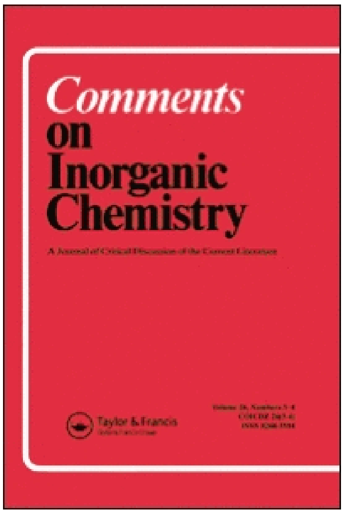

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Inorganometallic Chemistry

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Inorganometallic Chemistry

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The term inorganometallic chemistry has been defined to draw attention to an emerging body of knowledge consisting of the chemistry of compounds containing main group elements other than carbon interacting directly with metals. In a real sense, this chemistry mirrors that of organometallic chemistry. That is, the reactivity of main group element fragments is changed on interaction with metals, intrinsically unstable main group element fragments are stabilized by coordination and transition metals promote main group compound reactions via the formation of main group–metal intermediates. The scope of inorganometallic chemistry is outlined and illustrated with selected examples. The close connection with organometallic chemistry is emphasized with detailed, isoelectronic comparisons.

Key Words: *metallaboranes, cobaltaboranes, ferraboranes, hydrocarbyl clusters, main group–metal clusters, boranes, metal clusters*

INTRODUCTION

Although one can trace the development from a much earlier beginning, about a quarter of a century ago there was a burst of activity in the preparation and characterization of compounds containing organic moieties bound to transition metals in low oxidation states via direct carbon–metal interactions.[1] Continued growth and development gave rise to the thriving area known as organometallic chemistry. Chemistry departments are not considered complete

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these days if the faculty lacks an organometallic chemist and practitioners of organometallic chemistry arise from both the organic and inorganic areas. Indeed, as chairman, I have heard the need expressed for an "organic" organometallic course besides the "inorganic" organometallic course presently being offered. Despite this conservative sense of origin so typical of chemists, the use of metals for the manipulation of organic fragments and the use of organic fragments for the coordination of metals in new ways continues unabated.[2,3] This hybrid field has given a new dimension to both classical transition metal chemistry and organic chemistry.

Inorganic chemistry as a whole consists of a loose confederation of areas each of which has a rich chemistry. In some, for example silicon chemistry, the chemistry has been developed to an impressive degree.[4] The same can be said for metal chemistry.[5] In the United States chemists involved in the study of transition metal chemistry in some form probably constitute the largest fraction of inorganic chemists. It is not unreasonable then to consider three general types of chemisty—organic, metal and main group element chemistry. In Fig. 1 these three areas are denoted by the vertices of a "freshman chemistry" triangle. The combination of metal and carbon chemistries is known as organometallic chemistry while that

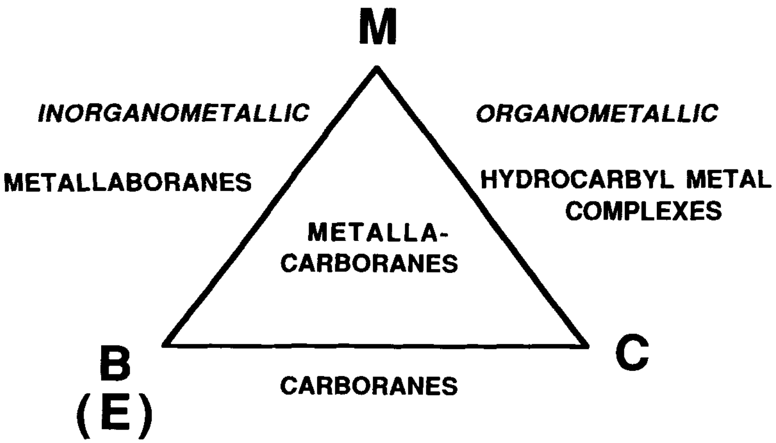


FIGURE 1 Relationship of metal–carbon, metal–boron (main group) and carbon–boron (main group) chemistry.

of carbon and main group elements has been called organometalloid chemistry,[6] e.g., organoboron or carborane chemistry. In recent years more and more compounds that combine fragments containing main group elements, e.g., boron, with transition metals have been synthesized. These compounds correspond to the third combination possible in Fig. 1. Although these species certainly can be considered as metal complexes with "unusual" ligands, there is reason (see below) for separating them from those in which main group moieties act as simple Lewis bases in coordinating to a metal, i.e., one separates organometallic chemistry from coordination chemistry despite the fact that a coordinated ligand can form a metal carbon bond (orthometalation) so as to act towards the metal in both senses.[7] Hence, we suggest that metal–main group chemistry be called inorganometallic chemistry. Among other things this descriptor emphasizes the fact that the potential for innovative advances here is similar to that existing for organometallic chemistry 25 years ago. By analogy with organometallic compounds, one can expect transition metals to stabilize intrinsically unstable main group moieties as well as facilitate chemical transformations involving main group compounds. Likewise, the main group fragments are expected to vary the properties of a transition metal moiety in new and interesting ways.

Still, "What's in a name? That which we call a rose, by any other name would smell as sweet."[8] A name draws connections that, while always present, may not be clearly perceptible. That is, chemists categorize compounds to provide organization and to draw attention to similarities of structure, bonding and reactivity. Sometimes this filing procedure obscures interesting and potentially important connections. For example, in a classical view there is little connection between the boranes and transition metal clusters but the work of Wade,[9] Mingos[10] and others[11] has pointed out fundamental similarities that has stimulated work in both areas. In fact the close relationship of main group and transition metal clusters to organometallic compounds has been defined as well.[9] The purpose of this essay is to draw attention to a developing area that may well become a significant independent field. After a brief example of compounds that express the close link between organo- and inorganometallic chemistry, a selection of characterized compounds that can be called inorganometallic will be presented. Examples from the author's own work in metallaborane chemistry are then used to interrelate more closely organometallic and inorganometallic chemistries. Note that the area denoted inorganometallic could equally well be named metallo–main group element chemistry or even metalloid–metal chemistry. However, the term inorganometallic, though redundant in the sense that inorganic includes metallic, expresses the close relationship with organometallic chemistry described below.

