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A Report on the "New Frontiers in Group 13 Chemistry" Symposium from the 88th Canadian Society for Chemistry Conference and Exhibition

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ABSTRACT: *The 88th Canadian Society for Chemistry Conference and Exhibition was held in Saskatoon, Saskatchewan, during the period of May 28–June 1, 2005. More than 250 chemists from various academic institutes and industries enjoyed five plenary lectures, thirteen oral presentations and a plethora of poster presentations.* © 2007 Wiley Periodicals, Inc. Heteroatom Chem 18:323–332, 2007; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20287

INTRODUCTION

The 88th Canadian Society for Chemistry Conference and Exhibition (www.csc2005.ca) was held from May 28 until June 1, 2005, in the city of Saskatoon, Saskatchewan, Canada. Over one thousand delegates attended this year's annual national chemistry meeting. One feature of the conference was a special symposium entitled "New Frontiers in Group 13 Chemistry," which featured presentations from a number of prominent scientists both from academia and industry, representing 16 universities and companies, from Canada and around the world. Described in this report is a review of the symposium that includes a summary of the symposium's plenary lectures, a compilation of all of the abstracts from the oral presentations, and a synopsis of the poster session contributions.

PLENARY LECTURES

The first plenary lecture was given by Herbert W. Roesky (University of Göttingen, Germany) on "Reactions and Catalysis of Aluminum(I) and Aluminum(III) Compounds." When describing his approach to organoaluminum chemistry, Prof. Dr. Roesky quoted Ralph Waldo, "Research is the art of seeing what others see, but thinking what others don't think." Prof. Dr. Roesky gave a very stimulating and intriguing lecture on the preparation and properties of LAl ($L = HC(CMeNAr)_2$, $Ar = 2,6\text{-}i\text{-}Pr_2C_6H_3$). The reactions of LAl with $Me_3SiC{\equiv}CSiMe_3$, $HC{\equiv}CH$, N_3R (Scheme 1), RCN, S_8, P_4, and $B(C_6F_5)_3$ were also reported. A new synthetic approach to heterobimetallic systems was discovered using organometallic hydroxides such as LAl(Me)OH, LGa(Me)OH, and LGe(OH). The synthesis of $LAl(Me)OZrCp_2Me$ demonstrates that this heterobimetallic compound is an efficient catalyst for the polymerization of ethylene. Finally, it was

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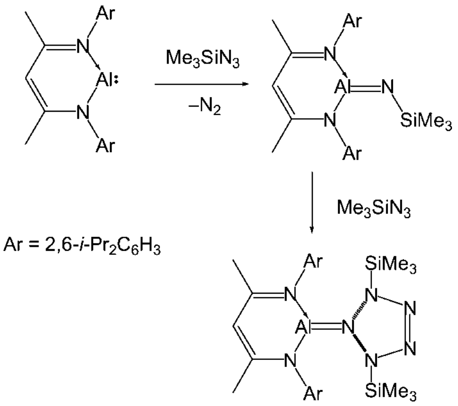


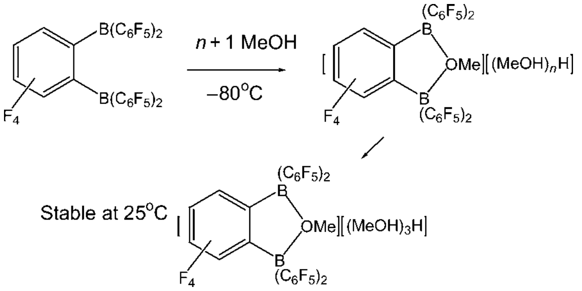
Ar = 2,6-*i*-$Pr_2C_6H_3$

SCHEME 1

shown that $AlH_3 \cdot NMe_3$ is a powerful hydroalumination reagent for acetylenes, nitriles, and isonitriles [1].

