In all cases probed by X-ray crystallography, it ligates the metal through π-interactions with one of its phenyl rings (i.e., interactions with C–H bonds have not been observed).[22a,25] With one exception, all of the structures exhibit η^6-coordination. A typical example is shown in Figure 4.[25b] In these η^6-structures, the coordinated phenyl ring is sometimes planar and sometimes distorted from planarity. In $Ru(Cp)(BPh_4)$, for example, the ring in question is planar to within 0.01 Å.[25d] In $Co(BPh_4)(PMe_3)_2$, the ipso carbon atom is displaced, away from cobalt, by 0.044 Å from the plane of the remaining five carbon atoms.[25a] In $Rh(BPh_4)(P(OMe)_3)_2$, both the ipso and para carbon atoms are displaced, in this case by ~0.08 Å, from the plane of the remaining four carbon atoms and away from rhodium,[25e] while in $Rh(BPh_4)$(diphos), the ipso and para carbon atoms are displaced toward rhodium by ~0.07 Å. (In the cases of $Co(BPh_4)(py)_2$[22a] and $Ru(\eta^3\text{-}1,2,3\text{-}\eta^2\text{-}5,6\text{-}(1,5\text{-cyclooctadienyl}))(BPh_4)$,[25c] the coordinated phenyl ring was refined as a planar rigid body or its degree of planarity was not discussed in the paper, respectively.)

The structural results allow the strength of the interaction between a given metal ion and BPh_4^- to be compared with the interaction of the metal ion and a neutral arene. The result of this comparison is that a phenyl ring from anionic tetraphenylborate is not more strongly bound, as judged by M–C(arene) distances, than a neutral phenyl ring. For example, the range of Ru–C(arene) distances in $Ru(Cp)(BPh_4)$ is 2.181(6)–2.271(5) Å. In the complexes $Ru(\eta^5\text{-}1,2\text{-}C_5H_3(Ph)_2)(\eta^6\text{-}$

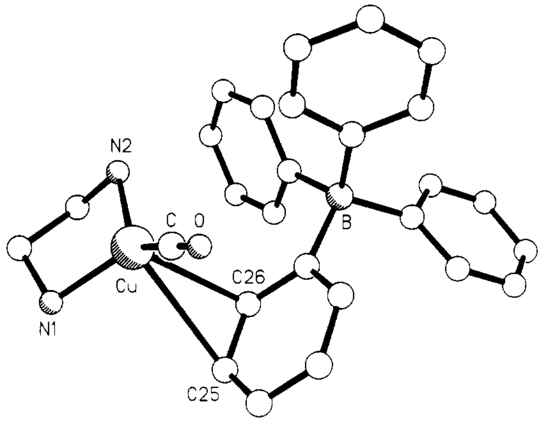

Figure 5. Structure of $Cu(BPh_4)(CO)(en)$. The unlabeled open spheres are carbon atoms. For clarity, hydrogen atoms have been omitted.

$C_6H_6)^{+}$ [26] and $Ru(Cp)((\eta^6-C_6H_5)P(O)Ph_2)^{+}$,[27] the respective ranges are 2.187(6)–2.200(8) Å and 2.191(4)–2.214(4) Å. Nevertheless, NMR data indicates that electrostatic interactions contribute to the stability of $(\eta^6-C_6H_5)BPh_3^-$ complexes in a way that they cannot in homologous complexes with neutral π-arene ligands: the coordinated BPh_4^- ligand in $Zr(CH_2Ph)_3((\eta^6-C_6H_5)BPh_3)$ is not displaced by toluene, hexamethylbenzene, or 1,3,5-tri-*tert*-butylbenzene.[28]

In $Cu(BPh_4)(CO)(en)$, shown in Figure 5, one of the phenyl groups is coordinated in η^2-fashion to copper.[29] In this case, the BPh_4^- anion is very weakly bonded to the Cu(I) ion. The Cu–C25 and Cu–C26 bond distances of 2.919(5) and 2.706(4) Å, respectively, are considerably longer than the Cu–C distances of 2.09(2) and 2.13(2) Å in $Cu(SO_3CF_3)(\eta^2-C_6H_6)$[30] or of 2.15(3) and 2.30(3) Å in $Cu(AlCl_4)(\eta^2-C_6H_6)$.[31,32] Another measure of the weakness of the interaction between the $Cu(CO)(en)^+$ moiety and the BPh_4^- anion is that the Cu(I) ion is only displaced by 0.26 Å from the plane defined by N1, N2, and C. An example of $(\eta^2-C_6H_5)BPh_3^-$ coordination to an early transition metal may be found in $Zr(Cp')_2(Me)(BPh_4)$, which was studied by NMR spectroscopy.[24b]

2. Reactions with Metal Ions

There are a number of ways that BPh_4^- can react with electrophilic species, especially cations. These are (i) metalation, (ii) phenyl group transfer, and (iii) electron transfer. In addition, BPh_4^- is susceptible to photochemical decomposition. All of these reactions limit the usefulness of this anion and render it less than ideal for many applications.

There is only one study in which metalation has been clearly demonstrated.[24d] Treatment of $Zr(Cp^*)_2(Me)_2$ with *1* equiv of $[NH(n-Bu)_3][B(Ar)_4]$ (Ar = C_6H_5, $p-C_6H_4Me$, and $p-C_6H_4Et$) led to the evolution of *2* equiv of CH_4 and isolation of $Zr(Cp^*)_2((m-(p-C_6H_3R)B(p-C_6H_4R)_3)$ (R = H, Me, and Et). The structure of the *p*-Et compound is shown in Figure 6. The authors postulated that the agostic[33] Zr–H31 interaction (2.154(4) Å) might be electrostatic in origin, since the compound can be formulated as a zwitterion, with formal + and − charges on zirconium and boron, respectively. They noted that the isoelectronic neutral complex $Sc(Cp^*)_2(Ph)$ does not exhibit agostic interactions.[34] In any event, the structure shown in Figure 6

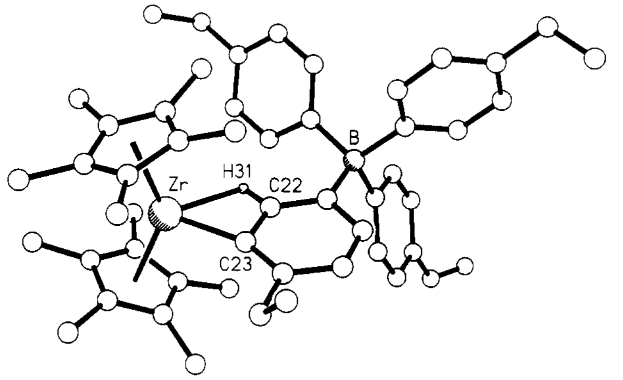

Figure 6. Structure of $Zr(Cp^*)_2((m-(p-C_6H_3Et)B(p-C_6H_4Et)_3)$. The unlabeled open spheres are carbon atoms. Except for H31, hydrogen atoms have been omitted for clarity.

is the first example of any bonding interaction between a metal center and the hydrogen atoms of tetraphenylborate, showing that this type of interaction is viable. It stands in contrast to the many cases of simple, reversible π-coordination of BPh_4^- discussed above.

Examples of phenyl group transfer from BPh_4^- to metal centers are far too numerous to allow a complete discussion here of every case.[24b,35] The metals involved in this chemistry include Fe(II),[35c] Fe(III),[35e] Ni(II),[35f] Zr(IV),[24b] Rh(I),[25b] Rh(III),[35b] Ru(II),[35g] Pd(II),[35a] W(IV),[35d] Pt(II),[35h] and Hg(II).[35i] It can be seen that metals from all regions of the *d* block can abstract a phenyl group from this rather reactive counterion. This is not surprising, given that BPh_4^- also readily reacts with Brønsted acids.[36] The relative reactivities of BPh_4^- and fluoro anions are dependent on the respective cationic metal complexes. The cations $W(Cp)(NO)_2^+$,[35d] $Fe(TPP)^+$,[35e] and $Ni(L)^+$ (L = tris[2-(diphenylarsino)ethyl]amine)[35f] all yield isolable complexes with coordinated BF_4^- as the counterion, but undergo phenylation with BPh_4^- as the counterion. In contrast, $Zr(Cp)_2(Me)(THF)^+$ [21e,37] and $Cr(Cp)(Me)(THF)_2^+$ [38] are stable in the presence of BPh_4^- but abstract fluoride ion from BF_4^- or PF_6^-, respectively.

The electrochemical oxidation of tetraphenylborate has been studied in aqueous and nonaqueous media.[22c,39] The anodic peak potential for [TBA][BPh_4] in acetonitrile (0.1 M [TBA][ClO_4]) is 1.16 V vs NHE. Although biphenyl was an isolated product,[37] no evidence for free Ph• radicals was observed.[22c] Instead, the authors of these studies concluded that biphenyl must be formed by an intramolecular coupling of two phenyl groups in the neutral •BPh_4 radical.

While the electrochemical oxidation is relevant to the use of BPh_4^- salts as supporting electrolytes, the chemical oxidation of BPh_4^- by metal ions is relevant to its use as a weakly coordinating anion. It has been shown that Ce(IV),[22d,39] Ir(IV),[22e] and Fe(III)[22d] ions will oxidize BPh_4^-, with biphenyl observed as one of the products. More surprisingly, metals in relatively low oxidation states, such as Co(II)[22a] or Ni(II),[40] can be reduced by BPh_4^- to Co(I) or a dimeric nickel complex with apparent oxidation state +1.5, respectively. In the former case, heating the Co(II) compound $[Co(THF)_3(py)_3][BPh_4]_2$ to 60 °C in the solid state produced biphenyl and $Co(BPh_4)(py)_2$. (The structure of this Co(I) complex was described above.) In the latter case, refluxing NiX_2 (X = Br, I) with 1,8-naphthyridine (napy) and $NaBPh_4$ in 1-butanol produced [Ni_2-

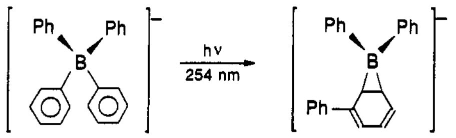

Figure 7. Scheme showing the primary product formed when BPh_4^- is irradiated at 254 nm.

$(napy)_4X_2][BPh_4]$, which contains a Ni–Ni bond (2.415(4) Å). The second equivalent of tetraphenylborate anion is apparently the reducing agent, since reduction of nickel did not occur upon substitution of $NaPF_6$ for $NaBPh_4$.

The photochemical decomposition of BPh_4^- in aqueous solution has been studied.[22f,41] In the presence of oxygen, biphenyl is the principal product. In its absence, 1-phenyl-1,4-cyclohexadiene predominates. In contrast, irradiation of $[NMe_4][BPh_4]$ in oxygen-free acetonitrile or tetrahydrofuran gave one major primary product, as shown in the reaction depicted in Figure 7.[42] Clearly, one must avoid using BAr_4^- ions in situations where intentional or adventitious exposure to UV radiation will occur.

There is one report of phenyl group cleavage from a coordinated BPh_4^- anion. Treatment of $Ru(\eta^3$-1,2,3-η^2-5,6-(1,5-cyclooctadienyl))(BPh_4) dissolved in acetonitrile with the protic acids HF, HBF_4, or HPF_6 resulted in the formation of $Ru(\eta^3$-1,2,3-η^2-5,6-(1,5-cyclooctadienyl))$(\eta^6$-$C_6H_5BF_3)$.[25c] Not surprisingly, this hybrid borate anion is bonded to the soft Ru(II) center via its phenyl ring and not through one or more of its fluorine atoms.

3. *Comparisons with BF_4^-, PF_6^-, and ClO_4^-*

There are two published reports that compare the reactivity of metal complexes in the presence of BPh_4^- with the same complexes in the presence of some of the more classical weakly coordinating anions. In one study, the replacement of chloride ions in $PtCl_4^{2-}$ by an acyclic tetraphosphine ligand yielded exclusively one product with BF_4^- as the counterion. In the presence of the BPh_4^- anion, however, two completely different platinum complexes were isolated.[43] In the other study, a series of cationic Rh(I) hydride complexes were much more active hydrogenation catalysts in the presence of PF_6^- and ClO_4^- than in the presence of BPh_4^-.[44]

B. Fluorinated Derivatives of BPh_4^-

In order to reduce the coordinating ability and/or the reactivity of BPh_4^-, several derivatives containing fluorine or trifluoromethyl substituents on the phenyl groups have been explored. These include $B(p$-$C_6H_4F)_4^-$, $B(C_6F_5)_4^-$, and $B(3,5$-$C_6H_3(CF_3)_2)_4^-$. The structure of the latter anion, which will be referred to as $TFPB^-$, is shown in Figure 8.[45] The counterion, which is not shown, is a centrosymmetric, dimeric Rh(I) dication with four bridging diisocyanide ligands. The closest Rh···F contact is 3.31 Å, which is just outside the sum of van der Waals radii for rhodium and fluorine.[46,47] Therefore, it is sensible to conclude that $TFPB^-$ is not bonded to the rhodium atoms in this compound. This conclusion is in harmony with the observation that the closest Rh···F contact in the homologous PF_6^- salt is ~5.5 Å.[48] As was the case with BPh_4^-, a primary application of these relatively new anions is to generate active catalysts, whether for olefin polymerization,[24,49] carbon monoxide and olefin copolymerization,[50] or the production of adipic acid by methyl acrylate dimerization.[51] In addition, salts of these fluorinated tetraarylborates show extraordinary solubilities,[51] a useful property but one that sometimes frustrates their crystallization.[52]

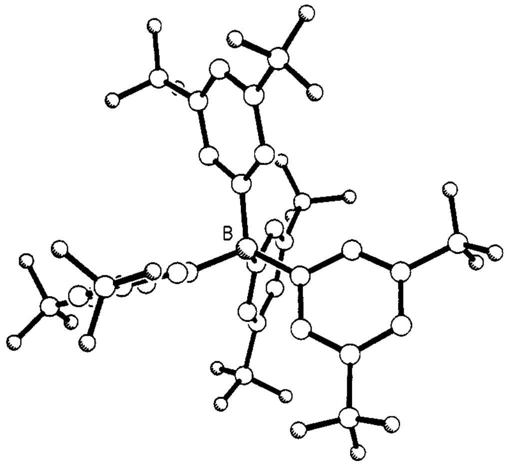

Figure 8. Structure of the $B(3,5$-$C_6H_3(CF_3)_2)_4^-$ anion ($TFPB^-$). The unlabeled open spheres are carbon atoms and the unlabeled highlighted spheres are fluorine atoms. Hydrogen atoms have been omitted for clarity.