1. A SIMPLE EXAMPLE

A classic example of an organometallic compound and one that is described by the Dewar–Chatt–Duncanson model of a metal–olefin interaction is $(CO)_4FeC_2H_4$ which is shown in Fig. 2.[12] Ethylene is a stable molecule in the sense that it has a long lifetime under normal conditions although its low ionization potential (10.5 eV) suggests available electron density for coordination to a Lewis acid. The iron tetracarbonyl fragment, on the other hand, is an extremely reactive, unsaturated species that can only be examined for short periods of time or in matricies at low temperatures.[13] The combination of C_2H_4 and $Fe(CO)_4$ to yield $(CO)_4FeC_2H_4$ results in changes in the structures of both compared to the free state thereby reflecting perturbations in electronic structure upon coordination.[12] As a consequence, the reactivity of the bound olefin (and the metal carbonyl fragment) is significantly changed from that in the free state.[14]

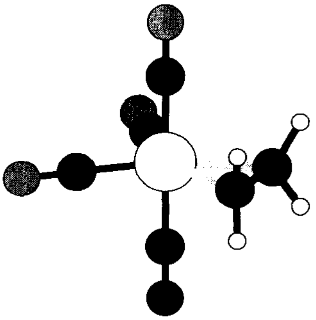


FIGURE 2 Representation of the structure of $(CO)_4FeC_2H_4$ (Ref. 12).

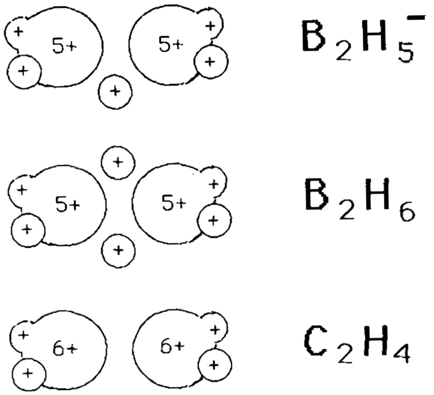


FIGURE 3 The distribution of protons in C_2H_4, B_2H_6 and $[B_2H_5]^-$.

Diborane, B_2H_6, is isoelectronic with C_2H_4 and an early view presented diborane as an ethylenic $[B_2H_4]^{2-}$ with one proton buried in each of the lobes of the B–B π bond (Fig. 3).[15] Because the π lobes are coordinated with protons, B_2H_6 itself has little tendency to coordinate with a Lewis acid (IP = 12.6 eV). However, if one removes one of the bridging protons to form $[B_2H_5]^-$ (Fig. 4) a site of available electron density is created. Recently, Shore and co-workers reported the $[(CO)_4FeB_2H_5]^-$ anion prepared from $[Fe(CO)_4]^{2-}$ and $BH_3{\cdot}THF$.[16] The $Fe(CO)_4$ fragment, which possesses an empty valence orbital, can be viewed as re-

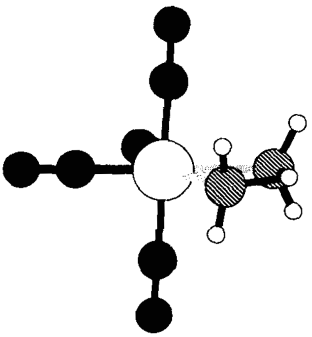


FIGURE 4 Proposed structure of $[(CO)_4FeB_2H_5]^-$ (Ref. 16).

placing a bridging proton in B_2H_6 and, hence, the compound is a direct analogue of $(CO)_4FeC_2H_4$. The structure was confirmed by a single crystal X-ray diffraction study of $CpFe(CO)_2B_2H_5$ in which the $[CpFe(CO)_2]^+$ cation formally replaces one bridging proton in B_2H_6.[17]

Despite the similarities between $[(CO)_4FeB_2H_5]^-$ and $(CO)_4$-FeC_2H_4 in terms of structure and number of valence electrons, the actual electronic structures exhibit significant differences. Using photoelectron spectroscopy and Fenske–Hall molecular orbital calculations, we compared the electronic structures of $Cp(CO)_2FeB_2H_5$ and $(CO)_4FeC_2H_4$.[18] In doing so it became clear that whereas in the latter case both the π and π^* orbitals of the C_2H_4 ligand are important in describing the FeC_2 interaction, in the former case the FeB_2 interaction occurs principally in a single molecular orbital. This bonding orbital, which is well balanced in terms of metal and boron character, has all the appearances of a three-center two-electron bond.

The origin of the difference between the metal–main group element bonding in these two compounds can be most easily seen by comparing the molecular orbitals of tetrahedral $[BH_4]^-$ and CH_4 (Fig. 5). These isoelectronic species have four filled MO's, a t_2 symmetry set of three and an a_1 symmetry orbital. Despite the same number and symmetry types of MO's, the MO energies of BH_4^- are much higher than those of CH_4 and the a_1–t_2 splitting is less. These differences are caused by the different effective nuclear charges of the central atoms as well as the different overall charges. In the case of $[B_2H_5]^-$ vs. C_2H_4 as ligands, the orbital equivalent to the π^* orbital in C_2H_4 is too high in energy to interact effectively with the metal. In the absence of the backbonding interaction that is so important in the organometallic compound, one might expect the borane to be very weakly bound to the metal. However, two factors mitigate the situation. First, the higher donor orbital energy of $[B_2H_5]^-$ results in a better energy match with the acceptor orbital of the iron fragment. Second, the B–H–B proton orients, as it were, the hybrids on boron such that they point directly at the iron atom thereby increasing overlap with the acceptor orbital on iron. There are many examples of metallaborane analogues of organometallic π complexes (Fig. 6).[19] Simple extended Hückel calculations show that in all these cases the B–H–