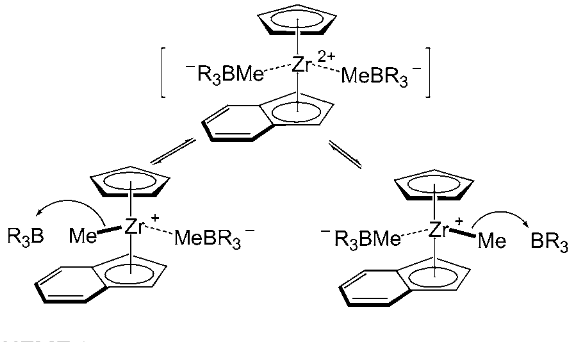
The second plenary lecture entitled “Bifunctional Boranes: Two Borons Are Better Than One” by Warren E. Piers (University of Calgary, Canada) was linked between the Group 13 Chemistry symposium and a Canadian Society for Chemistry Award presentation (“The 2005 Alcan Award Lecture”). The Alcan Award is an annual honour for “a contribution to the field of inorganic chemistry or electrochemistry while working in Canada.” This plenary lecture by Prof. Piers adds to the numerous awards that he has won during his career (e.g., Royal Society of Canada Rutherford Medal in Chemistry (2000), the Catalysis Lecture Award (2002), and the 2003 Merck Frosst Centre for Therapeutic Research Award). Professor Piers noted that chelating Lewis acids are far less studied than their Lewis base counterparts owing to the synthetic challenges associated with preparing bidentate Lewis acids. Piers’ group has been interested in a couple of families of bifunctional boranes, inspired by the common chelating ligands such as diphos and bipy. Professor Piers reported elegant synthetic routes to Lewis acid analogs belonging to two families of bifunctional boranes: the perfluoroaryl boranes 1,2-C_6F_4-$(BAr^F)_2$ and related compounds (Scheme 2), and the nonfluorinated 2,2-diborabiphenyl bipyridine analogs [2].

The next plenary lecture was given by Scott Collins (University of Akron, USA), who asked the question “Are Two Heads Better Than One (in Dinuclear Activators and Initiators in Polymerisation Processes)?” Professor Collins gave an excellent talk on his group’s search for weakly coordinating anions (WCA) in olefin polymerization. The introduction of his talk discussed the use of activators bearing two group 13 atoms in conjunction with metallocene catalysts. These activators can function in either a chelating or bridging capacity and some of these activators are known to give rise to exceptionally active polymerization catalysts compared with those formed using conventional mononuclear activators. Professor Collins discussed the possible involvement of WCAs in propene polymerization using *ansa*-metallocenium ions and mononuclear borane activators (Scheme 3), and the use of dinuclear borane co-initiators in isobutene polymerization [3].

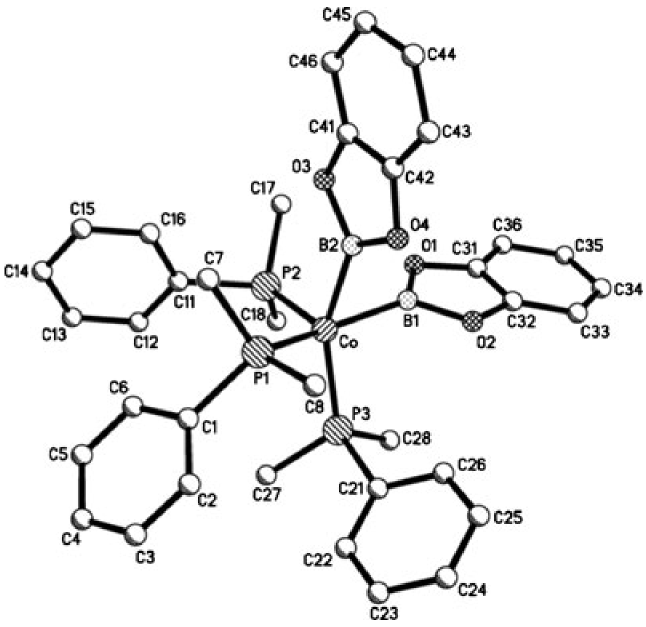


SCHEME 2

The fourth plenary lecture was provided by Professor Nicholas C. Norman (University of Bristol, UK), whose interesting talk entitled “Cobalt Boryl Compounds: Synthesis, Structure and Reactivity” focused on their recent work in this area. This paper was part of a collaboration with Professors Todd B. Marder (Durham University, UK) and Zhenyang Lin (Hong Kong University of Science and Technology, China). The neutral Co(0) species $[Co(PR_3)_4]$ ($PR_3 = PMe_3$ or PMe_2Ph) react with the diborane (4) compound B_2cat_2 (cat = catecholate) to give the paramagnetic Co(II) boryl species $[Co\{B(cat)\}_2(PR_3)_3]$. The structures of these compounds and related derivatives, determined by X-ray crystallography, comprise a five-coordinate, square-based pyramidal Co center with an apical phosphine and cis basal boryl groups with a short $B \cdots B$ distance (example below). Electron spin resonance



SCHEME 3

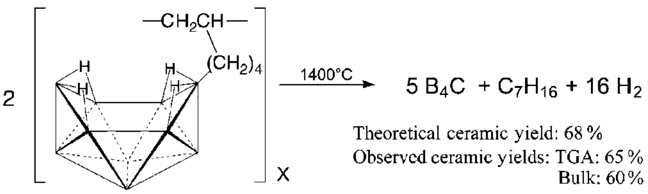


(ESR) spectroscopic data and theoretical calculations were also presented and discussed with the results of other experiments which yield Co(I) and Co(III) boryls. Finally, some preliminary catalyzed alkyne diboration and boryl transfer reactions were presented [4].