In principle, the incorporation of electron-withdrawing substituents should suppress π-coordination of the phenyl groups as well as raise the reduction potential for the $B(Ar)_4^{0/-}$ couple. In practice, this is exactly what has been found. None of the fluorinated tetraphenylborates have been found to coordinate to a metal via a π-phenyl interaction,[53] and the reduction potentials of $TFPB^{0/-}$ and $B(C_6F_5)_4^{0/-}$ are some 1.2 and 1.5 V, respectively, more positive than that of BPh_4^-.[45]

The incorporation of electron-withdrawing substituents should also reduce the tendency for B–Ar cleavage, by decreasing the amount of negative charge at the ipso carbon atoms. This is certainly the case for Brønsted acid cleavage: $TFPB^-$ is inert to aqueous methanolic sulfuric acid for conditions under which BPh_4^- is hydrolyzed with a half-life of less than 30 min.[36] To some extent, this has been found to be true for Lewis acid cleavage as well. The electrophilic cation $Fe(Cp)(CO)_2(THF)^+$ is phenylated in the presence of BPh_4^- but is not arylated in the presence of $TFPB^-$.[21c] Similarly, there is no evidence for arylation of $Zr(Cp')_2(R)^+$ complexes in the presence of $B(C_6F_5)_4^-$.[54] However, $Zr(Cp')_2(Me)^+$ is converted to $Zr(Cp')_2(Me)(p$-$C_6H_4F)$ at 25 °C in the presence of $B(p$-$C_6H_4F)_4^-$.[49d] Furthermore, pentafluorophenyl transfer does occur in the following reaction:[55]

$$XeF_2 + B(C_6F_5)_3 \rightarrow [Xe(C_6F_5)][BF_2(C_6F_5)_2]$$

Since this reaction probably occurs via the intermediacy of $[XeF][BF(C_6F_5)_3]$, pentafluorophenyl transfer from a four-coordinate tetrahedral borate species to at least some cationic metal centers can be anticipated if the thermodynamics are favorable.

The two tetraarylborates with aromatic C–F bonds can coordinate to metal ions through fluorine atom lone pairs. Fluorine-19 NMR spectroscopy suggested that there is a single Zr–F–C bridge in $Zr(Cp^*)_2(Me)(B(p$-$C_6H_4F)_4)$.[49d] In another example, $Th(Cp^*)_2(Me)(B$-

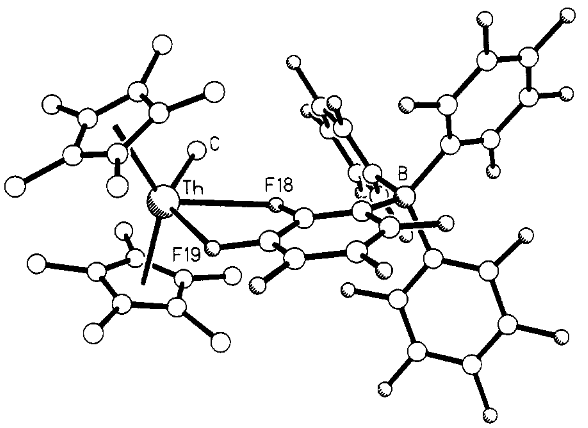

Figure 9. Structure of $Th(Cp^*)_2(Me)(B(C_6F_5)_4)$. The unlabeled open spheres are carbon atoms and the unlabeled highlighted spheres are fluorine atoms. Hydrogen atoms have been omitted for clarity.

$(C_6F_5)_4)$, X-ray crystallography proved that there are two Th–F–C bridges, involving an ortho,meta pair of fluorine atoms, as shown in Figure 9.[56] The Th–F18 and Th–F19 distances, 2.757(4) and 2.675(5) Å, respectively, are shorter than the sum of van der Waals radii for these two atoms but are considerably longer than the sum of Th^{4+} and F^- ionic radii (~2.3 Å).[57] This compound is more than 3 orders of magnitude more reactive for olefin polymerization than $Th(Cp^*)_2(Me)(BPh_4)$, for which low-temperature ^1H NMR spectra have been interpreted as suggesting π-phenyl coordination.[24g] While this comparison of bulk catalytic activity as a function of anion is interesting, it will be equally important to measure other factors, such as the rate of catalyst deactivation, as a function of anion.

An elegant experimental procedure to measure the relative coordinating ability of anions has been developed.[20a] The degree of disproportionation of the mixed-valence, dimeric rhodium isocyanide complex $Rh_2(TM4)_4^{3+}$ (TM4 = 2,5-diisocyano-2,5-dimethylhexane) was measured using spectroelectrochemistry. It had earlier been shown that the thermodynamic driving force for this and related disproportionations of other dimeric rhodium complexes derives from complexation of the d^7–d^7 dimer by anions, X^-.[58] Therefore, comparison of K_{disp} for $Rh_2(TM4)_4^{3+}$ in the presence of various anions provides a relative measure of the thermodynamic stabilities of the d^7–d^7 $Rh(TM4)_4X_2^{2+}$ complexes, and hence a relative measure of the ability of X^- to stabilize electrophilic centers, as shown below:[59]

$$\underset{d^7\text{–}d^8}{2Rh_2(TM4)_4^{3+}} + 2X^- \rightleftharpoons \underset{d^8\text{–}d^8}{Rh_2(TM4)_4^{2+}} + \underset{d^7\text{–}d^7}{Rh_2(TM4)_4X_2^{2+}}$$

The results, listed in Table II, establish the order of coordinating ability $ClO_4^- \approx BF_4^- > PF_6^- > SbF_6^- \gg TFPB^-$. While the results are specific for this particular rhodium system, they show that single-site metathesis reactions such as the following can have ΔG values of < –5 kcal mol⁻¹ $([\Delta G_{disp}(SbF_6^-) - \Delta G_{disp}(TFPB^-)]/2)$:

$$L_{n-1}M(TFPB) + SbF_6^- \rightleftharpoons L_{n-1}M(SbF_6) + TFPB^-$$

In a more recent development, it has been shown that $B(C_6F_5)_4^-$ is more strongly coordinating, than $TFPB^-$.[45]

Table II. Disproportionation Data for $[Rh(TM4)]^{3+}$ in 0.1 M TBA^+X^- [a,b]

X^-	K_{disp} [c]	ΔG_{disp}, kcal mol⁻¹ [d]
Cl^-	$>10^6$	<–8.2
ClO_4^-	18(2)	–1.7
BF_4^-	4(3)	–0.8
PF_6^-	$9(2) \times 10^{-2}$	1.5
SbF_6^-	$8(3) \times 10^{-3}$	2.8
$TFPB^-$ [e]	$<10^{-10}$	13.6

[a] Data from ref 20a. TM4 = 2,5-diisocyano-2,5-dimethylhexane. [b] Dichloromethane, 25 °C. [c] See text for definition. [d] Calculated from K_{disp}. [e] $TFPB^- = B(3,5\text{-}C_6H_3(CF_3)_2)_4^-$.

A related class of weakly coordinating anions, $B(R)(C_6F_5)_3^-$ (R = Me, Bz), are formed when complexes such as $M(Cp')_2R_2$, $M(Cp')R_3$, and MR_4 (M = Ti, Zr) are treated with $B(C_6F_5)_3$.[60] The resulting metal complexes are active homogeneous olefin polymerization catalysts. One of them, $Zr(1,2\text{-}C_6H_3Me_2)(Me)(B(CH_3)(C_6F_5)_3)$ has been structurally characterized.[60c] The borate is linked to the cationic zirconium moiety by its $B\text{–}CH_3$ group (Zr–C(B) = 2.549(3) Å, Zr–H(C(B)) = 2.25(3), 2.30(3), and 2.71(3) Å), not by the fluorine atoms of the perfluorophenyl groups.

C. $Ph_3BCNBPh_3^-$

This anion was introduced as a "potentially useful new anion for crystallizations", since it is essentially the anionic structural equivalent of the PPN^+ cation (cf. $Ph_3P{=}N{=}PPh_3^+$ with $Ph_3BC{\equiv}NBPh_3^-$).[61] It was crystallographically characterized in conjunction with a coordinatively saturated metal cation, so its efficacy as a weakly coordinating anion has not been tested. While the negative charge on each phenyl group should be lower than in BPh_4^-, one can expect that this anion will behave similarly to BPh_4^- in most ways, especially with respect to η^6-phenyl coordination and phenyl group transfer. Furthermore, $Ph_3BCNBPh_3^-$ is slightly dissociated in methanol to the presumably more strongly coordinating $B(CN)Ph_3^-$ anion and BPh_3, something that could limit the usefulness of this anion in basic solvents.

IV. 1-Carba-closo-dodecaborate(1–) ($CB_{11}H_{12}^-$) and Related Anions

A. $CB_{11}H_{12}^-$

There is an extensive literature on the coordination chemistry of BH_4^-.[62] It has been shown to coordinate strongly to metal ions with one, two, or three of its hydrogen atoms[62] or, in an agostic-type three-center interaction, with one B–H bond.[63] In an effort to distribute the charge over a larger number of hydrogen atoms and therefore make each hydrogen atom an intrinsically weaker donor, considerable effort has gone into studying large, polyhedral carborane and metallacarborane anions. As with fluorinated derivatives of tetraphenylborate, two practical goals of this research have been the development of active polymerization catalysts[64] and obtaining highly soluble salts.[65]

From the standpoint of weakly coordinating anions, the best studied of these polyhedral anions is $CB_{11}H_{12}^-$. In a series of landmark studies, it has been shown to be extremely weakly coordinating as well as an ex-

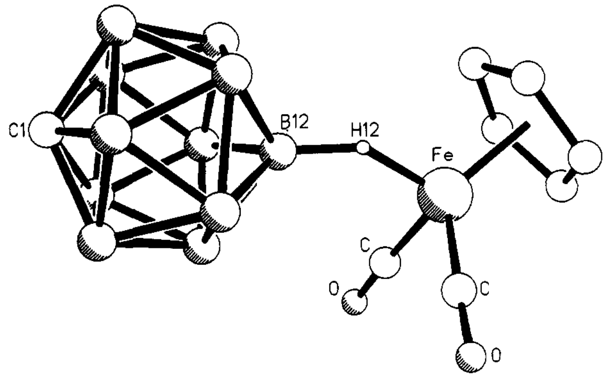

Figure 10. Structure of $Fe(Cp)(CB_{11}H_{12})(CO)_2$. The unlabeled open spheres are carbon atoms and the unlabeled highlighted spheres are boron atoms. Except for H12, hydrogen atoms have been omitted for clarity.

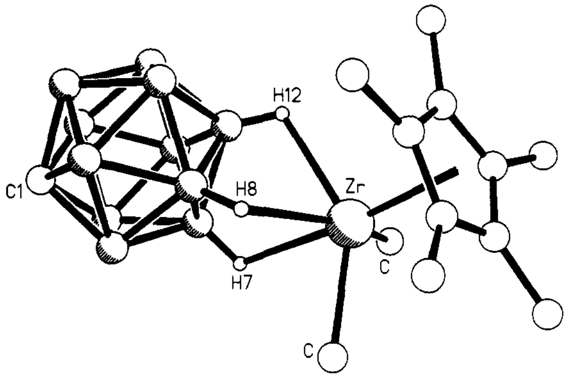

Figure 11. Structure of $Zr(Cp^*)(Me)_2(CB_{11}H_{12})$. The unlabeled open spheres are carbon atoms and the unlabeled highlighted spheres are boron atoms. Except for H7, H8, and H12, hydrogen atoms have been omitted for clarity.

tremely weak nucleophile.[32a,66] Structural studies have shown that the most hydridic hydrogen atom (i.e., H12, the one attached to the boron atom antipodal to the unique carbon atom[67]) is always involved in metal–$CB_{11}H_{12}^-$ bonding.[68] For example, in $Fe(Cp)(CB_{11}H_{12})(CO)_2$, shown in Figure 10, the only link between the carborane anion and the Fe(II) center is H12.[66a,69] The compounds $IrCl(CO)(PPh_3)_2(AgCB_{11}H_{12})$[66c] and $Fe(TPP)(CB_{11}H_{12})$[66b,d] also contain a single M-H-B linkage. In the compound $Ag(CB_{11}H_{12})(C_6H_6)$,[32a] each anion bridges two Ag(I) ions through the most hydridic B12–H12 bond and one of the five B–H bonds adjacent to it (i.e., one of the next most hydridic B–H bonds). While bidentate coordination of $CB_{11}H_{12}^-$ has not yet been observed, tridentate coordination occurs in $Zr(Cp^*)(Me)_2(CB_{11}H_{12})$, as shown in Figure 11.[70] This structure, in which the metal caps a triangular face consisting of the B12–H12 bond and two adjacent ones (Zr–H = 2.52(3) (H12), 2.81(3) (H7), and 2.83(3) Å (H8)),[69] demonstrates the potential electronic and structural flexibility of this weakly coordinating anion, properties that may prove useful in catalytic applications.

Table III. Structural, Spectroscopic, and Magnetic Results for Fe(TPP)X Complexes

X^-	Fe–N, Å[a]	Ct···N, Å[b]	Fe···Ct, Å	g[c]	ΔE_Q,[d] mm/s	% $S = {}^3/_2$
Cl^-	2.049(9)[e]	2.013[d]	0.38[e]	5.9[f]	0.46[g]	0
ClO_4^- [h]	2.001(5)	1.981	0.30	4.75	3.50	65
SbF_6^- [i]	1.978(3)	1.974	0.15	4.05	4.29	98
$CB_{11}H_{12}^-$ [j]	1.961(5)	1.955	0.10	4.15	4.12	92

[a] Average of four values (N = porphyrinate nitrogen atom). [b] Ct = center of the mean plane of the 24-atom porphyrinate core. [c] Electronic g value (from EPR spectra). [d] Quadrupole splitting (from Mössbauer spectra). [e] Reference 72c. [f] Reference 71. [g] Reference 72b. [h] Reference 72a. [i] Reference 7b. [j] References 66b,d.