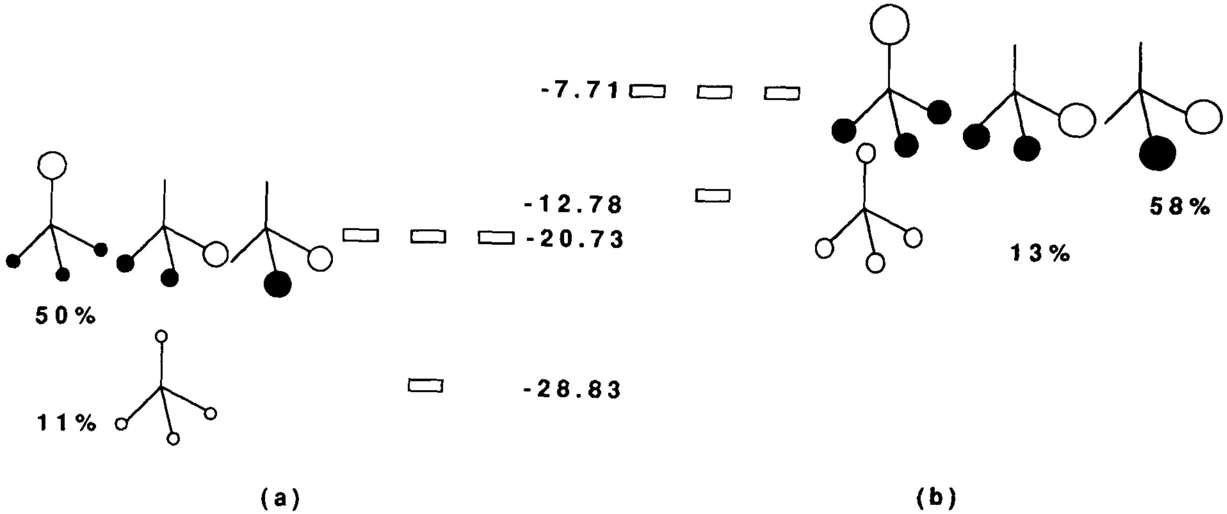


FIGURE 5 Comparison of the molecular orbitals of (a) CH_4 and (b) $[BH_4]^-$. Eigenvalues and H(1s) atomic orbital contributions to the MO's from Fenske–Hall MO calculations (Ref. 84).

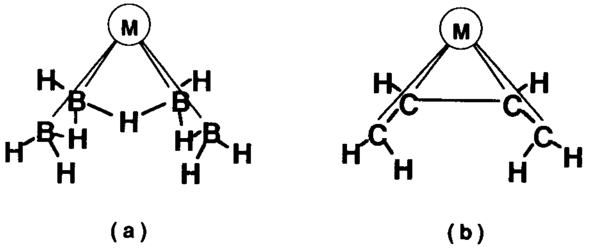


FIGURE 6 Comparison of the structure of $L_2(CO)IrB_4H_9$ with that of a 1,3-butadiene complex of a transition metal (Ref. 18, 73).

B bridging protons play an important role in orienting the donor orbitals of the borane towards the site occupied by the metal fragment.[18] No doubt this contributes substantially to the stability of the metal–boron interaction in these compounds.

The $[B_2H_5]^-$ ligand has been observed in other bonding modes. For example in $[(CO)_6Fe_2B_2H_5]^-$ (Fig. 7) the diborane anion bridges a "sawhorse" $Fe_2(CO)_6$ fragment.[20] The structure of this isomer can be easily generated from that of $[(CO)_4FeB_2H_5]^-$ by replacing one CO on the iron atom with a $Fe(CO)_3$ fragment (Both are two-electron donors.). In doing so the $[B_2H_5]^-$ fragment forms B–H–Fe bonds between formerly terminal B–H's and the incoming iron atom. A comparison of the compositions of the MO's of CH_4 and BH_4^- shows that the polarization of electronic charge towards hydrogen is larger in the case of BH_4^- than CH_4. Indeed, the use of BH_4^- as a ligand coordinating via 1–3 B–H bonds is well established and reflects the B–H bond polarity.[21] The compound analogous to $[(CO)_6Fe_2B_2H_5]^-$, $(CO)_6Fe_2C_2H_4$, has not been characterized perhaps because the C–H bond polarity is less favorable

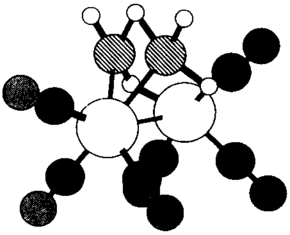


FIGURE 7 Proposed structure of one tautomer of $[(CO)_6Fe_2B_2H_5]^-$ (Ref. 20).

for the formation of C–H–Fe interactions. On the other hand, C–H–M interactions are well established at the present time[22] and $(CO)_6Fe_2C_2H_4$ might be accessible to a clever synthetic chemist.

The compounds $Pt_2(PMe_2Ph)_2(B_2H_5)(B_6H_9)$[23] and $Cp_2Co_2(PPh_2)B_2H_5$[24] contain the B_2H_5 fragment in another bonding mode. The structure of the latter compound is shown in Fig. 8 where it can be seen that the B_2H_5 fragment is asymmetrically bridging the Co–Co bond of a $Cp_2Co_2PPh_2$ fragment. One boron with a single terminal hydrogen is bound to both cobalt atoms while the other with two terminal hydrogens is bound to only one. A hydrogen atom bridges the two borons and one also bridges a cobalt–boron edge. In a formal sense, if the bridging protons are buried in the boron nuclei, a C_2H_3 fragment is produced and this fragment would be considered to be coordinated in a σ, η^2 mode (σ–π). The structural parameters of $Cp_2Co_2(PPh_2)B_2H_5$ suggest that multicenter Co_2B_2 bonding is important, i.e., the compound can be reasonably considered as a dimetallatetraborane. Comparison of the metallaborane structure with structures of multinuclear compounds containing a σ, η^2 C_2H_3 ligand suggests that multicenter Co_2C_2 bonding is important in the organometallic compounds as well. Hence, the inorganometallic compound provides additional insight into the organic analogue.

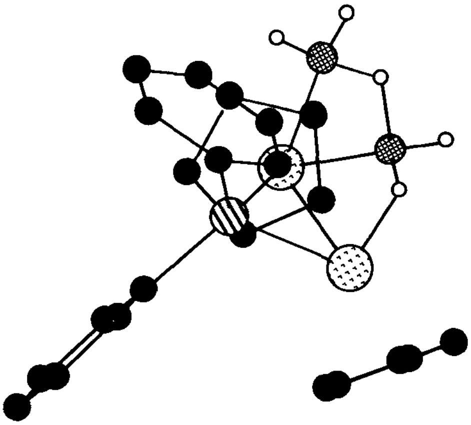


FIGURE 8 Structure of $Cp_2CO_2(PPh_2)B_2H_5$ (Ref. 24).

2. EXAMPLES OF INORGANOMETALLIC COMPOUNDS

Capped Trinuclear Metal Clusters

The potential scope of inorganometallic chemistry in terms of compound types is nicely illustrated by the variety of known examples of main group element capped trinuclear metal compounds having the fundamental cluster structure shown in Fig. 9 (Table I). Viewed as heteroatom tetranuclear clusters these all have 12 skeletal electron pairs (polyhedral electron count of 50); however, they can also be viewed as trinuclear metal clusters with a μ_3-capping ligand and an electron count of 48.[10,11] Table I gives at least one example for each main group capping atom. For some capping elements several compounds with different metals have been characterized. This is illustrated for sulfur in Table I.

