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Some past vignettes of and future prospects for Main Group chemistry

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Abstract

The present article traces, from the author's perspective, some of the important developments in the chemistry of the Group 13 and 15 elements that have taken place over the past three decades. Included in the review are compounds that feature multiple bonding between heavier Main Group elements, the coordination chemistry of Group 13 and 15 carbene analogues, and novel ring systems involving these elements. Some materials science and medicinal aspects of this area of chemistry are also presented.

Keywords: Steric crowding; Multiple bonding; Main Group elements

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1. Some past vignettes

Main Group chemistry is enjoying a considerable resurgence of interest. Apart from intrinsic interest in the field, this renaissance is driven to a large extent by the demands of materials science, catalysis, and medical science, along with the continuing need for the development of new reagents. It was, in fact, intrinsic interest in Main Group chemistry that first stimulated my interest. When I started an independent research program in the early 1960s, much of the emphasis in transition-metal organometallic chemistry was placed on low oxidation state, low coordination number systems. On the other hand, the chemistry of the p-block elements was concerned principally with the chemistry of high oxidation state, high coordination number compounds, some of the major issues of the day being the preparation of noble gas compounds and studies of hypervalent fluxional molecules. It seemed therefore that areas of future challenge might be high oxidation state transition-metal organometallic chemistry and low oxidation state, low coordination number Main Group chemistry. One of the earliest interests of our group in the latter context focused on the insertion of CF_3P units into e.g. As–As bonds [1]. In this sense the CF_3P unit behaved as a carbenoid and its relationship to some other six-valence-electron species is shown in Scheme 1. Clearly, dimerization of the entities shown in Scheme 1 should afford analogues of alkenes. However, despite the fact that diphosphenes (RP=PR), diarsenes (RAs=AsR) and disilenes (R_2Si=SiR_2) had been claimed in the early literature [2], subsequent studies showed that the products were, in fact, oligomeric. To thwart the tendency toward oligomerization, it would be necessary to employ appropriately bulky substituents, R, to afford kinetic stabilization of these dimeric species. In 1981, West et al. [3] reported tetramesityldisilene, the first structurally authenticated compound with a silicon–silicon double bond. This development heralded the development of a remarkable number of compounds with multiple bonds between the heavier Main

Group 13	Group 14	Group 15
R_2B^-	$\boxed{R_2C}$	RN
R_2Al-	R_2Si	RP
R_2Ga^-	R_2Ge	RAs
R_2In^-	R_2Sn	RSb
R_2Tl^-	R_2Pb	RBi

Scheme 1.

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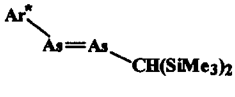
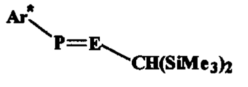
Group elements. For example, in our group we were able to prepare **1**, **2a**, and **2b**, the first compounds with arsenic–arsenic [4], phosphorus–arsenic [5], and phosphorus–antimony [6] double bonds.



$Ar^* = 2,4,6\text{-}t\text{-}Bu_3C_6H_2$

1



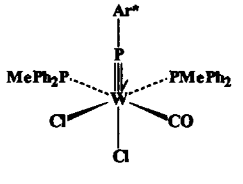
2a (E = As); **2b** (E = Sb)

In the case of the phosphastibene, **2b**, it was only possible to effect characterization spectroscopically; however, since that time Twamley and Power [6] have been able to carry out X-ray crystallographic studies on such compounds. Moreover, the first examples of distibenes and dibismuthenes have been isolated recently by employing the very bulky substituent, 2,4,6-tris(bis(trimethylsilyl)methyl)phenyl [7], and Group 13 dianions $[R_2BBR_2]^{2-}$, which are isoelectronic with substituted ethenes, have been shown to possess bond orders greater than unity [8]. Naturally, a question that underlies the foregoing work is 'Are they really double bonds?' In an effort to answer this question in the context of diphosphenes, we carried out electron density distribution (EDD) studies on Ar*P=PAr* (Ar* = $2,4,6\text{-}t\text{-}Bu_3C_6H_2$) [9] and $(Me_3Si)_3CP{=}PC(SiMe_3)_3$ in collaboration with Krüger, Ziegler and co-workers [10]. It was found that there is a build-up of electron density on each phosphorus atom that corresponds to the phosphorus lone pairs. Moreover, the P–P σ-bonds are clearly apparent in both molecules, and the non-cylindrical nature of the cross sections of the electron densities along the P–P axes is consistent with the existence of π-bonds.