Probably the best test of the relative coordinating ability of $CB_{11}H_{12}^-$, as well as its relative ligand field strength, was the preparation and characterization of $Fe(TPP)(CB_{11}H_{12})$.[66b,d] Iron porphyrins are among the most studied and best characterized metal complexes.[71] Since there are no truly noncoordinating anions or noncoordinating solvents, a cationic four-coordinate Fe(III) porphyrin has never been prepared. However, $Fe(TPP)(CB_{11}H_{12})$ contains the weakest interaction yet reported between the elusive $Fe(TPP)^+$ cation and any counterion. The results listed in Table III are revealing.[7b,66b,d,72] The compound $Fe(TPP)(CB_{11}H_{12})$ exhibits the shortest Fe–N distances, the smallest porphyrinate core, and the smallest out-of-plane displacement of the iron atom of any other Fe(TPP)X complex. Thus, the carborane species is the least coordinating anion in the group Cl^-, ClO_4^-, SbF_6^-, and $CB_{11}H_{12}^-$. Nevertheless, the magnetic and spectroscopic data suggest that it is the hexafluoroantimonate complex that exhibits the least high-spin ($S = {}^5/_2$) and the most intermediate-spin ($S = {}^3/_2$) character, suggesting that the ligand field strength of $CB_{11}H_{12}^-$ is greater than that of SbF_6^-, even though $CB_{11}H_{12}^-$ is the weaker binding of the two. The difference in ligand field strengths was attributed to the p_π donor capability of the bridging fluorine atom in $Fe(TPP)(SbF_6)$. (The carborane anion is incapable of p_π donation.[66b])

There are two potential limitations to the widespread use of $CB_{11}H_{12}^-$ as a weakly coordinating anion. One is that the trityl (CPh_3^+) salt cannot be prepared, presumably because the trityl cation abstracts hydride from the otherwise stable carborane anion.[73] Quite possibly, other cationic electrophiles might abstract a hydride ion from $CB_{11}H_{12}^-$. The second limitation is that while the anion is stable to electrochemical oxidation at potentials >1.7 V (vs NHE) at a platinum electrode in acetonitrile, it undergoes irreversible oxidation at ~0.5 V at the same electrode in dichloromethane.[73]

B. Other Related Anions

A number of derivatives of $CB_{11}H_{12}^-$ have been prepared,[73,74] partly in an effort to circumvent the inherent limitations mentioned above.[73] The most important of these are substituted at the 12-position (i.e., the position farthest removed from the carbon atom), since it is the B12–H12 bond that is the most hydridic[67] and hence the most prone to heterolytic cleavage (hydride transfer). These relatively new ions include $12\text{-}CB_{11}H_{11}Cl^-$,[73] $12\text{-}CB_{11}H_{11}Br^-$,[73] $12\text{-}CB_{11}H_{11}I^-$,[74] $12\text{-}CB_{11}H_{11}(C_6F_5)^-$,[73] $7,12\text{-}CB_{11}H_{10}Cl_2^-$,[73] $7,12\text{-}CB_{11}H_{10}Br_2^-$,[73] $7,12\text{-}CB_{11}H_{10}I_2^-$,[74] $7,8,9,10,12\text{-}CB_{11}H_7Cl_5^-$,[74] and $7,8,9,10,11,12\text{-}CB_{11}H_6X_6^-$ (X = Cl, Br).[74]

The structure of $Ag(12\text{-}CB_{11}H_{11}Br)(C_6H_6)$ has been determined.[73] Each monobrominated anion is bonded to three $Ag(C_6H_6)^+$ moieties, through its Br, H7, and H8 atoms.[69] The Ag–Br bond distance of 2.642 Å is considerably shorter than the distances in AgBr[75] or in $Ag(BrCH_2SO_3)$,[76] 2.8878(5) and 2.970(5) Å, respectively. The Ag–H distances of 2.20 and 2.27 Å are longer than the Ag–H7 and Ag–H12 distances in $Ag(CB_{11}H_{12})(C_6H_6)$, both of which are 1.97 Å.[32a,69] It is possible that the Ag–H distances in $Ag(12\text{-}CB_{11}H_{11}Br)(C_6H_6)$ are longer than those in $Ag(12\text{-}CB_{11}H_{11}Br)(C_6H_6)$ because the Ag(I) ion in the former compound, by virtue of its bond to a relatively strongly coordinating bromine atom, is less electrophilic than the Ag(I) ion in the latter compound.

There are a large number of other compounds in which metal ions form bonds with polyhedral borane or carborane anions.[62a–c] In nearly all cases, however, the cage anion cannot be considered a weakly coordinating anion because the metal ions interact with both hydrogen and boron atoms (in many cases the metal ions are part of the cage framework).[77] An exception is $[Th(Cp^*)_2Me]_2[Fe(C_2B_9H_{11})_2]$, in which the $Fe(C_2B_9H_{11})_2^{2-}$ anion bridges two $Th(Cp^*)_2Me^+$ cations.[78] The only cation–anion interactions are three relatively week Th–H bonds (2.42(3), 2.50(3), and 2.67(4) Å). Nevertheless, despite the seemingly weak Th–H interactions, this thorium complex is a much less active ethylene polymerization catalyst than an analog with two Th–F bonds, $Th(Cp^*)_2(Me)(B(C_6F_5)_4)$ (see Figure 9).[56]

V. Pentafluorooxotellurate ($OTeF_5^-$) and Related Anions

A. $OTeF_5^-$

Pentafluorooxotellurate, or teflate, has been used for some time as a hard and very electronegative substituent for main group elements.[79] Most notable is the recent low-temperature generation of $Kr(OTeF_5)_2$, one of only a handful of krypton compounds and the first one with Kr–O bonds.[80] The structure of the free teflate anion is a slightly distorted octahedron, with Te–O and average Te–F bond distances of 1.786(3) and 1.853(3) Å, respectively, and an average $O\text{–}Te\text{–}F_{eq}$ bond angle of 95.2(2)°.[81] Therefore, teflate is nearly isostructural and isodimensional with SbF_6^- (Sb–F (av) = 1.844(8) Å in $KSbF_6$[82]).

A number of binary (homoleptic) metal teflates have been prepared, including $MOTeF_5$ (M = Li–Cs),[83] $AgOTeF_5$,[84] $TlOTeF_5$,[85] $Zn(OTeF_5)_2$,[86] $Hg(OTeF_5)_2$,[83,87] $Fe(OTeF_5)_3$,[88] $Au(OTeF_5)_3$,[89] $Ti(OTeF_5)_4$,[90] $M(OTeF_5)_5$ (M = Nb, Ta),[91] $W(OTeF_5)_6$,[91] and $U(OTeF_5)_6$.[92] At the same time, a number of complexes containing teflates as well as traditional ancillary ligands have been prepared and characterized, including $Mn(OTeF_5)(CO)_5$,[93] $Fe(Cp)(OTeF_5)(CO)_2$,[93] $Fe(TPP)(OTeF_5)$,[94] and $Pt(OTeF_5)_2(NBD)$.[95] For the latter class of compounds, it has been found that the coordinating ability of $OTeF_5^-$ is considerably less than Cl^- and slightly greater than ClO_4^- or $SO_3CF_3^-$. Despite the measurable differences in coordinating ability, teflate is *not* unique relative to perchlorate or triflate as a terminal, monodentate ligand in complexes such as $Mn(OTeF_5)(CO)_5$.

The significant difference between $OTeF_5^-$ and the seemingly similar traditional weakly coordinating anions ClO_4^-, SO_3F^-, $SO_3CF_3^-$, BF_4^-, SbF_6^-, etc. becomes evident when comparing the reactivities of simple binary compounds such as AgX, TlX, and FeX_3. For example, solubilities of AgX salts in dichloromethane at 22 °C follow the order $AgClO_4$ (0.0006 M)[96] < $AgBF_4$ (0.010 M)[97] < $AgSbF_6$ (0.16 M)[98] < $AgOTeF_5$ (> 2.5 M).[96] Since teflate is a stronger donor than perchlorate, the extremely high solubility of $AgOTeF_5$ in this weakly coordinating solvent seems anomalous. In another study, it was found that $AgOTeF_5$ absorbed carbon monoxide in the solid state to form an unprecedented, isolable silver carbonyl, $Ag(OTeF_5)(CO)$ ($\nu(CO) = 2189\ cm^{-1}$).[99] The compound $AgSbF_6$, on the other hand, did not interact with carbon monoxide.[100] In yet another study, the solubility of $TlOTeF_5$ in toluene was determined to be 0.39 M. In contrast, $TlClO_4$ is completely insoluble in this solvent.[85] Finally, Mössbauer spectra indicate a major structural difference between $Fe(OTeF_5)_3$ and $Fe(SO_3CF_3)_3$. The former compound apparently has a trigonal-planar FeO_3 coordination geometry[88] while the latter has a routine octahedral FeO_6 coordination geometry.[101]

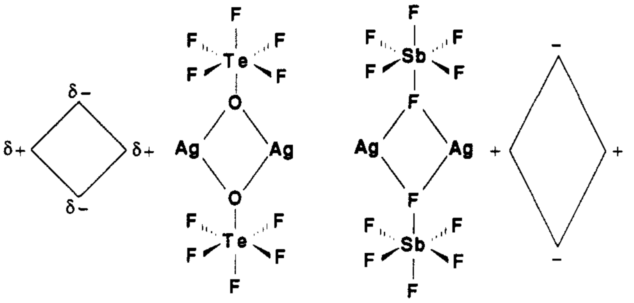

Figure 12. Diagram showing possible charges and charge separations for $Ag_2(OTeF_5)_2$ and $Ag_2(SbF_6)_2$ fragments.

These results can be understood as follows. With only one reasonably strong donor atom, teflate cannot form insoluble lattices with three-dimensional extended bridging, as can perchlorate and sulfonates. Since teflate's negative charge is concentrated on the oxygen atom,[81] its fluorine atoms are undoubtedly weaker donors than the fluorine atoms of the common fluoroanions. Furthermore, since teflate forms relatively strong M–O bonds, a $M(OTeF_5)_n$ or $M_2(OTeF_5)_{2n}$ fragment is probably more molecular (i.e., has lower charges) than a $M(SbF_6)_n$ or $M_2(SbF_6)_{2n}$ fragment, as depicted in Figure 12. Therefore, binary teflate compounds *should* be soluble in any solvent that can coordinate to the metal ion, even if the dielectric constant of the solvent is very low. The coordination of several weakly donating solvents has been studied by X-ray crystallography in isolable complexes such as $Ag(OTeF_5)(CH_2Cl_2)$,[96] $Ag(OTeF_5)(1,2\text{-}C_2H_4Cl_2)$,[96] $Ag(OTeF_5)(1,2,3\text{-}C_3H_5Cl_3)$,[102] $Tl(OTeF_5)(mes)_2$ (mes = mesitylene),[85] $Zn(OTeF_5)_2(C_6H_5NO_2)_2$,[103] and $Zn(OTeF_5)_2(C_6H_5NO_2)_3$.[103] With the exception of the last compound, which is a monomer, all of these complexes are dimeric with $M_2(OTeF_5)_2$ cores. For example, the structure of $Zn(OTeF_5)_2(C_6H_5NO_2)_2$, which contains both bridging and terminal teflate groups, is shown in Figure 13. Note that nitrobenzene can coordinate to metal ions both as a monodentate and as a bidentate ligand.[104] Suffice it to say, solvents such as chloroalkanes, aromatic hydrocarbons, and nitroarenes should not be referred to as "noncoordinating" solvents.

As discussed above, the major disadvantage of fluoroanions such as BF_4^-, SbF_6^-, etc. is the potential for fluoride ion abstraction by electrophiles. This is

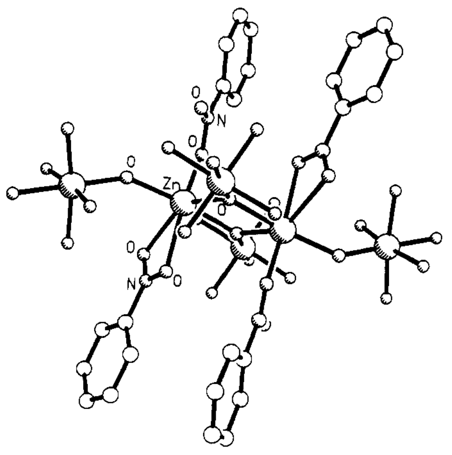

Figure 13. Structure of the centrosymmetric $[Zn(OTeF_5)_2(C_6H_5NO_2)_2]_2$ dimer. Each Zn(II) ion is coordinated to one bridging and one terminal $OTeF_5^-$ anion and to one monodentate and one bidentate nitrobenzene ligand. The unlabeled open spheres are carbon atoms, the unlabeled large highlighted spheres are tellurium atoms, and the unlabeled small highlighted spheres are fluorine atoms. Hydrogen atoms have been omitted for clarity.

not a problem for the teflate anion, however. There is *no evidence for fluoride ion or fluorine atom loss from free or bound* $OTeF_5^-$ at temperatures below 200 °C.[105]

B. $M(OTeF_5)_n^{m-}$

In an effort to obtain larger and more weakly coordinating anions, several $M(OTeF_5)_n^{m-}$ complexes ($n = 4, 6$; $m = 1, 2$) have been studied.[85a,96,99,100,106,107] It was anticipated that having the negative charge delocalized over a large number of fluorine atoms would diminish the interaction of any given fluorine atom and a cationic metal center. In an effort to further minimize cation–anion interactions, the soft monovalent cations Ag(I) and Tl(I) were chosen for initial studies. An additional reason for choosing these particular cations is that the set of $Ag_mM(OTeF_5)_n$ and $Tl_mM(OTeF_5)_n$ salts would then be available as Cl^-/X^- metathesis reagents.