In principle, considerable variation in the nature of the fragments making up the cluster is possible while retaining 12 skeletal pairs, i.e., variation in the metal and main group atom identities is possible as is variation of the ligands on each. In addition, endo-hydrogens or bridging carbonyls serve to make up the difference in electron count when the metal and main group fragments themselves do not contribute a sufficient number of electrons. However, despite the range of formally possible trimetal-capped clusters,[9] experimentally most metal atoms come from groups 6–9 and most main group atoms from groups 13–16. This is reasonable as there are limits to the number of ligands that can be gathered around a four-atom cluster core.[25] There are usually three terminal ligands in the case of the metal (Cp is considered to occupy three coordination positions) and zero or one in the case of the main group atom. The number of endo-hydrogens ranges from 0 to 4 while bridging carbonyls range from 0 to 3. This means that the cluster

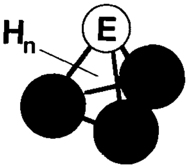


FIGURE 9 Schematic representation of a main group atom capped trimetal cluster with *n* endo-hydrogens.

TABLE I

Selected examples of main group atom capped trimetal clusters for different main group atoms.

13	14	15	16	17
$H(CO)_9Fe_3BH_4$[a]	$H_3(CO)_9Fe_3CR$[b]	$H_2(CO)_9Fe_3NR$[c]	$[(CO)_9Fe_3O]^{2-}$[d]	
	$(CO)_9Co_3SiCo(CO)_4$[e]	$H_2(CO)_9Fe_3PPh$[f]	$H_2(CO)_9Ru_3S$[g]	
			$H(CO)_9Fe_3SR$[h]	
			$(CO)_9Co_2FeS$[i]	
			$H_2(CO)_9Os_3S$[j]	
	$(CO)_9Co_3GeMn(CO)_5$[k]	$(CO)_9CO_3As$[l]	$(CO)_9Co_2FeSe$[m]	
		$H_3(CO)_9Bi$[n]	$(CO)_9Co_2FeTe$[o]	$HRu_3(CO)_9I$[p]

[a] Ref 39. [b] Ref 41. [c] Ref 74. [d] Ref 75. [e] Ref 20. [f] Ref 76. [g] Ref 77. [h] Ref 78. [i] Ref 79. [j] Ref 80. [k] Ref 68. [l] Ref 81. [m] Ref 82. [n] Ref 65a. [o] Ref 82. [p] Ref. 83.

core atoms must contribute from 6 to 12 electrons. Experimentally, in terms of isolobal main group analogues, the cluster fragments generally contribute 0–4 electrons to the cluster electron count. A greater variation would also induce a large polarity into the cluster bonding which would be expected to inhibit delocalized cluster bonding and reduce cluster stability. The situation is analogous to that of benzene and borazine.[26] Polarization of the out of plane $p\pi$ orbitals in the latter molecule severely disrupts the delocalized π system. This is not to say that other examples cannot be prepared but that, in contrast to the compounds in Table I, such clusters may be less stable and/or more reactive. This makes them more difficult in a synthetic sense but attractive in terms of carrying out chemistry. Note that a skeletal electron count of 8 is also possible for a tetrahedral cluster and this bonding situation has not been considered in the above.[27]

Unusual Bonding Modes

It is natural to draw attention to the similarities between new inorganometallic compounds and known organometallic systems simply because so many organometallic systems have been characterized. But it should be expected and, indeed is found, that some examples of inorganometallic compounds exhibit modes of bonding that are essentially different than those established for carbon moieties.

The situation with arsenic provides an instructive example. Let us begin by comparing the ligand properties of C_2R_2, N_2 and As_2. Alkynes, the organic analogues of N_2 and As_2, serve as two- and four-electron donors[28] and are coordinated in an η^2 fashion. Likewise one finds many examples of N_2 as a two- or four-electron donor in metal complexes.[29] However, for N_2 coordination is almost exclusively end-on, i.e., via the lone pairs on nitrogen although a side-on bound N_2 is postulated as a reaction intermediate[30] and an example of a compound exhibiting complex η^2 coordination is known.[31] The As_2 moiety, like N_2, has a formal triple bond. It is only observed in the free state as a component of arsenic vapors at high temperatures but, when coordinated to metals, As_2 is found as a 4, 6 or 8 electron donor ligand. Examples are shown in Fig. 10[32,33] where representative examples of both side-on and end-on (lone pair) coordination are shown. Perhaps the most interesting

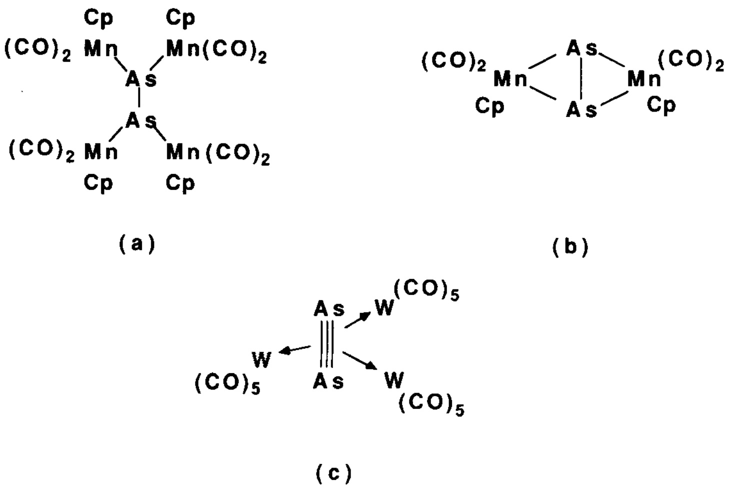


FIGURE 10 Schematic drawings of (a) $[CpMn(CO)_2]_4As_2$, (b) $[CpMn(CO)_2]_2As_2$ and (c) $[W(CO)_5]_3As_2$ (Refs. 32–34).