Special interest is associated with the monomeric carbenoid species. An important clue to the existence of a phosphinidene was provided by the observation that the phosphaketene, Ar*P=C=O, is photosensitive and, in addition to the evolution of CO, results in two species with half lives of 1 and 6 μs. MO calculations on the model phosphinidene PhP indicated that the ground state is a triplet, leading to the surmise that the shorter- and longer-lived species are attributable to singlet and triplet Ar*P, respectively [11]. Subsequent collaborative work with Gaspar's group [12] revealed that it is possible to matrix isolate mesitylphosphinidene and that, since an ESR signal is detectable, this phosphinidene exists in a triplet ground state.

The work described above involves six-valence-electron species. In more recent times, we have turned our attention to the corresponding four-valence-electron entities from Group 13, viz. RB, RAl, RGa, and RIn. Typically, the aggregation of these moieties results in tetramers or hexamers as exemplified by the formation of $[InC(SiMe_3)_3]_4$ from the metathetical reaction of $LiC(SiMe_3)_3$ with InCl [13]. The C_5Me_5 substituent is also effective for the stabilization of these clusters and $[AlC_5Me_5]_4$ [14], $[GaC_5Me_5]_6$ [15], and $[InC_5Me_5]_6$ [16] have all been prepared and structurally characterized. Attempts have been made in our laboratory to prepare the 'missing member' of empirical composition BC_5Me_5. However, our lack of success in this endeavor is probably due to the small covalent radius of boron.

Like the carbenes themselves, silylenes, phosphinidenes and their heavier congeners, as well as Group 13 fragments of the type RM (M = B, Al, Ga, In), should be able to function as ligands toward a wide variety of transition-metals. Our first success in this area was realized by treatment of the phosphaketene Ar*P=C=O with $WCl_2(PMePh_2)_4$ [17]. The resulting complex, $(Ph_2MeP)_2(CO)(Cl)_2W{\equiv}PAr^*$ (**3**), represented the first example of a linear terminal phosphinidene complex, thus complementing the earlier report by Lappert and co-workers [18] of the synthesis of the first angular terminal phosphinidene complexes. The short W–P bond distance and large $^{183}W—^{31}P$ coupling constant for **3** are consistent with the proposed triple-bonding description.



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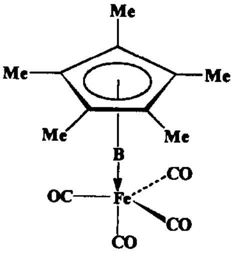

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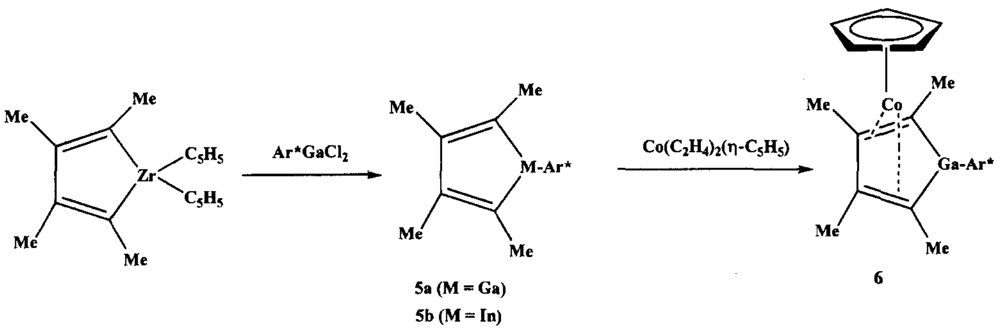
The first terminal boranediyl (borylene) complex, $(\eta^5\text{-}C_5Me_5)BFe(CO)_4$ (**4**), was synthesized by treatment of $(C_5Me_5)BCl_2$ with $K_2[Fe(CO)_4]$ [19]. The boranediyl moiety is located in the axial position of a trigonal bipyramidal $Fe(CO)_4$ fragment with a B–Fe bond distance of 2.010(3) Å. The nature of the bonding between Group 13 RM ligands and transition-metals is one that has spurred considerable recent discussion [20,21]. Four bonding models, **A**–**D**, can be considered for the covalent interaction between Group 13 (RM) and transition-metal ($M'L_n$) fragments. Structures **A**, **B**, and **C** imply that the RM ligand coordinates in a singlet state.