A subset of these anions, $M(OTeF_5)_4^{2-}$ (M = Co,[107] Ni,[107] Cu,[107] Zn,[100] and Pd[96]), will be considered first. Their Ag(I) salts have proven to be the most interesting. For example, crystalline $Ag_2Zn(OTeF_5)_4$ binds 2 equiv of carbon monoxide at 22 °C and pressures < 1 atm. (Recall that $AgOTeF_5$ takes up only 1 equiv and $AgSbF_6$ does not form a complex with CO under these conditions.[100]) Another interesting example is $Ag_2Pd(OTeF_5)_4$, which absorbs up to 2 equiv of dichloromethane vapor in the solid state, as shown in Figure 14. Both a 1:1 (Ag/CH_2Cl_2) and a 1:2 complex are evident. As can be seen, the 1:2 complex has an equilibrium vapor pressure of dichloromethane above the crystals of ~350 Torr, which is nearly the vapor pressure of neat dichloromethane at 22 °C. The structure of the 1:2 complex is shown in Figure 15. Each Ag(I) ion in this centrosymmetric complex is coordinated to two bidentate dichloromethane ligands. The Ag–Cl bond distances range from 2.775(2) to 2.882(2) Å. These distances are much shorter than the sum of van der Waals radii for Ag and Cl atoms, 3.45 ± 0.05 Å.[46] Considering that the chlorine atoms do not bear a full negative charge, the Ag–Cl bonds are quite short—they can be compared with Ag–Cl distances involving a terminal chloride ion, 2.512(1) Å in Ag(diphos)Cl,[108] chloride ions that bridge Ag(I) and Pt(II) ions, 2.408(8) and 2.724(8) Å in $Ag_2Pt_2Cl_4(C_6F_5)_4$,[109] and an octahedral array of chloride ions, 2.77512(5) Å in AgCl.[75]

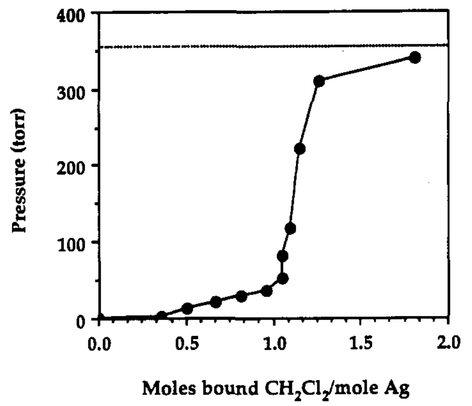

Figure 14. Tensimetric titration of $Ag_2Pd(OTeF_5)_4$ with dichloromethane. The pressure in the apparatus is due to dichloromethane vapor only. The dotted horizontal line at 353.3 Torr represents the vapor pressure of dichloromethane at 20.0 °C.

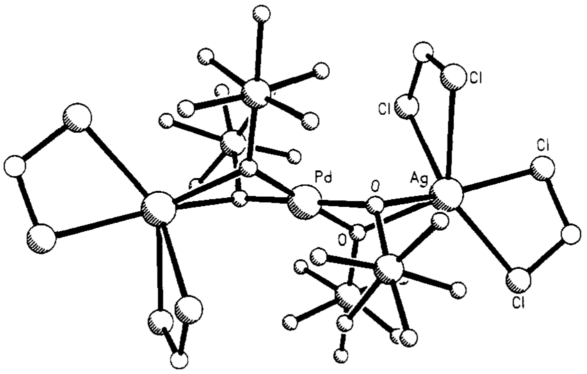

Figure 15. Structure of the centrosymmetric $[Ag(CH_2Cl_2)_2]_2[Pd(OTeF_5)_4]$ formula unit. The unlabeled open spheres are carbon atoms, the unlabeled large highlighted spheres are tellurium atoms, and the unlabeled small highlighted spheres are fluorine atoms. Hydrogen atoms have been omitted for clarity.

Note that each Ag(I) ion in $[Ag(CH_2Cl_2)_2]_2[Pd(OTeF_5)_4]$ is bonded to two of the oxygen atoms of the $Pd(OTeF_5)_4^{2-}$ counterion. Evidently, the teflate oxygen atoms in this compound are too sterically accessible to allow only weak Ag–F interactions to exist. In order to gauge the strength of the cation–anion interaction in $[Ag(CH_2Cl_2)_2]_2[Pd(OTeF_5)_4]$, equivalent conductances were measured for $Ag_2Pd(OTeF_5)_4$, $AgOTeF_5$, and related compounds.[96] The results are shown in Table IV. They suggest that a much higher proportion of Ag(I) ions are dissociated from $Pd(OTeF_5)_4^{2-}$ than from $OTeF_5^-$, so it is the former anion that is the more weakly coordinating. The results in Table IV also require that specific solvation of Ag(I) ions (i.e., coordination to Ag(I) ions) must be stronger with 1,2-dichloroethane than with dichloromethane, a conclusion that was corroborated by ^{13}C NMR experiments.[96]

A logical extension of the chemistry described above was the exploration of the $B(OTeF_5)_4^-$ anion as a very bulky and less coordinating alternative to BF_4^-. It was thought that the relatively short B–O bonds might

Table IV. Equivalent Conductances (22 °C) in Dichloromethane and 1,2-Dichloroethane[a]

compd	concentration, M	10^3 × equivalent conductance, Ω^{-1} cm^{-1} M^{-1} CH$_2$Cl$_2$	10^3 × equivalent conductance, Ω^{-1} cm^{-1} M^{-1} 1,2-C$_2$H$_4$Cl$_2$
$AgOTeF_5$	0.0101	0.14	0.52
$Ag_2Pd(OTeF_5)_4$	0.0100	2.9	14.4
$N(n\text{-}Bu)_4{}^+ClO_4{}^-$	0.0100	13.8	
$N(n\text{-}Bu)_4{}^+OTeF_5{}^-$	0.0100	14.8	15.2
$(N(n\text{-}Bu)_4{}^+)_2Pd(OTeF_5)_4{}^{2-}$	0.0100	15.6	16.4

[a] Data from ref 96. The specific conductance of both of the pure solvents was ≤3 × 10^{-7} Ω^{-1} cm^{-1}.

prevent strong B–O–M bridges from forming. Five compounds have been structurally characterized: $[Tl(mes)_2][B(OTeF_5)_4]$,[85] $[Tl(1,2\text{-}C_2H_4Cl_2)][B(OTeF_5)_4]$,[106c] $AgB(OTeF_5)_4$,[106b] $[Ag(CO)][B(OTeF_5)_4]$,[99] and $[Ag(CO)_2][B(OTeF_5)_4]$.[100] In the two Tl(I) compounds, the only cation–anion interactions are relatively long Tl–F secondary[111] bonds. In the compound $[Tl(mes)_2][B(OTeF_5)_4]$, which contains two η^6-mesitylene ligands for each Tl(I) ion, the four closest Tl–F contacts are made with two borate counterions and are 3.17(1), 3.25(1), 3.47(1), and 3.83(1) Å.[85] The last two distances are longer than the sum of van der Waals radii for thallium and fluorine, ~3.35–3.50 Å.[46,47] In the compound $[Tl(1,2\text{-}C_2H_4Cl_2)][B(OTeF_5)_4]$, the presence of a simple chelating bidentate 1,2-dichloroethane ligand instead of two η^6-mesitylene ligands leads to a greater number of Tl–F contacts.[106c] In this case, four anions donate nine fluorine atoms, and the distances range from 2.950(5) to 3.981(8) Å. For comparison, the Tl–F distances in TlF, which possesses a very distorted rock salt structure, range from 2.25(2) to 3.90(2) Å.[112] Another relevant comparison can be made with $[Tl(C_9H_{21}N_3)][PF_6]$, in which the Tl(I) ion has an N_3F_3 donor set ($C_9H_{21}N_3$ = *N,N′,N″*-trimethyl-1,4,7-triazacyclononane).[113] In this compound, the Tl–F distances are 3.23(1), 3.27(1), and 3.54(1) Å.

In the silver dicarbonyl complex, there are three discrete, linear $Ag(CO)_2{}^+$ cations, each surrounded by $B(OTeF_5)_4{}^-$ anions.[100] The Ag–F distances range from 2.75(1) to 3.20(1) Å, 3.02(1) to 3.54(1) Å, and 2.95(1) to 3.57(2) Å for the three cations. The Ag–F distances in $AgSbF_6$[114] and in AgF,[115] both of which have AgF_6 coordination spheres, are 2.62 and 2.467(3) Å, respectively. Clearly, in $[Ag(CO)_2][B(OTeF_5)_4]$ and in the two Tl(I) compounds, the $B(OTeF_5)_4{}^-$ anion is extremely weakly coordinating.

Nevertheless, in both $AgB(OTeF_5)_4$ and in $[Ag(CO)][B(OTeF_5)_4]$ there are Ag–O–B bridges, indicating that the borate anion can coordinate more strongly under some circumstances. In the structure of $[Ag(CO)][B(OTeF_5)_4]$, which is shown in Figure 16, there are two Ag–O bonds (Ag–O1 = 2.324(6) Å, Ag–O2 = 2.436(7) Å) and four Ag–F contacts (not shown) which range in distance from 2.959(6) to 3.076(8) Å.[99] The Ag(I) ion in $AgB(OTeF_5)_4$ is bonded to O1 (2.500(5) Å) and O2 (2.601(5) Å) from one borate anion and more weakly bonded to O3′ (2.756(5) Å) from another.[106b] Six Ag–F contacts, 2.644(5)–3.017(5) Å, round out the coordination sphere of the cation. Differences in ionic radii may explain why Tl(I) does not coordinate to $B(OTeF_5)_4{}^-$ oxygen atoms. The six-coordinate radii of Ag(I) and Tl(I) are 1.15 and 1.50 Å, respectively.[57] Clearly, the oxygen atoms are sterically less accessible than the fluorine atoms, and the larger Tl(I) ion may not be able to form Tl–O–B bridge bonds without requiring a severe distortion of the borate anion.

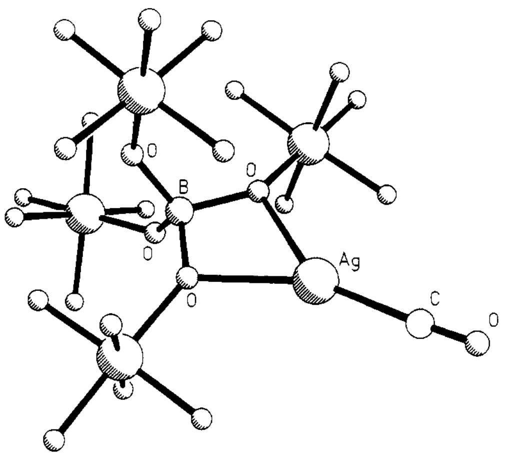

Figure 16. Structure of $[Ag(CO)][(B(OTeF_5)_4)]$. The unlabeled large highlighted spheres are tellurium atoms, and the unlabeled small highlighted spheres are fluorine atoms.

Similar bridge bonds to the oxygen atoms of the borate anion may explain how cationic electrophiles abstract a teflate anion from $B(OTeF_5)_4{}^-$. For example, attempts to prepare $[Fe(TPP)][B(OTeF_5)_4]$, $[Fe(OEP)][B(OTeF_5)_4]$, or $[SiPh_3][B(OTeF_5)_4]$ by metathesis reactions between Fe(TPP)Cl, Fe(OEP)Cl, or $SiClPh_3$ and $AgB(OTeF_5)_4$ or $TlB(OTeF_5)_4$, or between $SiHPh_3$ and $[CPh_3][B(OTeF_5)_4]$, led only to the isolation of $Fe(TPP)(OTeF_5)$, $Fe(OEP)(OTeF_5)$, or $SiPh_3(OTeF_5)$.[106b] The elusive cations $Fe(TPP)^+$, $Fe(OEP)^+$, and $SiPh_3{}^+$ were not observed. Presumably, intermediates such as $[(TPP)FeO(TeF_5)B(OTeF_5)_3]$ are involved in these reactions. Control experiments proved that $OTeF_5{}^-$ did not readily dissociate from $B(OTeF_5)_4{}^-$: there was no isotope exchange, even after weeks, when $[TBA][{}^{17}OTeF_5]$ was mixed with $[TBA][B({}^{16}OTeF_5)_4]$ in dichloromethane at 22 °C.[106b] The presence of an electrophile was definitely required to effect the exchange. For example, ^{17}O NMR experiments showed that complete isotope exchange occurred within 1 h when $H^{17}OTeF_5$ or $Ag^{17}OTeF_5$ were mixed with $[TBA][B({}^{16}OTeF_5)_4]$.[106b] Therefore, despite the large size and diffuse charge of the $B(OTeF_5)_4{}^-$ anion, its usefulness as a weakly coordinating anion is limited: it too easily fragments into $OTeF_5{}^-$ and $B(OTeF_5)_3$ in the presence of strong electrophiles.