compound is $As_2[W(CO)_5]_3$ prepared by the reaction of $AsCl_3$ with either $[W(CO)_5THF]$ or $Na_2[W_2(CO)_{10}]$.[33] Conventional electron counting requires the As_2 fragment to contribute six electrons to the metal atoms even though all three metals are η^2 to the As_2 fragment. This means the one σ and two π electron pairs of the formal triple bond must become involved in the metal–main group atom coordination. Note also that not only are the two arsenic atoms still within bonding distance but that the bond distance (2.279 Å) is shorter than that expected for an AsAs single bond. Hence, one can view the As_2 moiety as a triply bonded diarsine whose bond is lengthened by η^2 coordination to three metal fragments acting as Lewis acids just as the triple bond of C_2H_2 is lengthened by η^2 coordination to one or two metal centers. Huttner *et al.* have modeled the bonding using extended Hückel theory and the three principle MO's that were suggested to account for the bonding of the Lewis acids to As_2 are sketched in Fig. 11.[34]

The principle reason for the different behavior of C_2H_2, N_2 and As_2 again lies in the differences in the energies and compositions of the highest lying donor orbitals. These differences are most easily seen by comparing ionization behavior. First compare N_2, PN and P_2. Consistent with the behavior of N_2 as a donor, the

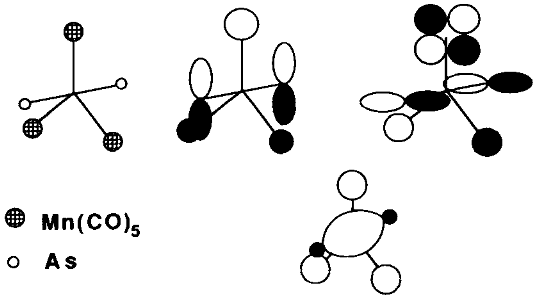


FIGURE 11 Schematic representation of the principle As_2 metal bonding orbitals for $[W(CO)_5]_3As_2$ (Ref. 34).

lowest ionization potential (ip) of N_2 results from loss of an electron from a σ MO ("lone pair") while 1.1 eV additional energy is required to remove an electron from the degenerate π orbitals.[35] Two changes occur as one moves to the heavier conjugers. First, the lowest ionization potential decreases. (The first ip of PN is 11.9 eV and that of P_2 is 10.8 eV.) and the difference in the ip's of σ and π orbitals decreases (0.8 eV in PN an 0.2 eV in P_2). Hence, in going to P_2 there is less distinction between the σ and π electrons in terms of donor ability and P_2 is known to act as a π donor, e.g., $(CO)_6Co_2P_2$. Although the ionization potentials of As_2 are not available, they will be closer to those of P_2 than N_2. Finally, the highest lying σ MO for N_2 has significant amplitude lying between the nitrogen nuclei as well as at each "end." Hence, an incoming Lewis acid might attack either "end-on" or "broad-side." Apparently, for As_2 in $As_2[W(CO)_5]_3$ the coordination of three Lewis acids leads to "broad-side" coordination for both σ and π donor MO's. The difference between N_2 (or As_2) and C_2H_2 is also revealed by a comparison of ip's. In going from N_2 to C_2H_2 a proton is formally removed from each N nucleus and placed in an "end-on" position. The net result is a large destabilization of the π MO's of C_2H_2 (11.40 vs. 16.7 eV) due to a reduction in effective nuclear charge and a large stabilization of the former σ orbital of N_2 due to the presence of the protons. Hence, only the π MO's of C_2H_2 are readily available for coordination to Lewis acids.

An even more unusual example of the behavior of As_2 is shown in Fig. 12 where the structure of CpMo[μ-(η^4-As_5)]MoCp is de-

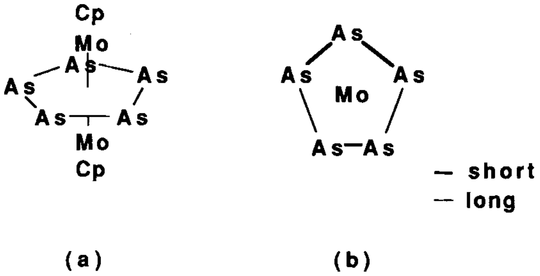


FIGURE 12 Schematic drawings of (a) $Cp_2Mo_2As_5$ and (b) the As_5 ring showing two long and three short As–As distances (Ref. 36).

picted.[36] At first sight this compound looks like an analogue of a triple decker sandwich compound and, in fact, it can be viewed that way if one ignores some significant distortions in the As_5 ring and the short Mo–Mo distance of 2.764 Å. (This value is intermediate between those observed for single and double bonds.) Because of the latter observations, the compound has been described differently. That is, the ring exhibits three short and two long distances such that a partitioning into μ-(η^2-As_3) and μ-(η^2-As_2) ligands is possible. Hence, the compound is viewed as an example of a binuclear transition metal fragment bridged by ligands exhibiting two different bridging geometries. Contrast CpMo[μ-(η^4-As_5)MoCp with $As_2[W(CO)_5]_3$. In the former a multiply bonded dinuclear Lewis acid is coordinated by basic As_n ligands in a bridging fashion. In the latter a dinuclear multiply bonded Lewis base is coordinated by acidic $W(CO)_5$ fragments in a bridging fashion. CpMo[η^4-As_5)]MoCp is, in a sense, an inside out version of $As_2[W(CO)_5]_3$!

By noting the existence of $Co_2(CO)_6As_2$[37] and $Co(CO)_3As_3$[38] (Fig. 13) we complete the circle begun in this section with the discussion of M_3E clusters which included an example of an M_3E cluster with E = As. $Co_2(CO)_6As_2$ can be considered as a As_2 molecule coordinated to a $Co_2(CO)_6$ fragment and is therefore analogous to the well studied $C_2H_2Co_2(CO)_6$ cluster. Alternatively, it can also be viewed as a 6 skeletal electron pair heteronuclear cluster. Likewise, $Co(CO)_3As_3$ can be viewed as an As_3 ring coordinated to cobalt or as a 6 electron pair heteronuclear cluster. Indeed, as pointed out by Dahl as early as 1969,[37,38] in all

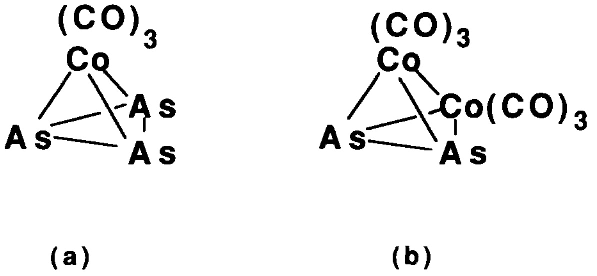


FIGURE 13 Schematic representation of the structures of (a) $(CO)_3CoAs_3$ and (b) $(CO)_6Co_2As_2$ (Refs. 37, 38).

these cluster systems one can envision series having compositions ranging from completely main group atoms to transition metal atoms, i.e., the other two members of this series are As_4 and $Co_4(CO)_{12}$.