A **B** **C** **D**

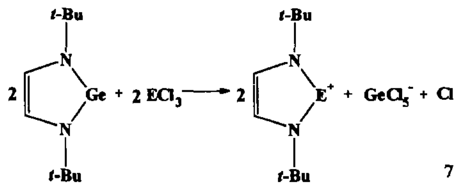
In structure **A** there is a simple donor–acceptor bond between M and M′, while structures **B** and **C** feature one and two additional backbonding interactions from the transition-metal to the Group 13 element, thereby developing double and triple bonds, respectively, between M and M′. The double-bonded structure, **D**, implies that the RM fragment bonds as a triplet state.



Scheme 2.

Density functional calculations on free and $Fe(CO)_4$-complexed boranediyls and their heavier congeners revealed that, regardless of the substituent R (R = η^5-C_5H_5, η^5-C_5Me_5, Me, $(H_3Si)_2NB$), the ground state of each RM fragment is a singlet, thus eliminating the double-bonded model, **D** [21]. In general, the univalent RM species are found to be two-electron donors (bonding model **A**). In principle, the RM ligands with non-π-donating R groups could possess some π-acceptor capability, which is appropriate for metal–ligand backbonding (bonding models **B** and **C**). However, evidence for this was found only in the case of $MeBFe(CO)_4$ and not for the heavier Group 13 analogues.

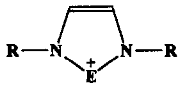
An alternative way to stabilize Group 13 and 15 RM fragments is to incorporate them into cyclic structures. For example, the novel galla- and indacyclopentadienes **5a,b** were prepared by treatment of the appropriate zirconacyclic transfer reagent with Ar^*GaCl_2 or Ar^*InBr_2 (Scheme 2) [22]. Furthermore, the gallacyclopentadiene reacts with $Co(\eta^5\text{-}C_5H_5)(C_2H_4)_2$ to afford a cyclopentadienylcobalt complex (**6**) with a somewhat short gallium–cobalt contact. The cyclic germylene **7** [23] is also a useful transfer reagent as demonstrated by the reaction with PCl_3 or $AsCl_3$, which affords the cyclic phosphenium or arsenium cations **8a** and **8b** [24]. It is also possible to prepare the same cations by the metathetical reactions of dilithiodiazabutadiene with ECl_3 (E = P, As).



8a (E=P); 8b (E=As);

7

It is noteworthy that in the latter synthetic approach autoionization of the P–Cl bond takes place. In turn, this raises the possibility of the existence of circumannular delocalization in cations **8a,b**. Indeed, the same questions arise in regard to the analogous Group 14 and 13 species shown below since each of these is, in principle, a 6-π-electron system. However, in the case of the phosphenium and arsenium cations, the metrical parameters provide little support for aromatic-type delocalization because e.g. the C–C bond distances of 1.330(6) and 1.36(2) Å in **8a** and **8b**, respectively correspond to localized double bonds [25].



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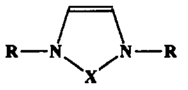
(E = N, P, As)



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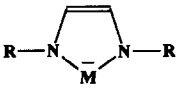
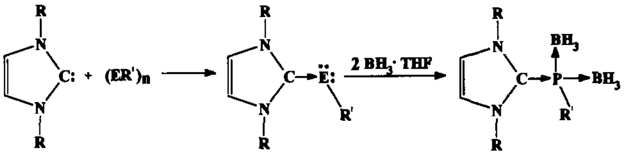
(X = C, Si, Ge)



11
(X = B, Al, Ga [25])

The isolation of a stable carbene by Arduengo et al. [26] has prompted a flurry of interest in the use of such compounds as reagents. Being strongly nucleophilic, the imidazol-2-ylidenes behave somewhat like phosphines. For example, they react with cyclopolyphosphines and cyclopolyarsines to afford carbene-phosphinidenes and -arsenidenes **9a,b** as indicated below [27]. The presence of two lone pairs on the phosphinidene, **9a**, was demonstrated by the isolation of the bis(borane) complex, **10** [28].