A limited amount of information is available on even larger $M(OTeF_5)_n{}^{m-}$ anions with sterically less accessible oxygen atoms, such as $Ti(OTeF_5)_6{}^{2-}$,[90a,106a] $Nb(OTeF_5)_6{}^-$,[116] $Ta(OTeF_5)_6{}^-$,[116] and $Sb(OTeF_5)_6{}^-$.[117] Silver(I) salts of the first two have been prepared and studied,[106a] and the initial interpretation is that these hexacoordinate anions are superior to $B(OTeF_5)_4{}^-$ in three important respects. First, as the structure of $[Ag(CH_2Cl_2)_3]_2[Ti(OTeF_5)_6]$, shown in Figure 17, demonstrates, there are no Ag–O–Ti bridge bonds and only two relatively weak Ag–F interactions (Ag–F1 = 3.028(7) Å, Ag–F6 = 3.034(7) Å). Second, IR experiments showed no exchange between $Ag^{18}OTeF_5$ and $AgNb({}^{16}OTeF_5)_6$, even after several days. Finally, the solubilities of $AgSbF_6$, $AgOTeF_5$, $AgB(OTeF_5)_4$, and $AgNb(OTeF_5)_6$ in 1,1,2-trichlorotrifluoroethane (CFC-113)

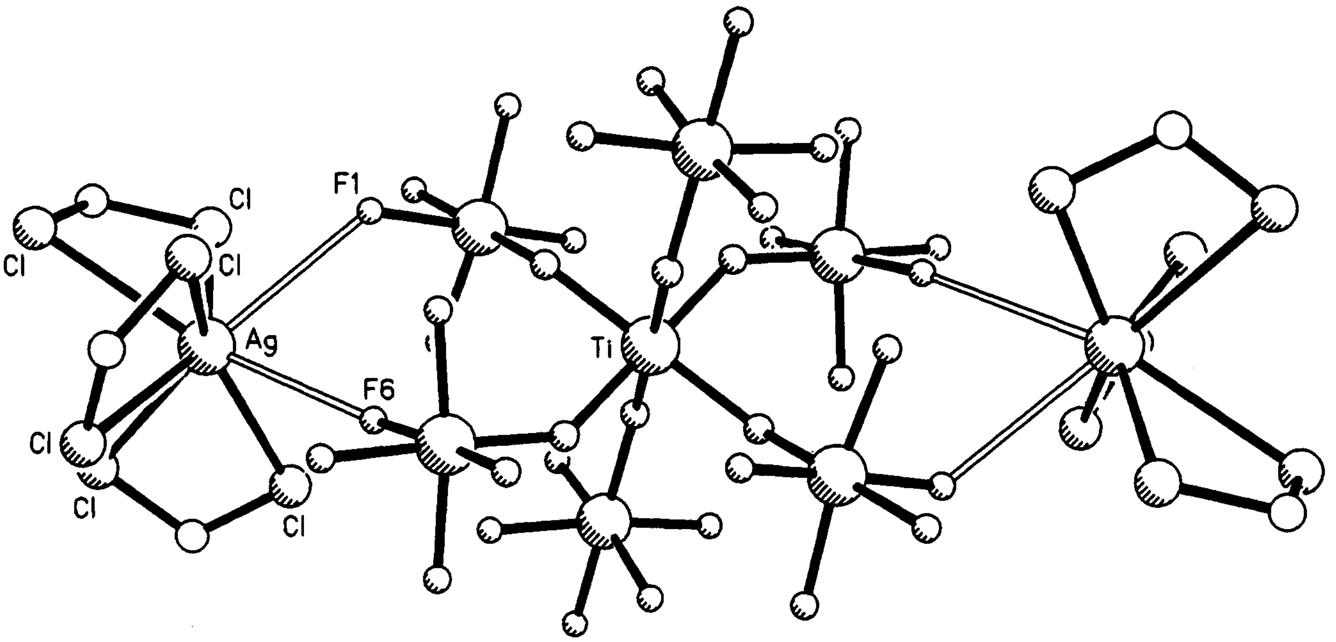

Figure 17. Structure of the centrosymmetric $[Ag(CH_2Cl_2)_3]_2[Ti(OTeF_5)_6]$ formula unit. The unlabeled open spheres are carbon atoms, the unlabeled large highlighted spheres are tellurium atoms, and the unlabeled small highlighted spheres are fluorine atoms. Hydrogen atoms have been omitted for clarity.

at 22 °C are 0, 0, 0.004, and 0.40 M, respectively, showing that appreciable concentrations of metal ions can be produced in solvents that are even more weakly coordinating than dichloromethane if the counterion is large enough and weakly coordinating enough. Whether complex ion salts such as $[Fe(Por)][Nb(OTeF_5)_6]$ and $[SiR_3][Nb(OTeF_5)_6]$ can be isolated and fully characterized remains to be seen.

VI. $PW_{12}O_{40}^{3-}$ and Related Anions

A number of reactive, cationic organometallic complexes have been isolated in the solid state using heteropolyanions (Keggin ions) such as $PW_{12}O_{40}^{3-}$ as their counterions. The first such complex studied was the $Rh(CO)(PPh_3)_2^+$ cation in $[Rh(CO)(PPh_3)_2]_3[PM_{12}O_{40}]$ and $[Rh(CO)(PPh_3)_2]_4[SiM_{12}O_{40}]$ (M = Mo, W).[118] These compounds were prepared by heating the $[Rh(CH_3CN)(CO)(PPh_3)_2]_n[EM_{12}O_{40}]$ precursors to >140 °C under vacuum, driving off the weakly bound acetonitrile ligands (E = P, $n = 3$; E = Si, $n = 4$). EXAFS results for $[Rh(CO)(PPh_3)_2]_4[SiW_{12}O_{40}]$ showed no Rh···W distance < 4 Å. On this basis, the authors proposed that there are no Rh–O(W) contacts in this class of compounds and that coordinatively unsaturated (i.e., 14-electron) $Rh(CO)(PPh_3)_2^+$ cations are located in interstitial sites between the $SiW_{12}O_{40}^{4-}$ cages.[118] An alternative interpretation is that one or more weak Rh–O(M) contacts with distances > 3 Å exist in these compounds, similar to the long Ag–F(Te) contacts in $[Ag(CH_2Cl_2)_3]_2[Ti(OTeF_5)_6]$ (see above). Such long Rh–O distances would give rise to Rh···W distances significantly greater than 4 Å and would not have been found in the analysis of the EXAFS data. Another alternative explanation is that a weak interaction with a phenyl group in $Rh(CO)(PPh_3)_2^+$ gives rise to a reactive yet saturated 16-electron complex. Such an interaction was discovered in the related complex $[Rh(PPh_3)_3][ClO_4]$.[119] Nevertheless, it has been found that solid-state, solvent-free compounds such as $[Rh(CO)(PPh_3)_2]_4[SiW_{12}O_{40}]$ are active catalysts for olefin hydroformylation and isomerization, the oxidation of carbon monoxide to carbon dioxide, and the reduction of nitric oxide to nitrous oxide by carbon dioxide.[120]

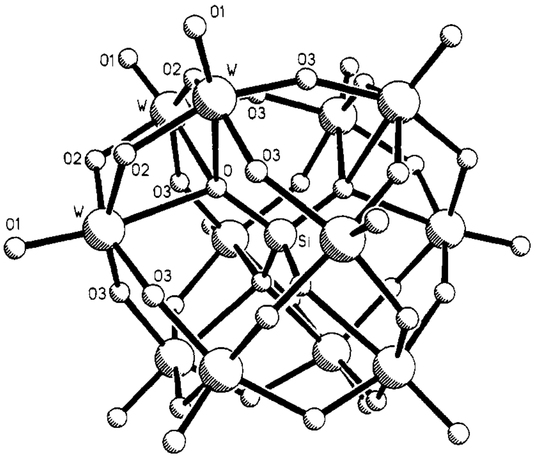

Figure 18. Structure of the $SiW_{12}O_{40}^{4-}$ anion. Only a portion of the anion has been labeled, showing the four types of oxygen atoms described in the text (O, O1, O2, and O3).

Therefore, even if Rh–O or $\overline{\mathrm{Rh{-}H{-}C}}_{\mathrm{ortho}}$ bonds exist in these species, they must be weak and labile interactions that allow the metal center to exhibit the observed catalytic activity. In other words, these novel materials contain virtual coordination sites.

The structure of the $SiW_{12}O_{40}^{4-}$ anion in $[BEDT\text{-}TTF]_8[SiW_{12}O_{40}]$[121] is shown in Figure 18. The heteropolyanion, which has effective T_d symmetry, is representative of the structure of all four $EM_{12}O_{40}^{n-}$ anions mentioned above. There are four types of oxygen atoms, of which three could potentially form bridges to cations. (Each of the four oxygen atoms forming the central SiO_4 core, labeled O in Figure 18, cannot form bridges with cations, since they are already four-coordinate.) Besides the terminal M═O oxygen atoms (labeled O1), there are two types of M–O–M bridging oxygen atoms. One type (O2) bridges pairs of edge-shared MO_6 octahedra and the other type (O3) bridges pairs of vertex-shared MO_6 octahedra. It has been shown that O2 is more basic than O1: treatment of $[N(n\text{-}C_6H_{13})_4]_3[PMo_{12}O_{40}]$ with $[O(CH_3)_3][BF_4]$ results in methylation of an O2 atom in preference to an O1 atom and the formation of a $M\text{–}O(CH_3)\text{–}M$ unit.[122] Since O3 is sterically less accessible than O2, this experiment may not have probed its relative basicity. As far as intrinsic basicity is concerned, it has been shown that $PMo_{12}O_{40}^{3-}$ and $SiMo_{12}O_{40}^{4-}$ are considerably less basic than perchlorate. This fact can be understood by representing these ions as $(PO_4)^{3-}(Mo_{12}O_{36})^0$ and $(SiO_4)^{4-}(Mo_{12}O_{36})^0$, which denote the highly charged cores in a metal oxide sheath possessing zero surface formal charge.[123] Nevertheless, metal ions such as Ca^{2+} and Eu^{3+} bind, with substantial affinity, to some heteropolyanions in aqueous solution, including $SiMo_{12}O_{40}^{4-}$.[123b]

The concept of trapping soft organometallic cations in a lattice of hard, very large, weakly nucleophilic heteropolyanion clusters has also been nicely exploited in a number of other systems involving rhodium, iridium, and platinum.[124] Many of these systems display catalytic activity. In some cases, such as $[PtH(PEt_3)_2]_3[PW_{12}O_{40}]$,[124e] virtual coordination sites are generated by thermally removing solvent molecules bound to the metal in the precursor. In other cases, such as $[IrH_2(PPh_3)_2]_3[PW_{12}O_{40}]$,[124f] these sites are created by hydrogenation of olefins bound to the metal in the precursor.

VII. $HC(SO_2CF_3)_2^-$ and Related Anions

There have been numerous reports of the use of carbon and nitrogen Brønsted acids such as $CH_2(SO_2CF_3)_2$, $CH(Ph)(SO_2CF_3)_2$, $NH(SO_2CF_3)_2$, and homologues with longer perfluoroalkyl chains to prepare (i) catalytically active rhodium and iridium complexes,[125] (ii) protonated late transition metal complexes,[126] and (iii) η^2-H_2 complexes of ruthenium[127] and iridium.[128] The acids possess a number of useful properties:[125d] they are volatile, crystalline, air-stable solids; they are soluble in weakly coordinating solvents such as toluene and dichloromethane (replacement of the CF_3 groups with longer perfluoroalkyl chains results in significantly enhanced solubilities in aromatic hydrocarbons of salts of the conjugate bases); they are nonoxidizing, strong acids (the pK_a of $CH_2(SO_2CF_3)_2$ was estimated to be approximately −1 in water); their conjugate bases appear to be very weakly coordinating toward soft metal ions. For example, treatment of $RhH(PPh_3)_4$ with $CH_2(SO_2CF_3)_2$ resulted in the formation of $[Rh(PPh_3)_3][CH(SO_2CF_3)_2]$.[125d] NMR and IR data strongly suggested that the $CH(SO_2CF_3)_2^-$ ion is not coordinated to Rh(I) in this compound, which is not surprising since perchlorate does not coordinate to Rh(I) in $[Rh(PPh_3)_3][ClO_4]$.[119]

Nevertheless, anions such as $CH(SO_2CF_3)_2^-$ can coordinate strongly to oxophilic early transition metal cations and to later transition metal cations without additional ligands. In fact, the formation of relatively stable chelate rings can make $CH(SO_2CF_3)_2^-$ and related anions more strongly coordinating than triflate and other sulfonates in some cases. For example, the structure of $Zr(Cp)_2(CH(SO_2CF_3)_2)_2$, shown in Figure 19, revealed the presence of two coordinated $CH(SO_2CF_3)_2^-$ anions.[129] Note that one of these ligands is O-monodentate and the other is O,O′-bidentate, the latter forming a six-membered Zr–O–S(O)–C(H)–S(O)–O chelate ring. A similar chelate ring was found in $Ti_2(i\text{-}PrO)_6(CH(SO_2CF_3)_2)_2$.[130] The related anion $C(SO_2C_2H_5)_3^-$ was used to prepare binary salts such as $Co(C(SO_2C_2H_5)_3)_2$ and $Ni(C(SO_2C_2H_5)_3)_2$.[131] Ligand field spectra and magnetic moments were consistent with octahedral coordination of the metal ions, suggesting the presence of not only O-coordination but of O,O′-chelation as well. In some cases involving low-valent, soft metal ions,[126c,f] the $CH(SO_2CF_3)_2^-$ anion can coordinate through its central carbon atom, making it superficially similar to the acetylacetonate anion.

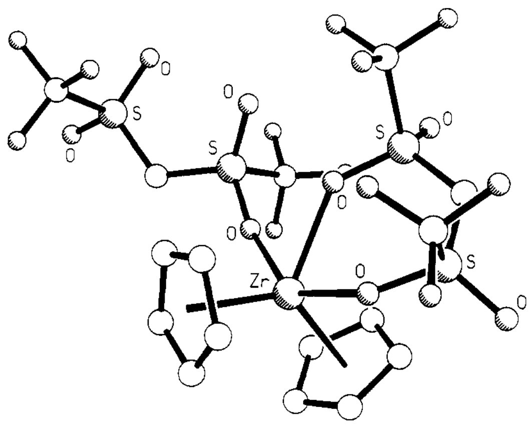

Figure 19. Structure of $Zr(Cp)_2(CH(SO_2CF_3)_2)_2$. The unlabeled open spheres are carbon atoms and the unlabeled small highlighted spheres are fluorine atoms. Hydrogen atoms have been omitted for clarity.

VIII. Miscellaneous Anions

A. C_{60}^-

There is only one report of the use of the fulleride ion C_{60}^- as a counterion for a cationic metal complex. Treatment of Cr(TPP) with C_{60} in THF produced crystalline $Cr(TPP)(C_{60})(THF)_3$.[132] Based on the available spectroscopic and magnetic data, the product is best formulated as $[Cr(TPP)(THF)_2]^+[C_{60}]^-\cdot THF$.[132] The reaction is highly solvent dependent and does not occur in toluene solution. Apparently, a coordinating solvent like THF is necessary to stabilize the cationic Cr(III) product that results from electron transfer from Cr(II) to C_{60}.