The last plenary lecture was by Prof. Larry G. Sneddon (University of Pennsylvania, USA), who provided an outstanding lecture on the "Design, Synthesis and Applications of Chemical Precursors to Advanced Boron-Based Ceramic Materials." Prof. Sneddon noted that the production of complex structural and electronic materials in useable forms is one of the most challenging problems of modern solid-state chemistry and materials science. Indeed, an important new route to producing film, fiber, and nanostructured materials involves the use of the chemical-precursor approach, in which a polymeric or molecular precursor is first formed into the desired shape and then decomposed to the final material with retention of this shape. Their recent work directed toward the syntheses, characterizations, and applications of new boron-based polymeric and molecular precursor systems was presented with a focus on the use of these precursors to generate technologically important non-oxide ceramics, such as boron carbide (Scheme 4) and metal borides, in processed forms [5].

ORAL PRESENTATIONS

There were a total of 19 oral presentations that were directly linked to the symposium. These are listed below in order of appearance.



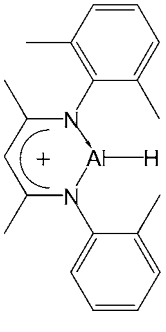
Theoretical ceramic yield: 68 %
Observed ceramic yields: TGA: 65 %
Bulk: 60 %

SCHEME 4

OP01

"Reactivity of Low Coordinate Group 13 Species: Carbocation and Methyl Radical Derivative" by J. A. C. Clyburne (Simon Fraser University, Canada), D. A. Dickie, T. Ramnial, I. D. McKenzie, P. W. Percival, and G. Schatte.

Abstract: Our interest in the reactivity of nucleophilic carbenes, specifically the imidazol-2-ylidenes, has led us to study the reactivity of carbenes with simple reagents, including radicals and protic agents. Recently there have been some exciting advances in the preparation of group 13 carbene analogs. Neutral Ga [6a] and Al [6b] carbene analogs have been reported and these compounds are stabilized by the β-ketiminato ligand. The availability of a lone pair of electrons on the metal site has been illustrated by formation of donor–acceptor complexes [6c]. This report will extend our studies on carbene analogs to the related group 13 compounds. For example, a computational study has been performed to examine the reactions of a model β-ketiminatoaluminum(I) complex with the hydrogen atom and with the electron. It was found that the hydrogen atom adds to the metal center exothermically ($H_{rxn} = -202$ kJ mol^{-1}), and the spin density in the resulting radical resides entirely on the β-ketiminato ligand. The spin density of the corresponding radical anion is very similar to that of the H-adduct. We have also started to examine the structural chemistry of cations derived from the group 13 carbene analogs, and results will be reported soon [6d].



OP02

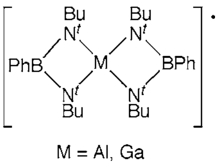
"Kinetic Evidence for Five-Coordination in the $\mathrm{AlOH(aq)^{2+}}$ Ion: Implications for the Reactivity and Toxicity of Aluminum(III) in Water" by W. H. Casey, B. L. Phillips, J. Rosenquist, P. Yu, E. Bylaska, and T. W. Swaddle (University of Calgary, Canada).

Abstract: In dilute aqueous solution, $\mathrm{Al^{3+}}$ exists essentially as octahedral $\mathrm{Al(H_2O)_6^{3+}}$ at pH <3.0 and as tetrahedral $\mathrm{Al(OH)_4^-}$ at pH >7.0. It has been traditionally assumed that hydrolytic species such as $\mathrm{AlOH(aq)^{2+}}$ that exist in the biologically and geologically important pH range 3–7 are hexacoordinate. The exchange of solvent water via $\mathrm{AlOH(aq)^{2+}}$, however, is extraordinarily fast relative to that of $\mathrm{Al(H_2O)_6^{3+}}$, and the apparent volume of activation (-0.7 $\mathrm{cm^3\ mol^{-1}}$) is inconsistent with the accepted mechanism whereby water exchange on the conjugate base of an aqua ion occurs in a rate-determining dissociatively activated step following rapid proton loss. The data are fully explained if the stable form of $\mathrm{AlOH(aq)^{2+}}$ is *five-coordinate* $\mathrm{Al(H_2O)_4OH^{2+}}$, formed by rapid loss of water following *rate-determining* proton loss. Thus, the observed volume of activation is that for proton exchange, and Al(III) stands unique among aqueous metal ions. Dynamic Car-Parrinello simulations confirm that removal of one $\mathrm{H^+}$ from aqueous $\mathrm{Al(H_2O)_6^{3+}}$ is followed within 1 ps by loss of one water molecule to form $\mathrm{Al(H_2O)_4OH^{2+}}$. The implications for the geochemistry and toxicity of aqueous $\mathrm{Al^{3+}}$ will be briefly discussed [7].