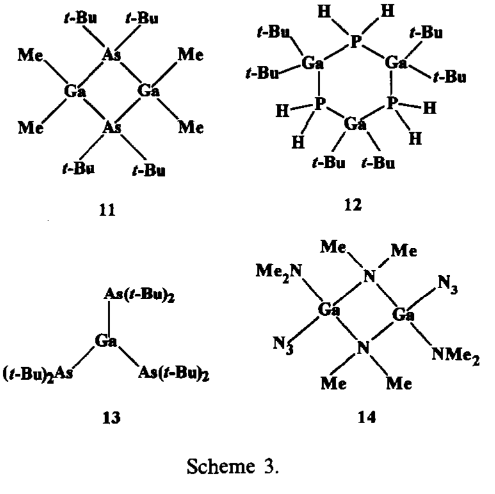


9a (E = P); 9b (E = As)

10

Interestingly, there is a nexus between the foregoing discussion and materials science in the sense that compounds of the general type MeGaEH (E = P, As) have been implicated in mechanistic studies of the thermal reactions of Me_3Ga with EH_3. Such compounds presumably involve Ga–E bond orders greater than unity. Although the thermal reaction of Me_3Ga and AsH_3 represents the basis of the industrially employed chemical vapor deposition (CVD) process, this two-source approach possesses a number of disadvantages that include stoichiometry control issues, the necessity for elevated reaction temperatures, and environmental concerns associated with the use of toxic, volatile components. Starting in the mid-1980s my colleague, Richard Jones, and I launched a program aimed at the synthesis, characterization, and CVD studies of Group 13/15 compounds of the general type $L_nMEL'_n$ (M = Al, Ga, In; E = N, P, As, Sb) [29]. The overall strategy was to maximize the M–E bond strengths to prevent loss of stoichiometry during deposition and to employ substituents L and L′ that were capable of facile thermal or photochemical decomposition. Initial effort was focused on gallium–arsenic, gallium–phosphorus, and indium–phosphorus ring compounds of the general type $(R_2MER'_2)_n$. With sterically demanding substituents, dimers tended to be formed ($n = 2$), while the use of smaller groups resulted in the formation of trimers ($n = 3$); some representative examples are shown in Scheme 3. The *t*-Bu substituent was chosen because of its well-known capacity to undergo facile alkene elimination via the classical β-hydride mechanism. Gallium arsenide film growth from **11** took place at 525°C. XPS examination of the films revealed that the Ga:As ratios were 1:1 and that the carbon contamination was less than 1000 ppm. Precursor **12** underwent thermolysis at significantly lower temperatures. In fact, refluxing a toluene solution of **12** resulted in the formation of amorphous GaAs (albeit containing trapped organic impurities). Interestingly, however, the best quality GaAs film that we have obtained thus far were obtained from the tris(arsino)gallane, **13** [30]. The 1:3 stoichiometry was employed both to avoid the presence of Ga–C bonds and also to ensure the presence of an excess of arsenic on the growing surface. Epitaxial GaAs growth was achieved under modest reactor conditions (480°C at 6×10^{-5} Torr) and the resulting films had significantly less carbon contamination than those deposited from 1:1 stoichiometry precursors.

In more recent times, the focus of our film deposition studies has changed to Group 13 and transition-metal nitrides. In order to minimize carbon contamination we chose to explore the synthesis and film deposition study of single-source precursors with all-nitrogen coordination environments. This design principle was demonstrated initially by the isolation of **14** [31], the idea being that this precursor features a labile dimethylamido leaving group and an azide nitrogen source. Indeed, this precursor produces epitaxial GaN with smooth, crack-free morphology at 580°C. The estimated oxygen and carbon contents of the film were 5×10^{20} and 2×10^{21} atoms cm^{-3}, respectively. However, **14** exists in the solid state as a polymer of dimers thus diminishing the volatility of this precursor. In the hope of disrupting the polymer, **14** was treated with pyridine. Unexpectedly, however, a rearrangement took place and $Ga(N_3)(py)_3$, the tris(pyridine) adduct of gallium tris(azide), was isolated [32]. Subsequently, Fischer et al. [33] have isolated $(Et_3N)Ga(N_3)_3$ which is reported to deposit hexagonal monocrystals of GaN via detonation! In the meantime we are continuing to explore other classes of Group 13 nitride precursors with all-nitrogen coordination environments such as tris(primary amides), tris(hydrazides) and related systems [34].