Despite this interesting result, C_{60}^- will probably not find widespread use as a weakly coordinating anion for two reasons. First, reduction potentials for the $C_{60}^{0/1-}$ couple, which are solvent dependent, are always more negative than 0 V vs NHE.[133] This means that C_{60}^- is even more prone to oxidation by electrophiles than BPh_4^- (see above). Second, neutral C_{60} has been found to coordinate to metals as a bulky olefin.[134] The addition of a negative charge could make it an even better ligand for cationic, electrophilic metal complexes that have an affinity for olefins. The second point may not be relevant in all cases, however: it has been shown that for neutral, soft metal complexes such as $Pt(PPh_3)_2$, the order of affinity is $C_{60} > C_{60}^- > C_{60}^{2-}$.[134b]

B. $B(o\text{-}C_6H_4O_2)_2^-$

This relatively stable borate anion has been used to generate cationic π-allyl nickel complexes that are catalysts for stereospecific butadiene polymerization.[135] It was found that $B(o\text{-}C_6H_4O_2)_2^-$ is more strongly coordinating than PF_6^- and less strongly coordinating than sulfonates such as triflate and tosylate. It seems likely that the catecholate oxygen atoms coordinate to the Ni(II) ions in these compounds.

C. $H(1,8\text{-}(BMe_2)_2C_{10}H_6)^-$

The neutral diborane $1,8\text{-}(BMe_2)_2C_{10}H_6$ has been shown to abstract hydride from various triorganoborohydrides and from $Zr(Cp)_2(H)(Cl)$.[136] It has been called hydride sponge because of its similarity to Proton Sponge, 1,8-bis(dimethylamino)naphthalene.[136] The anion, $H(1,8\text{-}(BMe_2)_2C_{10}H_6)^-$, may be a potential weakly coordinating anion, since the hydridic hydrogen atom is firmly bound to two boron atoms and is sterically protected by the four methyl groups. The potential exists, however, for coordination of this anion through its delocalized π-system. The field of multidentate anion complexation has been recently reviewed.[137]

D. Anionic Methylalumoxanes

Active Ziegler–Natta polymerization catalysts have been prepared from soluble $M(Cp)_2(X)_2$ complexes and a large excess of methylalumoxane, which is a mixture of $[Al(CH_3)(\mu\text{-}O)]_n$ oligomers prepared by the controlled hydrolysis of $AlMe_3$.[24a,138] Little detail is known about the interactions between the poorly defined methylalumoxane and the metal complexes, but model studies suggest the formation of $[M(Cp)_2(X)]^+[X(Al(CH_3)(\mu\text{-}O))_n]$ ion pairs.[24a]

IX. Metathesis and Other Reactions: How Can Weakly Coordinating Anions Be Introduced?

An important issue that has not yet been addressed in this review is the limitations imposed by weakly coordinating anions on possible metathesis reactions. In other words, how are larger and more weakly coordinating anions going to be introduced in the first place? Several routes that have been widely reported, and have been used in the chemistry described in the references given above, are $L_{n-1}M\text{–}R$ bond protonolysis, R^- abstraction with Lewis acids, halide abstraction with Ag(I) or Tl(I) salts, H^- abstraction with the CPh_3^+ cation, and oxidation of $L_{n-1}M\text{–}R$ bonds by Ag(I) or $Fe(Cp)_2^+$ ions.

Halide abstraction is by far the most general approach to the synthesis of highly reactive cationic metal complexes. Mechanistic studies of Ag(I)-induced halide abstraction from alkyl halides[139] and iodide abstraction from $Fe(Cp)(I)(CO)_2$[140] have been reported. When common anions such as BF_4^- are used, the situation is believed to be well understood. When larger and more weakly coordinating anions are employed, however, halide abstraction is either very slow or does not occur. For example, when the complex $IrCl(CO)(PPh_3)_2$ was treated with $AgClO_4$ in benzene, a rapid Cl^-/ClO_4^- metathesis occurred and AgCl and $Ir(ClO_4)(CO)(PPh_3)_2$ were formed.[141] Similarly, the complex $Ir(SO_3CF_3)(CO)(PPh_3)_2$ was formed if $AgSO_3CF_3$ was used instead of $AgClO_4$.[66a] In contrast, when $AgBF_4$, $AgSbF_6$, $Ag(CB_{11}H_{12})$, $Ag(7,8,9,10,11,12\text{-}CB_{11}H_6Br_6)$, or $Ag(C(Ph)(SO_2CF_3)_2)$ were used, there was no precipitation of AgCl even after several days. Instead, an adduct with a Ir–Ag–X linkage was formed (X^- = the weakly coordinating counterion). Furthermore, when acetone was used as the solvent, the metathesis between $IrCl(CO)(PPh_3)_2$ and $Ag(CB_{11}H_{12})$ occurred rapidly, but the iridium complex formed was $Ir((CH_3)_2CO)(CO)(PPh_3)_2^+$.[66a]

Another example of arrested halide abstraction was observed when $Fe(Cp)(I)(CO)_2$ was treated with $Ag(CB_{11}H_{12})$ in benzene.[66a] A stable adduct with a Fe–I–Ag linkage was isolated and characterized. Only after one week was the metathesis reaction complete, yielding AgI and $Fe(Cp)(CB_{11}H_{12})(CO)_2$ (see Figure 10). If the counterion X^- was BF_4^-, SbF_6^-, ClO_4^-, or $SO_3CF_3^-$, the iodide-bridged adduct could be observed but decomposed much more rapidly to AgI and $Fe(Cp)(X)(CO)_2$.

Both of these examples demonstrate that the rates of halide/weakly coordinating anion metathesis reactions are very sensitive to the nucleophilicity of the anion and the solvent. Rather than halide abstraction by Ag(I), these reactions should be thought of as Ag(I)-assisted nucleophilic displacements of halide ions by X^- or by a solvent molecule. The paradox is that as anions and solvents become less and less coordinating, and hence less basic and less nucleophilic, simple $L_{n-1}M\text{–}Cl$ complexes will not be useful precursors to reactive, virtually unsaturated $L_{n-1}M^+$ cations. More clever ways to introduce weakly coordinating anions will have to be developed. Along with the synthesis of larger and more weakly coordinating anions, this is one of the most important challenges facing coordination chemists today.

X. Acknowledgments

I am pleased to acknowledge the fine work of the talented and dedicated graduate and undergraduate students, postdoctoral fellows, and colleagues who have worked with me in the area of weakly coordinating anions and whose names can be found in the references. Our work in this area has been supported by the Research Corporation, the Alfred P. Sloan Foundation, and the National Science Foundation. I am grateful for the enthusiastic and able assistance I received from Dawn Van Seggen, Jeff Rack, and Susie Miller in the preparation of this review, and for the correspondance and conversations I had with Maurice Brookhart, Rick Finke, Rich Jordan, Kent Mann, Tobin Marks, Chris Reed, Allen Siedle, and Howard Turner.

XI. Abbreviations

Cp	η^5-cyclopentadienyl anion
Cp*	η^5-pentamethylcyclopentadienyl anion
Cp′	any of several substituted η^5-cyclopentadienyl anions
diphos	1,2-bis(diphenylphosphino)ethane
mes	mesitylene
NBD	2,5-norbornadiene
NHE	normal hydrogen electrode (E = 0 V)
OEP	2,3,7,8,12,13,17,18-octaethylporphyrinate dianion
Por	any porphyrinate dianion
PPN^+	bis(triphenylphosphine)iminium cation

py	pyridine
TBA	tetra-*n*-butylammonium cation
TFPB$^-$	tetrakis[3,5-bis(trifluoromethyl)phenyl]borate(1−) anion
THF	tetrahydrofuran
TPP	5,10,15,20-tetraphenylporphyrinate dianion

XII. References and Notes

(1) Rosenthal, M. R. *J. Chem. Educ.* **1973**, *50*, 331.

(2) Gowda, N. M. N.; Naikar, S. B.; Reddy, G. K. N. *Adv. Inorg. Chem. Radiochem.* **1984**, *28*, 255.

(3) Lawrance, G. A. *Chem. Rev.* **1986**, *86*, 17.

(4) Representative examples: (a) Hersh, W. H. *Inorg. Chem.* **1990**, *29*, 713. (b) Cockman, R. W.; Hoskins, B. F.; McCormick, M. J.; O'Donnell, T. A. *Inorg. Chem.* **1988**, *27*, 2742. (c) Horn, E.; Snow, M. R.; Tiekink, E. R. T. *Aust. J. Chem.* **1987**, *40*, 761. (d) Hitchcock, P. B.; Lappert, M. F.; Taylor, R. G. *J. Chem. Soc., Chem. Commun.* **1984**, 1082.

(5) Representative examples: (a) Honeychuck, R. V.; Hersh, W. H. *Inorg. Chem.* **1989**, *28*, 2869. (b) Dartiguenave, M.; Dartiguenave, Y.; Mari, A.; Guitard, A.; Olivier, M. J.; Beauchamp, A. L. *Can. J. Chem.* **1988**, *66*, 2386.

(6) Representative examples: (a) Klapotke, T.; Thewalt, U. *J. Organomet. Chem.* **1988**, *356*, 173. (b) Buss, B.; Clegg, W.; Hartmann, G.; Jones, P. G.; Mews, R.; Noltemeyer, M.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1981**, 61.

(7) Representative examples: (a) Hersh, W. H. *J. Am. Chem. Soc.* **1985**, *107*, 4599. (b) Shelly, K.; Bartczak, T.; Scheidt, W. R.; Reed, C. A. *Inorg. Chem.* **1985**, *24*, 4325.

(8) Beck, W.; Sünkel, K. *Chem. Rev.* **1988**, *88*, 1405. This review focuses on organometallic complexes of the weakly coordinating anions BF_4^-, PF_6^-, AsF_6^-, and SbF_6^-.

(9) Lawrance, G. A. *Adv. Inorg. Chem.* **1989**, *34*, 145.

(10) Wells, J. R.; Weitz, E. *J. Am. Chem. Soc.* **1992**, *114*, 2783. See also: Weiller, B. H.; Wasserman, E. P.; Bergman, R. G.; Moore, C. B.; Pimentel, G. C. *J. Am. Chem. Soc.* **1989**, *111*, 8288.

(11) (a) Hop, C. E. C. A.; McMahon, T. B. *J. Am. Chem. Soc.* **1991**, *113*, 355. (b) Morse, J.; Parker, G.; Burkey, T. J. *Organometallics* **1989**, *7*, 2471. (c) Yang, G. K.; Vaida, V.; Peters, K. S. *Polyhedron* **1988**, *7*, 1619.

(12) (a) Yoon, K. B.; Kochi, J. K. *Inorg. Chem.* **1990**, *29*, 869. (b) Seppelt, K. *Chem. Unserer Zeit* **1978**, *12*, 27. (c) Kiso, Y. *Kagaku No Ryoiki* **1973**, *27*, 1017. (d) Appelman, E. H. *Acc. Chem. Res.* **1973**, *6*, 113. (e) Dasent, W. E. *Nonexistent Compounds*; Dekker: New York, 1965.

(13) We are not considering coordinatively unsaturated transition states or extremely short-lived intermediates in this discussion. Our focus is on whether *persistent* vacant coordination sites ever exist in cationic complexes in solution.

(14) This principle is the Lewis acid equivalent of the leveling effect. Just as the Brønsted acidity of a strong protic acid is leveled down to the acidity of H_3O^+ in water, so the Lewis acidity of a cationic complex with an exchangeable, extremely weak metal–ligand bond is leveled down to the Lewis acidity of the corresponding species with an exchangeable, but stronger, metal–solvent bond.

(15) (a) Gutmann, V. *Coord. Chem. Rev.* **1976**, *18*, 225. (b) Gutmann, V. *Coord. Chem. Rev.* **1967**, *2*, 239. (c) Gutmann, V. *Coordination Chemistry in Non-aqueous Solvents*; Springer Verlag: New York, 1969.

(16) *Handbook of Chemistry and Physics*, 71st ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 1991.

(17) Honeychuck, R. V.; Hersh, W. H. *J. Am. Chem. Soc.* **1989**, *111*, 6056.

(18) It will also depend on the hardness of the cationic center: what may be the weakest coordinating anion for a hard metal center may not be the weakest coordinating anion for a soft metal center.

(19) Bartlett, N.; Okino, F.; Mallouk, T. E.; Hagiwara, R.; Lerner, M.; Rosenthal, G. L.; Kourtakis, K. In *Electron Transfer in Biology and the Solid State*; Johnson, M. K., King, R. B., Kurtz, D. M., Jr., Kutal, C., Norton, M. L., Scott, R. A., Eds.; Advances in Chemistry Series 226; American Chemical Society: Washington, DC, 1990; p 391.

(20) (a) Hill, M. G.; Lamanna, W. M.; Mann, K. R. *Inorg. Chem.* **1991**, *30*, 4687. (b) Bond, A. M.; Ellis, S. R.; Hollenkamp, A. F. *J. Am. Chem. Soc.* **1988**, *110*, 5293. (c) Appel, M.; Schloter, K.; Heidrich, J.; Beck, W. *J. Organomet. Chem.* **1987**, *322*, 77. (d) Rhodes, M. R.; Mann, K. R. *Inorg. Chem.* **1984**, *23*, 2053.

(21) (a) Winter, C. H.; Zhou, X.-X.; Heeg, M. J. *Inorg. Chem.* **1992**, *31*, 1808. (b) Gorrell, I. B.; Parkin, G. *Inorg. Chem.* **1990**, *29*, 2452. (c) Bonnesen, P. V.; Puckett, C. L.; Honeychuck, R. V.; Hersh, W. H. *J. Am. Chem. Soc.* **1989**, *111*, 6070 and references therein. (d) Klapötke, T.; Gowik, P. *Monatsh. Chem.* **1989**, *120*, 711. (e) Bochmann, M.; Wilson, L. M.; Hursthouse, M. B.; Short, R. L. *Organometallics* **1987**, *6*, 2556. (f) Jordan, R. F.; Dasher, W. E.; Echols, S. F. *J. Am. Chem. Soc.* **1986**, *108*, 1718. (g) Reedijk, J. *Comments Inorg. Chem.* **1982**, *1*, 379. (h) Marks, T. J.; Seyam, A. M. *Inorg. Chem.* **1974**, *13*, 1624.

(22) (a) Fachinetti, G.; Funaioli, T.; Zanazzi, P. F. *J. Chem. Soc., Chem. Commun.* **1988**, 1100. (b) Morris, J. H.; Gysling, H. J.; Reed, D. *Chem. Rev.* **1985**, *85*, 51. (c) Bancroft, E. E.; Blount, H. N.; Janzen, E. G. *J. Am. Chem. Soc.* **1979**, *101*, 3692. (d) Eisch, J. J.; Wilcsek, R. J. *J. Organomet. Chem.* **1974**, *71*, C21. (e) Abley, P.; Halpern, J. *J. Chem. Soc., Chem. Commun.* **1971**, 1238. (f) Williams, J. L. R.; Doty, J. C.; Grisdale, P. J.; Regan, T. H.; Borden, D. G. *J. Chem. Soc., Chem. Commun.* **1967**, 109.