3. CLUSTER MIMETICS

Occasionally the organo- and inorganometallic analogues are strictly isoelectronic. In the case of some metallaboranes we have studied, this has permitted detailed physical–chemical comparisons of the properties of each pair of compounds. We have found that the metallaborane closely mimics the isoelectronic hydrocarbyl complex. But there are also interesting and characteristic differences that have permitted the development of a deeper understanding of the behavior of both. The following examples serve to illustrate the point.

The metallaborane $HFe_3(CO)_9(H_3BH)$ has been fully characterized and its solid state structure is shown in Fig. 14.[39] The hydrogen positions shown on the cluster framework are based on the low temperature ^1H NMR spectrum. Formally, the ferraborane can be described as a BH_4^- ligand triply bridging a 42-electron $[HFe_3(CO)_9]^+$ fragment. Each of the three B–H bonds of the borohydride ligand that forms a bridging interaction donates two electrons thereby yielding a 48-electron trimetal cluster. Alternatively, the compound can be viewed as a four-atom cluster with six skeletal electron pairs or a polyhdredral electron count of 50.

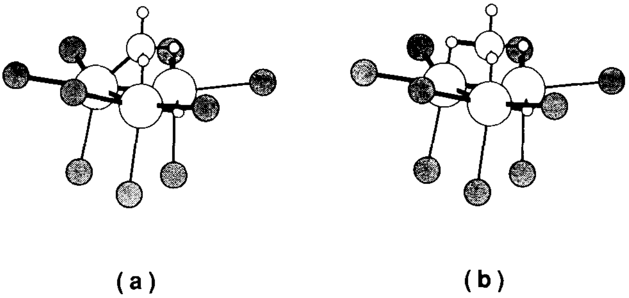


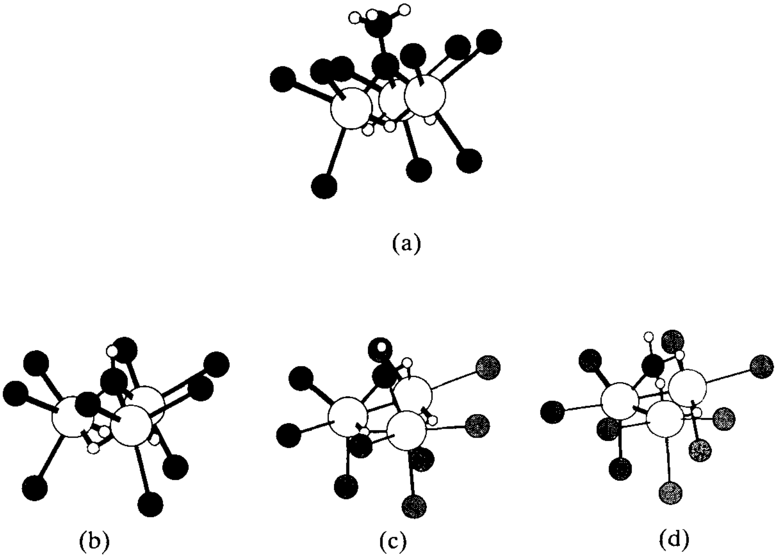
FIGURE 14 Proposed structure of (a) $[HFe_3(CO)_9(H_2BH)]^-$ and structure of (b) $HFe_3(CO)_9(H_3BH)$ (Ref. 39). The CO ligands are represented by the CO oxygen atoms alone for clarity.

The latter view is more consistent with the fluxional behavior of the compound. Variable temperature ^1H NMR demonstrates that exchange of the B–H–Fe and Fe–H–Fe hydrogens occurs in preference to that of B–H–Fe and B–H terminal hydrogens. This suggests that in the B–H–Fe interaction skeletal B–H bond breakage occurs in preference to Fe–H bond rupture. Contrast this with the behavior of most mononuclear borohydride complexes where the opposite holds true.[21] Hence, we have argued that $HFe_3(CO)_9(H_3BH)$ is better viewed as a tetranuclear cluster with four energetically similar endo-hydrogens.

Substitution of the terminal B–H hydrogen with CH_3 leads to $HFe_3(CO)_9(H_3BCH_3)$. Methyl substitution lowers the barrier for the exchange process resulting in the observed fluxional behavior of the endo-hydrogens. Deprotonation of $HFe_3(CO)_9(H_3BH)$ yields $[HFe_3(CO)_9(H_2BH)]^-$ in which the endo-hydrogens undergo an even more facile fluxional process. Spectroscopic studies have established in the latter case that the most stable static arrangement of the endo-hydrogens is that shown in Fig. 14.[39] Although a B–H–Fe proton is removed by base, two endo-hydrogens are still associated with the apical boron atom in this structure.

The structures of the clusters $H_3M_3(CO)_9CH$, M = Os, Ru, had been well established before we began our work[40] and, consequently, our characterization of $H_3M_3(CO)_9CCH_3$, M = Fe, as a cluster containing three Fe–H–Fe endo-hydrogens was not surprizing (Fig. 15).[41] On the other hand, the contrast between the ferraborane and hydrocarbyl analogues in terms of the endo-hydrogen locations was particularly striking because of the isoelectronic relationship between the compounds. Hence, we pursued a spectroscopic investigation of the system with the composition $Fe_3(CO)_9CH_4$ in order to provide an additional point of direct comparison. By utilizing IR, variable temperature ^1H and ^{13}C NMR, and low temperature protonation of the anionic conjugate base of $Fe_3(CO)_9CH_4$, we have demonstrated that this cluster exists in solution as a mixture of three tautomers: $H_3Fe_3(CO)_9CH$, **A**; $H_2Fe_3(CO)_9(HCH)$, **B**; and $HFe_3(CO)_9(H_2CH)$, **C** (Fig. 15).[42] Tautomers **B** and **C** both possess C–H–Fe interactions that are analogous to the B–H–Fe interactions in the isoelectronic ferraborane. In addition, these tautomers exhibit fluxional behavior with respect to the hydrocarbyl fragments but, in contrast to the ferraborane, for these C–H–Fe bridges it is the Fe–H rather than the C–H interaction which is most easily broken.