Scheme 3.

2. Some future prospects

It is my belief that Main Group chemistry will play an increasingly important role in the next century both as a source of new materials and also as a means of producing already known materials. In particular, the future of the single-source precursor concept is bright for several reasons. At the outset, it is important to recognize that many of the thermal deposition processes used currently require elevated temperatures and are therefore under thermodynamic control. Since the deposition temperatures that are achievable with the single-source precursor approach are considerably more modest, it should be possible to effect kinetic control of many deposition process(es), thereby providing potential access to unusual or metastable phases. Clearly, such kinetic control will depend on, e.g. the particularities of the relevant phase diagram. Indeed, there are already some examples in the literature of selective deposition by means of the molecular control afforded by the use of single-source precursors. Two such examples are the deposition of cubic GaN by thermolysis of the trimer, $(R_2GaNH_2)_3$ [35] and the production of previously unknown cubic In_xSe_y phases from indium selenolate precursors [36].

Single-source precursors also have a potentially important future role in regard to simplification of the production of ternary and higher-order materials. One possibility would be to have three elements incorporated into one source and to have the fourth element delivered by a second source. At the present time there are only a few single-source precursors for ternary or higher-order materials due, in part, to the challenge of preparing such precursors with the requisite stoichiometries.

Selective deposition represents another area of challenge for the single-source precursor approach. It would be of great interest, for example, to be able to switch at will from, e.g. [100] to [111] growth on a substrate or to deposit on some parts of the substrate and not others. Already, the phase, composition, and morphology of a deposited material have been shown to depend not only on the stoichiometry and degree of oligomerization of the single-source precursor, but also on the nature of the substituents and deposition techniques. It will therefore be highly important to learn as much as possible about the details of the processes whereby single-source precursors are transformed into solid-state materials.

The single-source precursor approach is already proving to be viable for the production of nanocrystalline materials [37]. The advantage of this approach compared to a separate source approach is that, providing the relevant prevenient bonds do not rupture, there is no stoichiometry control issue. A cornucopia of new nano materials that stem from the use of this approach can be anticipated.

Another exciting materials science prospect for Main Group chemistry relates to its use in the polymer field. Although polysiloxanes, polyphosphazenes, and polysilanes represent well-established examples of polymers with Main Group element backbones, new developments continue to be disclosed for all three systems. Interesting hybrid materials such as polyphosphazene/polysiloxanes and hydroxyapatite/polyphosphazene composites are beginning to emerge [38] as are systems based on other Main Group element backbones. Even more possibilities will be realized by the synthesis of polymers that feature both Main Group elements and transition elements in the backbone [39].

Main Group chemistry is also likely to sustain its emerging importance in the field of catalysis. One such 'hot topic' is the design and synthesis of new ligands, particularly those that are suitable for asymmetric catalysis. For example, several cleverly conceived phosphine ligands are now available commercially and, when coordinated to transition-metal moieties, are used for the catalytic production of chiral drugs and other value-added products. As pointed out in a recent news article [40] the global sales of single-enantiomer drugs is of the order of US $90 billion. In turn, this has created a brisk future demand for new ligands for asymmetric catalysis.

Another bright prospect for Main Group chemistry relates to the search for new Lewis acids and Brønsted-assisted Lewis acids. Lewis acids such as methylalumoxane (MAO) have been used for many years as cocatalysts for e.g. olefin polymerization. However, MAO is a complex system that is not well defined from a structural standpoint. Exciting opportunities therefore exist for the design of new Lewis acids, particularly those that are chiral, since these will have significant implications for asymmetric Diels–Alder reactions as well as a plethora of asymmetric ring-opening processes.