(23) A survey of the CAS Online database (1967 through the present) during August 1992 revealed more than 600 references to the chemistry of tetraphenylborate (CAS Registry Number 4358-26-3).

(24) (a) Jordan, R. F. *Adv. Organomet. Chem.* **1991**, *32*, 325. (b) Horton, A. D.; Frijns, J. H. G. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1152. (c) Bochmann, M.; Jaggar, A. J.; Nicholls, J. C. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 780. (d) Hlatky, G. G.; Turner, H. W.; Eckman, R. R. *J. Am. Chem. Soc.* **1989**, *111*, 2728. (e) Taube, R.; Krukowka, L. *J. Organomet. Chem.* **1988**, *347*, C9. (f) Turner, H. W. European Patent Appl. 277,004 (assigned to Exxon), 1988. (g) Lin, Z.; Le Marechall, J.-F.; Sabat, M.; Marks, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 4127. (h) Jordan, R. F.; Bajgur, C. S.; Willett, R.; Scott, B. *J. Am. Chem. Soc.* **1986**, *108*, 7410.

(25) (a) Ananias de Carvalho, L. C.; Dartiguenave, M.; Dartiguenave, Y.; Beauchamp, A. L. *J. Am. Chem. Soc.* **1984**, *106*, 6848. (b) Albano, P.; Aresta, M.; Manassero, M. *Inorg. Chem.* **1980**, *19*, 1069. (c) Ashworth, T. V.; Nolte, M. J.; Reimann, R. H.; Singleton, E. *J. Chem. Soc., Chem. Commun.* **1977**, 937. (d) Kruger, G. J.; du Preez, A. L.; Haines, R. J. *J. Chem. Soc., Dalton Trans.* **1974**, 1302. (e) Nolte, M. J.; Gafner, G.; Haines, L. M. *J. Chem. Soc., Chem. Commun.* **1969**, 1406.

(26) Lutsenko, Z. L.; Aleksandrov, G. G.; Petrovskii, P. V.; Shubina, E. S.; Andrianov, V. G.; Struchkov, Y. T.; Rubezhov, A. Z. *J. Organomet. Chem.* **1985**, *281*, 349.

(27) Uson, R.; Oro, L. A.; Ciriano, M. A.; Naval, M. M.; Apreda, M. C.; Foces-Foces, C.; Cano, F. H.; Garcia-Blanco, S. *J. Organomet. Chem.* **1983**, *256*, 331.

(28) Bochmann, M.; Karger, G.; Jaggar, A. J. *J. Chem. Soc., Chem. Commun.* **1990**, 1038.

(29) Pasquali, M.; Floriani, C.; Gaetani-Manfredotti, A. *Inorg. Chem.* **1980**, *19*, 1191.

(30) Dines, M. B.; Bird, P. H. *J. Chem. Soc., Chem. Commun.* **1973**, 12.

(31) Turner, R. W.; Amma, E. L. *J. Am. Chem. Soc.* **1966**, *88*, 1877.

(32) Asymmetric bidentate coordination of arenes to Cu(I) and Ag(I) is normal: (a) Shelly, K.; Finster, D. C.; Lee, Y. J.; Scheidt, W. R.; Reed, C. A. *J. Am. Chem. Soc.* **1985**, *107*, 5955 and references therein. (b) Strauss, S. H.; Noirot, M. D.; Anderson, O. P. *Inorg. Chem.* **1986**, *25*, 3850 and references therein.

(33) (a) Crabtree, R. H.; Hamilton, D. G. *Adv. Organomet. Chem.* **1988**, *28*, 299. (b) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395.

(34) Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santasiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203.

(35) (a) Crociani, B.; Di Bianca, F.; Canovese, L.; Uguagliati, P. *J. Organomet. Chem.* **1990**, *381*, C17. (b) Bianchini, C.; Meli, A.; Laschi, F.; Vizza, F.; Zanello, P. *Inorg. Chem.* **1989**, *28*, 227. (c) Bonnesen, P. V.; Puckett, C. L.; Honeychuck, R. V.; Hersh, W. H. *J. Am. Chem. Soc.* **1989**, *111*, 6070. (d) Legzdins, P.; Martin, D. T. *Organometallics* **1983**, *2*, 1785. (e) Reed, C. A.; Mashiko, T.; Bentley, S. P.; Kastner, M. E.; Scheidt, W. R.; Spartalian, K.; Lang, G. *J. Am. Chem. Soc.* **1979**, *101*, 2948. (f) Sacconi, L.; Dapporto, P.; Stoppioni, P. *Inorg. Chem.* **1976**, *15*, 325. (g) Haines, R. J.; du Preez, A. L. *J. Am. Chem. Soc.* **1971**, *93*, 2820. (h) Clark, H. C.; Dixon, K. R. *J. Am. Chem. Soc.* **1969**, *91*, 596. (i) Coates, G. E.; Green, M. L. H.; Wade, K. *Organometallic Compounds*; Methuen: London, 1967; Vol. I.

(36) Nishida, H.; Takada, N.; Yoshimura, M.; Sonoda, T.; Kobayashi, H. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2600 and references therein.

(37) Jordan, R. F. *J. Organomet. Chem.* **1985**, *294*, 321.

(38) Thomas, B. J.; Theopold, K. H. *J. Am. Chem. Soc.* **1988**, *110*, 5902.

(39) (a) Turner, W. R.; Elving, P. *Anal. Chem.* **1965**, *37*, 207. (b) Geske, D. H. *J. Phys. Chem.* **1962**, *66*, 1743. (c) Geske, D. H. *J. Phys. Chem.* **1959**, *63*, 1062.

(40) Sacconi, L.; Mealli, C.; Gatteschi, D. *Inorg. Chem.* **1974**, *13*, 1985.

(41) (a) Grisdale, P. J.; Williams, J. L. R.; Glogowski, M. E.; Babb, B. E. *J. Org. Chem.* **1971**, *36*, 544 and references therein. (b) Williams, J. L. R.; Doty, J. C.; Grisdale, P. J.; Searle, R.; Regan, T. H.; Happ, G. P.; Maier, D. P. *J. Am. Chem. Soc.* **1967**, *89*, 5153 and references therein.

(42) Wilkey, J. D.; Schuster, G. B. *J. Am. Chem. Soc.* **1991**, *113*, 2149.

(43) Brüggeler, P. *Inorg. Chim. Acta* **1989**, *155*, 45.

(44) Schrock, R. R.; Osborn, J. A. *Inorg. Chem.* **1970**, *9*, 2339.

(45) Mann, K. R. Personal communication, 1992.

(46) (a) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441. (b) Pauling, L. *The Nature of the Chemical Bond*; Cornell Univ. Press: Ithaca, NY, 1960; p 257.

(47) Precise definitions or measurements of van der Waals radii are problematic, as they are for another elusive but highly important chemical quantity, electronegativity. Even for the halogens, Bondi's[46a] and Pauling's[46b] values differ by as much as 0.15 Å. The

situation for metal ions is complicated by the fact that they are generally hidden from nonbonded contacts.[46a] Furthermore, the van der Waals radius of a metal ion, like its ionic radius, probably depends on the oxidation state, the coordination geometry, and the coordination number. This will necessarily lead to ambiguous conclusions about long M···L distances.

(48) Mann, K. R. *Cryst. Struct. Commun.* **1981**, *10*, 451.

(49) (a) Marks, T. J. *Acc. Chem. Res.* **1992**, *25*, 57 and references therein. (b) Pellecchia, C.; Longo, P.; Proto, A.; Zambelli, A. *Makromol. Chem., Rapid Commun.* **1992**, *13*, 265. (c) Taube, R.; Wache, S. *J. Organomet. Chem.* **1992**, *428*, 431. (d) Horton, A. D.; Orpen, A. G. *Organometallics* **1991**, *10*, 3910.

(50) Brookhart, M.; Rix, R. C.; DeSimone, J. M.; Barborak, J. C. *J. Am. Chem. Soc.* **1992**, *114*, 5894.

(51) Brookhart, M.; Sabo-Etienne, S. *J. Am. Chem. Soc.* **1991**, *113*, 2778.

(52) Jordan, R. F. Personal communication, 1992.

(53) It must be admitted, however, that the chemistry of fluorinated tetraphenylborates and metal ions is still not very well developed. It is certainly possible that π-interactions will be discovered, especially with soft metal ions.

(54) Hlatky, G. G. *Book of Abstracts*; 204th American Chemical Society National Meeting, Fall 1992, Washington, DC; American Chemical Society: Washington, DC, 1992; INOR387.

(55) (a) Naumann, D.; Wieland, T. *J. Chem. Soc., Chem. Commun.* **1992**, 47. (b) Frohn, H. J.; Jakobs, S. *J. Chem. Soc., Chem. Commun.* **1992**, 625.

(56) Yang, X.; Stern, C. L.; Marks, T. J. *Organometallics* **1991**, *10*, 840.

(57) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.

(58) Hill, M. G.; Mann, K. R. *Inorg. Chem.* **1991**, *30*, 1429.

(59) This model ignores differences in enthalpies and entropies of solvation.

(60) (a) Kesti, M. R.; Waymouth, R. M. *J. Am. Chem. Soc.* **1992**, *114*, 3565. (b) Pellecchia, C.; Proto, A.; Longo, P.; Zambelli, A. *Makromol. Chem., Rapid Commun.* **1992**, 277. (c) Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1991**, *113*, 3623.

(61) Giandomenico, C. M.; Dewan, J. C.; Lippard, S. J. *J. Am. Chem. Soc.* **1981**, *103*, 1407.

(62) (a) Grimes, R. N., Ed. *Metal Interactions with Boron Clusters*; Plenum: New York, 1982. (b) Grimes, R. N. *Adv. Inorg. Chem. Radiochem.* **1983**, *26*, 55. (c) Housecroft, C. M.; Fehlner, T. P. *Adv. Organomet. Chem.* **1982**, *21*, 57. (d) Marks, T. J.; Kolb, J. R. *Chem. Rev.* **1977**, *77*, 263.

(63) Jensen, J. A.; Wilson, S. R.; Girolami, G. S. *J. Am. Chem. Soc.* **1988**, *110*, 4977.

(64) (a) Hlatky, G. G.; Eckman, R. R.; Turner, H. W. *Organometallics* **1992**, *11*, 1413. (b) Turner, H. W.; Hlatky, G. G. European Patent Appl. 277,003 (assigned to Exxon), 1988.

(65) Plešek, J. *Chem. Rev.* **1992**, *92*, 269.

(66) (a) Liston, D. J.; Lee, Y. J.; Scheidt, W. R.; Reed, C. A. *J. Am. Chem. Soc.* **1989**, *111*, 6643. (b) Gupta, G. P.; Lang, G.; Young, J. Y.; Scheidt, W. R.; Shelly, K.; Reed, C. A. *Inorg. Chem.* **1987**, *26*, 3022. (c) Liston, D. J.; Reed, C. A.; Eigenbrot, C. W.; Scheidt, W. R. *Inorg. Chem.* **1987**, *26*, 2739. (d) Shelly, K.; Reed, C. A.; Lee, Y. J.; Scheidt, W. R. *J. Am. Chem. Soc.* **1986**, *108*, 3117.

(67) Hoffmann, R.; Lipscomb, W. N. *J. Chem. Phys.* **1962**, *36*, 3489.

(68) The unique carbon atom in $CB_{11}H_{12}^-$ can be distinguished from the boron atoms in this icosahedral anion because the five C–B bonds are significantly shorter than the B–B bonds ($\sim$1.70 Å vs $\sim$1.77 Å, respectively).[66]

(69) The atom numbers used here do not refer to the numbering scheme used in the references. Instead, they refer to the numbered positions of the icosahedral 1-carba-*closo*-dodecaborate(1−) anion, as defined in: Leigh, G. J. *Nomenclature of Inorganic Chemistry*; Blackwell: Oxford, 1990.

(70) Crowther, D. J.; Borkowsky, F. L.; Swenson, D. C.; Meyer, T. Y.; Jordan, R. F. Submitted for publication.

(71) (a) *Iron Porphyrins*; Lever, A. B. P., Gray, H. B., Eds.; VCH: New York, 1989; Part III. (b) *Iron Porphyrins*; Lever, A. B. P., Gray, H. B., Eds.; Addison-Wesley: Reading, MA, 1983; Parts I and II. (c) *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1978; Vols. I–VII.

(72) (a) Reed, C. A.; Mashiko, T.; Bentley, S. P.; Kastner, M. E.; Scheidt, W. R.; Spartalian, K.; Lang, G. *J. Am. Chem. Soc.* **1979**, *101*, 2948. (b) Dolphin, D. H.; Sams, J. R.; Tsin, T. B.; Wong, K. L. *J. Am. Chem. Soc.* **1978**, *100*, 1711. (c) Hoard, J. L.; Cohen, G. H.; Glick, M. D. *J. Am. Chem. Soc.* **1967**, *89*, 1992.

(73) Jelínek, T.; Baldwin, P.; Scheidt, W. R.; Reed, C. A. *Inorg. Chem.* **1993**, *32*, in press.

(74) Jelínek, T.; Plešek, J.; Heřmánek, S.; Štíbr, B. *Collect. Czech. Chem. Commun.* **1986**, *51*, 819.

(75) Berry, C. H. *Phys. Rev.* **1955**, *97*, 676.

(76) Charbonnier, F.; Faure, R.; Loiseleur, H. *Acta Crystallogr.* **1978**, *B34*, 3598.

(77) Two recent examples are: (a) Ng, L.-L.; Ng, B. K.; Shelly, K.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1991**, *30*, 4278. (b) Manning, M. J.; Knobler, C. B.; Hawthorne, M. F.; Do, Y. *Inorg. Chem.* **1991**, *30*, 3589.

(78) Yang, X., Ph.D. Dissertation, Northwestern University, 1991.