There are other differences between the boron and carbon capped clusters. The most stable structure of $[HFe_3(CO)_9(H_2BH)]^-$ corre-



(a)

(b) (c) (d)

FIGURE 15 Structure of (a) $H_3Fe_3(CO)_9CCH_3$ and proposed structures of (b) $H_3Fe_3(CO)_9CH$, (c) $H_2Fe_3(CO)_9(HCH)$ and (d) $HFe_3(CO)_9(H_2CH)$ (Refs. 41, 42). The CO ligands are represented by the CO oxygen atoms alone for clarity.

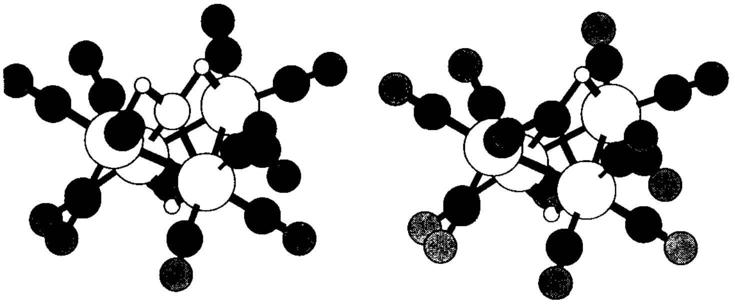
sponds to the structure of the least stable tautomer of $Fe_3(CO)_9CH_4$, i.e., **C**. This suggests that an isoelectronic ferraborane is an excellent model for the structure of an accessible high energy intermediate of the isoelectronic organometallic cluster. Convincing kinetic evidence has been published for the participation of $H_2Ru_3(CO)_9(HCH)$ as a high energy intermediate in the reductive elimination of the capping moiety from $H_3Ru_3(CO)_9CH$.[43] Likewise, $H_2Os_3(CO)_9(HCH)$ has been postulated as an intermediate in the exchange of the two types of hydrogen atoms in $H_3Os_3(CO)_9CH$.[44] The energy differences between the three tautomeric forms of $H_2Fe_3(CO)_9(HCH)$ are very small. This is interesting because only a small energy perturbation is required to drive the system from a structure with a coordinated methyne to one with a methylene to one with a methyl. Thus, the additional "push" provided by the presence of a Lewis base such as a phosphine is known to result in the release of CH_4.[42,45]

Naturally the question arises as to why tautomeric forms are observed for $Fe_3(CO)_9CH_4$ but not for $H_3Fe_3(CO)_9CCH_3$, $H_3M_3(CO)_9CH$, M = Ru, Os, or $[HFe_3(CO)_9(H_2BH)]^-$. The phenomenological explanation is that NMR spectroscopy does not have a large dynamic range and only a small energy difference favoring M–H–M bridging will preclude observing tautomeric forms containing C–H–M interactions. Hence, it is fortuitous in the case of $Fe_3(CO)_9CH_4$ that all factors balance so that the equilibria are observed. In the case of the ferraborane, the molecule is fluxional down to $^-90$°C and, because of the low barriers for hydrogen exchange, tautomeric forms, if present, can not be observed by NMR spectroscopy. A deeper explanation of what causes the differences is much more difficult to obtain. However, the various factors that control the balance between tautomers **A, B** and **C** are almost certainly related to those that control hydrogenation/dehydrogenation of a carbide atom on a metal surface site. Therefore, an understanding of these factors will help reveal what controls methane formation in the complex Fischer–Tropsch synthesis reaction. For this reason, as well as purely academic ones, we have explored the problem in some detail. Although the geometric characteristics of this type of cluster are very important,[46] one intrinsic electronic factor that affects endo-hydrogen position is the nuclear charge of the capping atom relative to that of the metal. For this reason we have sought further experimental evidence upon which to develop a more comprehensive model.

Reducing the effective nuclear charge of the main group capping atom relative to the metal promotes E–H–M, E = main group atom, M = metal atom, formation. It follows that increasing the effective nuclear charge of the metal relative to that of the capping atom should also promote E–H–M formation. Hence, we have reinvestigated the neutral mixed metal clusters with the composition $FeCo_2(CO)_9CHR$.[47,48] By selectively labeling the μ_3-carbon with ^{13}C we were able to show that the cluster with R = Ph exists in solution as a mixture of tautomers with the structures $HFeCo_2(CO)_9(CPh)$, **A′**, and $FeCo_2(CO)_9(HCPh)$, **B′**, which have 0 and 1 C–H–M interactions, respectively. More importantly, in contrast to the situation with $Fe_3(CO)_9CH_4$, tautomer **B′**, which is analogous to **B**, is the most abundant form of the cluster in solution.[49] Hence, as predicted, going from iron to cobalt while keeping the capping atom carbon promotes the formation of a E–H–M interaction. The change in metals with constant capping atom causes a much smaller shift in relative tautomer stabilities than keeping metals constant and changing the capping atom from carbon to boron. As expected, changes in the metals provide finer tuning of the electronic structure than changes in the main group atoms. Note also that just as in going from carbon to boron in the $Fe_3(CO)_9EH_x$ cluster, the barrier to tautomeric interconversion is reduced in going from iron to cobalt in the $Fe_xCo_y(CO)_9CH_z$ cluster. Therefore it appears that not only stabilities of the tautomers but also reaction barriers are sensitive to the relative capping atom–metal atom properties.

Note that changes in endo-hydrogen positions can be accomplished with boron as the capping atom as well as carbon. Shore has characterized the cluster $H_3Os_3(CO)_9BCO$ which is isolectronic with $H_2Os_3(CO)_9CCO$.[50] We have prepared the iron analogue, $HFe_3(CO)_9(\mu\text{-}CO)(HBH)$, which in contrast to the cluster with osmium has a B–H–M interaction and a bridging CO.[51] Presumably, the ruthenium analogue would lie somewhere in between. A change in the site of CO coordination on capped trimetal clusters with small chemical changes is known in other systems, e.g., protonation of $[Fe_3(CO)_9CCO]^{2-}$ leads to $[Fe_3(CO)_9(\mu\text{-}CO)CH]^-$.[52]