Finally, Main Group chemistry will continue to have important implications in the medical field, both in terms of diagnosis and therapy. For example, gallium-68 is used for positron emission tomography (PET) and gallium-67 is employed for X-ray imaging. Both gallium isotopes possess half lives in the appropriate domain for imaging. Moreover, indium-111 has found several diagnostic uses such as thrombosis monitoring and intra-abdominal imaging. A continuous improvement in delivery systems, i.e. the development of appropriate coordination environments, can be predicted. Likewise future developments can be predicted in terms of therapy. For example, there has been an important rekindling of interest in boron neutron capture therapy [41]. Several new compounds have become available, including novel polyhedral boranes and carboranes and boron analogues of amino acids.

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References

[1] (a) A.H. Cowley, J. Am. Chem. Soc. 89 (1967) 5990. (b) A.H. Cowley, D.S. Dierdorf, J. Am. Chem. Soc. 91 (1969) 5919.
[2] (a) H. Köhler, A. Michaelis, Ber. Dtsch. Chem. Ges. 10 (1877) 807. (b) P. Erlich, Lancet 173 (1907) 351. (c) F.S. Kipping, Proc. Chem. Soc. 27 (1911) 143.
[3] R. West, M.J. Fink, J. Michl, Science 214 (1981) 1343.
[4] A.H. Cowley, J.G. Lasch, N.C. Norman, M. Pakulski, J. Am. Chem. Soc. 105 (1983) 5506.
[5] A.H. Cowley, J.G. Lasch, N.C. Norman, M. Pakulski, B.R. Whittlesey, J. Chem. Soc. Chem. Commun. (1983) 881.
[6] B. Twamley, P.P. Power, Chem. Commun. (Cambridge) (1998) 1979.
[7] N. Tokitoh, Y. Arai, R. Okazaki, S. Nagase, Science 277 (1997) 78.
[8] (a) A. Moezzi, M.M. Olmstead, P.P. Power, J. Am. Chem. Soc. 114 (1991) 2715. (b) A. Moezzi, R.A. Bartlett, P.P. Power, Angew. Chem. Int. Ed. Engl. 31 (1992) 1082. (c) R.J. Wehmshulte, K. Ruhlandt-Senge, M.M. Olmstead, H. Hope, B.E. Sturgeon, P.P. Power, Inorg. Chem. 32 (1993) 2983.
[9] This compound was first reported by Yoshifuji and co-workers: M. Yoshifuji, I. Shima. N. Inamoto, I. Hirotsu, T. Higuchi, J. Am. Chem. Soc. 103 (1991) 4587.

[10] A.H. Cowley, A. Decken, N.C. Norman, C. Krüger, F. Lutz, H. Jacobsen, T. Ziegler, J. Am. Chem. Soc. 119 (1997) 3389.

[11] A.H. Cowley, F. Gabbaï, R.D. Schluter, D.A. Atwood, J. Am. Chem. Soc. 114 (1992) 3142.

[12] X. Li, S.I. Weissman, T.-S. Lin, P.P. Gaspar, A.H. Cowley, A.I. Smirnov, J. Am. Chem. Soc. 116 (1994) 7899.

[13] (a) R.D. Schluter, A.H. Cowley, D.A. Atwood, R.A. Jones, J.L. Atwood, J. Coord. Chem. 30 (1993) 35. (b) W. Uhl, R. Graupner, M. Layh, U. Schütz, J. Organometal. Chem. 493 (1995) C1.

[14] C. Dohmeier, C. Robl, M. Tacke, H. Schnöckel, Angew. Chem. Int. Ed. Engl. 30 (1991) 594.

[15] (a) D. Loos, E. Baum, A. Ecker, H. Schnöckel, A.J. Downs, Angew. Chem. Int. Ed. Engl. 36 (1997) 860. (b) A. Haaland, K.G. Martinsen, H.V. Volden, D. Loos, H. Schnöckel, Acta Chem. Scand. 48 (1994) 172.

[16] O.T. Beachley Jr., R. Blom, M.R. Churchill, K. Faegri Jr., J.C. Fettinger, J.C. Pazik, L. Victoriano, Organometallics 8 (1989) 346.

[17] A.H. Cowley, B. Pellerin, J.L. Atwood, S.G. Bott, J. Am. Chem. Soc. 112 (1990) 6734.