(79) (a) Seppelt, K. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 877. (b) Engelbrecht, A.; Sladky, F. *Adv. Inorg. Chem. Radiochem.* **1981**, *24*, 189. (c) Seppelt, K. *Acc. Chem. Res.* **1979**, *12*, 211.

(80) Sanders, J. C. P.; Schrobilgen, G. J. *J. Chem. Soc., Chem. Commun.* **1989**, 1576.

(81) Miller, P. K.; Abney, K. D.; Rappé, A. K.; Anderson, O. P.; Strauss, S. H. *Inorg. Chem.* **1988**, *28*, 2255.

(82) Kruger, G. J.; Pistorius, C. W. F. T.; Heyns, A. M. *Acta Crystallogr.* **1976**, *B32*, 2916.

(83) Sladky, F.; Kropshofer, H.; Leitzke, O.; Peringer, P. *J. Inorg. Nucl. Chem., Suppl.* **1976**, 69.

(84) Strauss, S. H.; Anderson, O. P.; Noirot, M. D. *Inorg. Chem.* **1985**, *24*, 4307.

(85) (a) Noirot, M. D.; Anderson, O. P.; Strauss, S. H. *Inorg. Chem.* **1987**, *26*, 2216. (b) Strauss, S. H.; Noirot, M. D.; Anderson, O. P. *Inorg. Chem.* **1986**, *25*, 3850.

(86) Rack, J. J.; Hurlburt, P. K.; Anderson, O. P.; Strauss, S. H. Manuscript in preparation.

(87) Seppelt, K.; Nothe, D. *Inorg. Chem.* **1973**, *12*, 2727.

(88) Drews, F.; Seppelt, K. *Z. Anorg. Allg. Chem.* **1992**, *606*, 201.

(89) Huppmann, P.; Hartl, H.; Seppelt, K. *Z. Anorg. Allg. Chem.* **1985**, *524*, 26.

(90) (a) Schröder, K.; Sladky, F. *Chem. Ber.* **1980**, *113*, 1414. (b) Seppelt, K. *Chem. Ber.* **1975**, *108*, 1823.

(91) Huppmann, P.; Labischinski, H.; Lentz, D.; Pritzkow, H.; Seppelt, K. *Z. Anorg. Allg. Chem.* **1982**, *487*, 7.

(92) (a) Templeton, L. K.; Templeton, D. H.; Bartlett, N.; Seppelt, K. *Inorg. Chem.* **1976**, *15*, 2720. (b) Seppelt, K. *Chem. Ber.* **1976**, *109*, 1046.

(93) Abney, K. D.; Long, K. M.; Anderson, O. P.; Strauss, S. H. *Inorg. Chem.* **1987**, *26*, 2638.

(94) Kellett, P. J.; Pawlik, M. J.; Taylor, L. F.; Thompson, R. G.; Levstik, M. A.; Anderson, O. P.; Strauss, S. H. *Inorg. Chem.* **1989**, *28*, 440.

(95) Colsman, M. R.; Manning, M. C.; Anderson, O. P.; Strauss, S. H. *Inorg. Chem.* **1987**, *27*, 3958.

(96) Colsman, M. R.; Newbound, T. D.; Marshall, L. J.; Noirot, M. D.; Miller, M. M.; Wulfsberg, G. P.; Frye, J. S.; Anderson, O. P.; Strauss, S. H. *J. Am. Chem. Soc.* **1990**, *112*, 2349.

(97) Crist, D. R.; Jordan, G. J.; Hashmall, J. A. *J. Am. Chem. Soc.* **1974**, *96*, 4927.

(98) Van Seggen, D. M.; Strauss, S. H. Unpublished observations, 1991.

(99) Hurlburt, P. K.; Anderson, O. P.; Strauss, S. H. *J. Am. Chem. Soc.* **1991**, *113*, 6277.

(100) Hurlburt, P. K.; Rack, J. J.; Dec, S. F.; Anderson, O. P.; Strauss, S. H. *Inorg. Chem.* **1993**, *32*, 373.

(101) Haynes, J. S.; Sams, J. R.; Thompson, R. C. *Can. J. Chem.* **1981**, *59*, 669.

(102) Van Seggen, D. M.; Anderson, O. P.; Strauss, S. H. *Inorg. Chem.* **1992**, *31*, 2987.

(103) Hurlburt, P. K.; Kellett, P. J.; Anderson, O. P.; Strauss, S. H. *J. Chem. Soc., Chem. Commun.* **1990**, 576.

(104) Complexes with nitrobenzene ligands had been reported earlier: Driessen, W. L.; Van Geldrop, L. M.; Groeneveld, W. L. *Recl. Trav. Chim. Pays-Bas* **1970**, *89*, 1271.

(105) Sladky, F.; Kropshofer, H.; Leitzke, O. *J. Chem. Soc., Chem. Commun.* **1973**, 135.

(106) (a) Van Seggen, D. M.; Hurlburt, P. K.; Anderson, O. P.; Strauss, S. H. *J. Am. Chem. Soc.* **1992**, *114*, 10995. (b) Van Seggen, D. M.; Hurlburt, P. K.; Noirot, M. D.; Anderson, O. P.; Strauss, S. H. *Inorg. Chem.* **1992**, *31*, 1423. (c) Hurlburt, P. K.; Anderson, O. P.; Strauss, S. H. *Can. J. Chem.* **1992**, *70*, 726.

(107) McQuiston, J. M.; Strauss, S. H. Manuscript in preparation.

(108) Barrow, M.; Burgi, H.-B.; Camalli, M.; Caruso, F.; Fischer, E.; Venanzi, L. M.; Zambonelli, L. *Inorg. Chem.* **1983**, *22*, 2356.

(109) Uson, R.; Fornies, J.; Menjon, B.; Cotton, F. A.; Falvello, L. R.; Tomas, M. *Inorg. Chem.* **1985**, *24*, 4651.

(110) Kropshofer, H.; Leitzke, O.; Peringer, P.; Sladky, F. *Chem. Ber.* **1981**, *114*, 2644.

(111) Alcock, N. W. *Adv. Inorg. Chem. Radiochem.* **1972**, *15*, 1.

(112) Alcock, N. W.; Jenkins, H. D. B. *J. Chem. Soc., Dalton Trans.* **1974**, 1907.

(113) Wieghardt, K.; Kleine-Boymann, M.; Nuber, B.; Weiss, J. *Inorg. Chem.* **1986**, *25*, 1309.

(114) Bode, H. *Z. Anorg. Allg. Chem.* **1951**, *267*, 62.

(115) Halleck, P. M.; Jarieson, J. C.; Pistorius, C. W. T. *J. Phys. Chem. Solids* **1972**, *33*, 769.

(116) Moock, K.; Seppelt, K. *Z. Anorg. Allg. Chem.* **1988**, *561*, 132.

(117) Schrobilgen, G. J. Personal communication, 1990.

(118) (a) Siedle, A. R.; Gleason, W. B.; Newmark, R. A.; Skarjune, R. P.; Lyon, P. A.; Markell, C. G.; Hodgson, K. O.; Roe, A. L. *Inorg. Chem.* **1990**, *29*, 1667. (b) Siedle, A. R.; Markell, C. G.; Lyon, P. A.; Hodgson, K. O.; Roe, A. L. *Inorg. Chem.* **1987**, *26*, 219.

(119) Yared, Y. W.; Miles, S. L.; Bau, R.; Reed, C. A. *J. Am. Chem. Soc.* **1977**, *99*, 7077.

(120) (a) Siedle, A. R. U.S. Patent 4,788,308 (assigned to 3M), 1988. (b) Siedle, A. R. U.S. Patent 4,673,753 (assigned to 3M), 1987.

(121) Davidson, A.; Boubekeur, K.; Pénicaud, A.; Auban, P.; Lenoir, C.; Batail, P.; Hervé, G. *J. Chem. Soc., Chem. Commun.* **1989**, 1373. BEDT-TTF = 3,4:3′,4′-bis(ethylenedithio)-2,2′,5,5′-tetrathiafulvalene.

(122) Knoth, W. H.; Harlow, R. L. *J. Am. Chem. Soc.* **1981**, *103*, 4265.

(123) (a) Barcza, L.; Pope, M. T. *J. Phys. Chem.* **1973**, *77*, 1795. (b) Saito, A.; Choppin, G. R. *Inorg. Chem.* **1991**, *30*, 4563.

(124) (a) Siedle, A. R.; Newmark, R. A.; Sahyun, M. R. V.; Lyon, P. A.; Hunt, S. L.; Skarjune, R. P. *J. Am. Chem. Soc.* **1989**, *111*, 8346. (b) Siedle, A. R.; Newmark, R. A. *J. Am. Chem. Soc.* **1989**, *111*, 2058. (c) Siedle, A. R.; Newmark, R. A. *Organometallics* **1989**, *8*, 1442. (d) Siedle, A. R. *New J. Chem.* **1989**, *13*, 719. (e) Siedle, A. R.; Newmark, R. A.; Gleason, W. B.; Skarjune, R. P.; Hodgson, K. O.; Roe, A. L.; Day, V. W. *Solid State Ionics* **1988**, *26*, 109. (f) Siedle, A. R.; Newmark, R. A.; Brown-Wensley, K. A.; Skarjune, R. P.; Haddad, L. C.; Hodgson, K. O.; Roe, A. L. *Organometallics* **1988**, *7*, 2078.

(125) (a) Siedle, A. R.; Newmark, R. A.; Howells, R. D. *Inorg. Chem.* **1988**, *27*, 2473. (b) Siedle, A. R. U.S. Patent 4,625,069 (assigned to 3M), 1986. (c) Siedle, A. R.; Newmark, R. A.; Pignolet, L. H.; Howells, R. D. *J. Am. Chem. Soc.* **1984**, *106*, 1510.

(126) (a) Siedle, A. R.; Newmark, R. A.; Gleason, W. B. *Inorg. Chem.* **1991**, *30*, 2005. (b) Siedle, A. R.; Newmark, R. A.; Korba, G. A.; Pignolet, L. H.; Boyle, P. D. *Inorg. Chem.* **1988**, *27*, 1593. (c) Siedle, A. R.; Gleason, W. B.; Newmark, R. A.; Pignolet, L. H. *Organometallics* **1986**, *5*, 1969. (d) Siedle, A. R.; Newmark, R. A.; Pignolet, L. H. *Inorg. Chem.* **1986**, *25*, 3412. (e) Siedle, A. R.; Newmark, R. A.; Pignolet, L. H. *Inorg. Chem.* **1986**, *25*, 1345. (f) Siedle, A. R.; Newmark, R. A.; Gleason, W. B. *J. Am. Chem. Soc.* **1986**, *108*, 767. (g) Siedle, A. R.; Newmark, R. A.; Pignolet, L. H.; Wang, D. X.; Albright, T. A. *Organometallics* **1986**, *5*, 38.

(127) Conroy-Lewis, F. M.; Simpson, S. J. *J. Chem. Soc., Chem. Commun.* **1987**, 1675.

(128) (a) Crabtree, R. H.; Lavin, M.; Bonneviot, L. *J. Am. Chem. Soc.* **1986**, *108*, 4032. (b) Crabtree, R. H.; Lavin, M. *J. Chem. Soc., Chem. Commun.* **1985**, 1661. (c) Crabtree, R. H.; Lavin, M. *J. Chem. Soc., Chem. Commun.* **1987**, 794.

(129) Siedle, A. R.; Newmark, R. A.; Gleason, W. B.; Lammana, W. M. *Organometallics* **1990**, *9*, 1990.

(130) Siedle, A. R.; Huffman, J. C. *Inorg. Chem.* **1990**, *29*, 3131.

(131) Beck, W.; Johansen, O.; Fehlhammer, W. P. *Z. Anorg. Allg. Chem.* **1968**, *361*, 147.

(132) Pénicaud, A.; Hsu, J.; Reed, C. A.; Koch, A.; Khemani, K. C.; Allemand, P.-M.; Wudl, F. *J. Am. Chem. Soc.* **1991**, *113*, 6698.

(133) (a) Jehoulet, C.; Bard, A. J.; Wudl, F. *J. Am. Chem. Soc.* **1991**, *113*, 5456 and references therein. (b) Dubois, D.; Kadish, K. M.; Flanagan, S.; Haufler, R. E.; Chibante, L. P. F.; Wilson, L. J. *J. Am. Chem. Soc.* **1991**, *113*, 4364 and references therein.

(134) (a) Fagan, P. J.; Calabrese, J. C.; Malone, B. *Acc. Chem. Res.* **1992**, *25*, 134. (b) Lerke, S. A.; Parkinson, B. A.; Evans, D. H.; Fagan, P. J. *J. Am. Chem. Soc.* **1992**, *114*, 7807.

(135) (a) Taube, R.; Gehrke, J.-P.; Böhme, P.; Scherzer, K. *J. Organomet. Chem.* **1991**, *410*, 403. (b) Taube, R.; Böhme, P.; Gehrke, J.-P. *Z. Anorg. Allg. Chem.* **1989**, *578*, 89. (c) Taube, R.; Gehrke, J.-P. *J. Organomet. Chem.* **1987**, *327*, 419.

(136) (a) Katz, H. E. *J. Org. Chem.* **1985**, *50*, 5027. (b) Katz, H. E. *J. Am. Chem. Soc.* **1985**, *107*, 1420.

(137) Katz, H. E. In *Inclusion Compounds*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Eds.; Oxford Univ. Press: Oxford, UK, 1991; Vol. 4, p 391.

(138) (a) Atwood, J. L. In *Coordination Chemistry of Aluminum*; Robinson, G. H., Ed.; VCH: New York, 1993; p 197. (b) Sishta, C.; Hathorn, R. M.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 1112 and references therein. (c) Ahlers, A.; Kaminsky, W. *Makromol. Chem., Rapid Commun.* **1988**, *9*, 457 and references therein.

(139) (a) Kevill, D. N. In *The Chemistry of Halides, Pseudo Halides, and Azides*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1983; Part 2, p 933. (b) Pocker, Y.; Wong, W.-H. *J. Am. Chem. Soc.* **1975**, *97*, 7097 and references therein.

(140) Mattson, B. M.; Graham, W. A. G. *Inorg. Chem.* **1981**, *20*, 3186.

(141) Peone, J., Jr.; Vaska, L. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 511.