Although deprotonation of the $Fe_3(CO)_9EH_x$, $E = B, C$; $x = 5, 4$, respectively, clusters leads to mono anions that have been studied, the deprotonation of the methyl derivatives, $Fe_3(CO)_9EH_xCH_3$, $E = B, C$; $x = 4, 3$, respectively, exhibits interesting differences. Instead of simply forming an anion, reaction of $H_3Fe_3(CO)_9CCH_3$ with a base results in quantitative loss of H_2 and the formation of $[HFe_3(CO)_9CCH_2]^-$.[53] In the presence of acid and H_2 the reaction is reversible. Mechanistic studies show that a simple anion is the initial product resulting from a second order reaction of $H_3Fe_3(CO)_9CCH_3$ with base but that H_2 is lost in a subsequent unimolecular decomposition of the transient anion initially formed. The formation of a coordinated vinylidene in $[HFe_3(CO)_9CCH_2]^-$ appears to be a significant driving force for the reaction. Deuterium labeling studies demonstrate that protonation/deprotonation takes place on the organic fragment while hydrogenation/dehydrogenation occurs on the triiron fragment. In contrast, the boron analogue $HFe_3(CO)_9(H_3BCH_3)$ deprotonates without H_2 elimination to form $[HFe_3(CO)_9(H_2BCH_3)]^-$. Dihydrogen elimination does occur on heating and, presumably, the boron analogue of $[HFe_3(CO)_9CCH_2]^-$ is formed.[54] Note that Shore has prepared the neutral osmium cluster, $[HOs_3(CO)_9(H_2BCH_2)$, which has been shown to contain a boron vinylidene fragment $(=B=CH_2)$.[55]



(a) (b)

FIGURE 16 Structures of $HFe_4(CO)_{12}BH_2$ and (b) $HFe_4(CO)_{12}CH$ (Ref. 56, 59).

We have also devoted considerable effort to a comparison of the properties of the two isoelectronic "butterfly" clusters $HFe_4(CO)_{12}BH_2$ and $HFe_4(CO)_{12}CH$ (Fig. 16).[56] The former contains two E–H–M interactions and the latter contains one. Deprotonation of $HFe_4(CO)_{12}BH_2$ leads to $[HFe_4(CO)_{12}BH]^-$ by loss of a B–H–M proton with the same structure as that of $HFe_4(CO)_{12}CH$. There is no evidence for tautomerization in either system. However, on going to the "butterfly" cluster with the composition $Ru_4(CO)_{12}CH_2$ two tautomers are observed in solution ($HRu_4(CO)_{12}CH$ and $H_2Ru_4(CO)_{12}C$).[57] Just as in the case of the capped-trimetal clusters, going from Fe to Ru promotes the stability of the M–H–M interaction relative to the E–H–M interaction. Further deprotonation of $[HFe_4(CO)_{12}BH]^-$ leads to $[Fe_4(CO)_{12}BH]^{2-}$ and then to $[Fe_4(CO)_{12}B]^{3-}$ [58]whereas deprotonation of $HFe_4(CO)_{12}CH$ leads to first $[HFe_4(CO)_{12}C]^-$ and then to $[Fe_4(CO)_{12}C]^{2-}$.[59] From this we would predict that the $[HRu_4(CO)_{12}B]^{2-}$ structure for the dianion would be promoted with respect to the $[Ru_4(CO)_{12}BH]^{2-}$ structure. Although the ruthenium analogue of $HFe_4(CO)_{12}BH_2$ has been reported, deprotonation has yet to be examined.[60] Disubstitution of $[HFe_4(CO)_{12}BH]^-$ with a phosphine at each of the two "wing-tips" leads to the $[Fe_4(CO)_{10}(PR_3)_2BH_2]^-$ structure.[57] Clearly, variation in the electronic properties of the metal fragments permits the rational control of stable endo-hydrogen position.

The fluxional behaviors of $HFe_4(CO)_{12}CH$ and $[HFe_4(CO)_{12}BH]^-$ in solution have been compared.[57] For both, variable temperature ^{13}C and ^{1}H NMR show the existence of two exchange processes. The first leads to scrambling of the Fe–H–Fe and E–H–Fe protons and the second leads to exchange of the E–H–Fe proton between the two Fe(wing-tip)–E sites (Fig. 16). The latter process is more facile for the hydrocarbyl cluster while the former is more facile for the ferraborane. The first exchange process involves breaking the main group–hydrogen interaction with retention of the hydrogen–metal interaction while the second retains the main group–hydrogen interaction while breaking the metal–hydrogen interaction. The structural parameters of the C–H–Fe and B–H–Fe interactions in $HFe_4(CO)_{12}CH$ and $HFe_4(CO)_{12}BH_2$[56,61] show that going from C to B results in weaker main group–hydrogen and stronger metal–hydrogen interactions. Thus, the difference in fluxional behavior lies in the relative strengths of main group–hydrogen and metal–hydrogen interactions in a three-center bond. This is congruent with what was observed in the comparison of the $Fe_3(CO)_9EH_x$ clusters reviewed above.

4. SUMMARY

The examples of inorganometallic chemistry described above constitute only a few of those available and are, naturally, biased by the author's own work. One could have presented equally exciting results from sulfur–metal,[62] phosphorus–metal,[63] silicon–metal,[64] bismuth–metal,[65] etc. Only clusters containing metal carbonyl fragments have been discussed. Compounds with $(\eta^5\text{-}C_5H_5)M$ fragments constitute another set of relevant species. Also, group 6 metal tri-tetrametal clusters with alkoxide rather than carbonyl exo-ligands are related in an interesting fashion to the compounds discussed herein.[66] There are just too many examples to cite them all in a short article such as this one but related reviews are available.[67,68] Just as many organic transformations are facilitated by the presence of transition metal complexes, so too the work of Sneddon, for example, has demonstrated the value of transition metal complexes for the promotion of main group reactions.[69] Inorganometallic compounds are almost certainly the active intermediates in these systems. Likewise, inorganometallic compounds have the potential of being valuable synthetic intermediates.[70] Finally, just as organometallic compounds have been found to be useful sources of materials, so too inorganometallic compounds have the potential of leading to carbon-free main group–metal materials.[71]

In his Nobel lecture[72] Hoffmann defined the close relationship between the bonding modes of main group and transition metal fragments. In beautiful agreement with his, and other's, predictions,[9–11], the fusion of main group and transition metal chemistry has already demonstrated the promise of fertile areas of research equal to that predicted for organometallic chemistry a quarter of a century ago. Just as "the" electron precise atom, carbon, is often our point of reference in main group chemistry, so too organometallic compounds serve as a point of reference for inorganometallic chemistry. The recognition of the ties relating them is not only a useful pedagogical tool but also one that points to new compounds while giving further insight into old ones.

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