[18] (a) P.B. Hitchcock, M.F. Lappert and W.-P. Leung, J. Chem. Soc. Chem. Commun. (1987) 1282. (b) P. Bohra, P.B. Hitchcock, M.F. Lappert, W.-P. Leung, Polyhedron 8 (1989) 1184.

[19] A.H. Cowley, V. Lomelí, A. Voigt, J. Am. Chem. Soc. 120 (1998) 6401.

[20] (a) See, for example, F.A. Cotton and X. Feng, Organometallics 17 (1998) 128. (b) J. Su, X.-W. Li, C. Crittendon, C.F. Campana, G.H. Robinson, Organometallics 17 (1998) 128. (c) C. Boehme, G. Frenking, Chem. Eur. J. 5 (1999) 2184.

[21] C.L.B. Macdonald, A.H. Cowley, J. Am. Chem. Soc. 121 (1999) 12113.

[22] A.H. Cowley, F.P. Gabbaï, A. Decken, Angew. Chem. Int. Ed. Engl. 33 (1994) 1370.

[23] W.A. Herrmann, M. Denk, J. Behm, W. Scherer, F.-R. Klingan, H. Bock, M. Soluki, M. Wagner, Angew. Chem. Int. Ed. Engl. 31 (1992) 1485.

[24] C.J. Carmalt, V. Lomelí, B.G. McBurnett, A.H. Cowley, Chem. Commun. (Cambridge) (1997) 2095.

[25] The first example of such an anion has been reported very recently: E.S. Schmidt, A. Jockisch, H. Schmidbaur, J. Am. Chem. Soc. 121 (1999) 9758.

[26] A.J. Arduengo III, R.L. Harlow, M. Kline, J. Am. Chem. Soc. 113 (1991) 361.

[27] A.J. Arduengo III, J.C. Calabrese, A.H. Cowley, H.V. Rasika Dias, J.R. Goerlich, W.J. Marshall, B. Riegel, Inorg. Chem. 31 (1997) 2151.

[28] A.J. Arduengo III, C.J. Carmalt, J.C. Clyburne, A.H. Cowley, R. Pyati, Chem. Commun. (Cambridge) (1997) 981.

[29] (a) A.H. Cowley, R.A. Jones, Angew. Chem. Int. Ed. Engl. 28 (1989) 1208. (b) A.H. Cowley, R.A. Jones, Polyhedron 13 (1994) 1149.

[30] V. Lakhotia, A.H. Cowley, R.A. Jones, J.G. Ekerdt, Chem. Mater. 6 (1994) 871.

[31] D.A. Neumayer, A.H. Cowley, A. Decken, R.A. Jones, V. Lakhotia, J.G. Ekerdt, J. Am. Chem. Soc. 117 (1995) 5893.

[32] C.J. Carmalt, A.H. Cowley, R.D. Culp, R.A. Jones, Chem. Commun. (Cambridge) (1996) 1453.

[33] A.C. Frank, F. Stowasser, H. Sussek, H. Pritzkow, C.R. Miskys, O. Ambacher, M. Giersig, R.A. Fischer, J. Am. Chem. Soc. 120 (1998) 3512.

[34] (a) J.S. Silverman, C.J. Carmalt, A.H. Cowley, R.D. Culp, R.A. Jones, B.G. McBurnett, Inorg. Chem. 38 (1999) 296. (b) J.S. Silverman, C.D. Abernethy, R.A. Jones, A.H. Cowley, Chem. Commun. (Cambridge) (1999) 1645.

[35] J.-W. Hwang, S.A. Hanson, D. Britton, J.F. Evans, K.F. Jensen, W.L. Gladfelter, Chem. Mater. 2 (1990) 342.

[36] H.J. Gysling, A.A. Wernberg, T.N. Blanton, Chem. Mater. 4 (1992) 900.

[37] R.L. Wells, W.L. Gladfelter, J. Cluster Sci. 8 (1997) 217.

[38] H.R. Allcock, S.E. Kuharcik, C.J. Nelson, Macromolecules 29 (1996) 3686, 3384.

[39] I. Manners, Polyhedron 15 (1996) 4311.

[40] Chemical and Engineering News, September 21, 1998, pp. 86–104.

[41] M.F. Hawthorne, Angew. Chem. Int. Ed. Engl. 32 (1993) 950.