OP03

"Group 13 Metal Complexes of the Boraamidinate Radical Anion" by T. Chivers (University of Calgary, Canada), C. Fedorchuk, D. J. Eisler, G. Schatte, H. M. Tuononen, and R. T. Boeré.

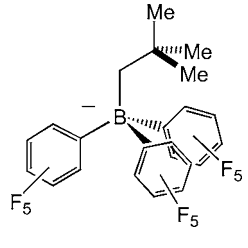
Abstract: Metal complexes of amidinate anions $\mathrm{[RC(NR')_2]^-}$ have been studied extensively in the context of novel structural chemistry or catalytic applications. By contrast, investigations of the coordination chemistry of the isoelectronic boraamidinate dianions $\mathrm{[RB(NR')_2]^{2-}}$ have been limited. The formation of anion radicals by a one-electron oxidation of these ligands was indicated by previous electron paramagnetic resonance (EPR) studies of Li derivatives [8a]. In this talk, the synthesis and X-ray structures of *stable* neutral spirocyclic radicals of the type $\mathrm{\{[PhB(\mu\text{-}N^tBu)_2]_2M\}\cdot}$ (M = Al, red; M = Ga, green) will be discussed [8b]. EPR spectra and density functional theory (DFT) calculations for these neutral radicals will also be described.



OP04

"Synthesis and Characterisation of the New Alkyl Borates $\mathrm{[RB(C_6F_5)_3]^-}$ ($\mathrm{R = CH_2Me}$, $\mathrm{CHMe_2}$ or $\mathrm{CH_2CMe_3}$): Utilisation of $\mathrm{[Me_3CCH_2B(C_6F_5)_3]^-}$ as a Weakly Coordinating Counterion During Zirconocene-Induced Catalysis of Propylene Polymerisation" by M. C. Baird (Queen's University, Canada) and N. Bavarian.

Abstract: Reactions of alkyl Li compounds RLi (R = Me, Et, *i*-Pr, neopentyl [Np]) with $\mathrm{B(C_6F_5)_3}$ result in the formation of the alkylborate salts $\mathrm{Li[RB(C_6F_5)_3]}$. Metathesis reactions of these with $\mathrm{Ph_3CCl}$ and chloride salts of $\mathrm{(Ph_3P)_2N^+}$, $\mathrm{PMePh_3^+}$, and $\mathrm{HNMe_2Ph^+}$ proceed with varying degrees of success, as shown by NMR spectroscopy and electrospray MS. In addition, the compounds $\mathrm{[PPN][EtB(C_6F_5)_3]}$ (PPN = bis(triphenylphosphoranylidene)ammonium), $\mathrm{[PMePh_3][NpB(C_6F_5)_3]}$, and $\mathrm{[HNMe_2Ph][NpB(C_6F_5)_3]}$ have been characterized crystallographically. All three anions assume the expected pseudotetrahedral structures with normal B-aryl bond lengths and R-B-aryl and aryl-B-aryl bond angles. The compound $\mathrm{[HNMe_2Ph][NpB(C_6F_5)_3]}$ reacts with $\mathrm{Cp_2ZrMe_2}$, $\mathrm{(indenyl)_2ZrMe_2}$ and $\mathrm{SBIZrMe_2}$ (SBI = *rac*-dimethylsilylbis(1-indenyl)) to give propylene polymerization catalysts that are significantly more active and give higher-MW polypropylene than do the catalysts obtained using $\mathrm{B(C_6F_5)_3}$. Thus the $\mathrm{[NpB(C_6F_5)_3]^-}$ anion is for steric reasons more weakly coordinating than is $\mathrm{[MeB(C_6F_5)_3]^-}$ [9].



OP05

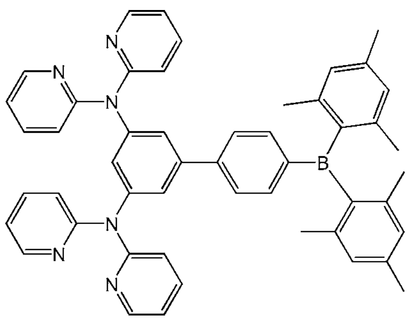
"Commercial Aspects of Boron Chemistry" by B. F. Spielvogel (BoroScience Canada Inc., Canada).

Abstract: BoroScience Canada Inc. is involved in the research, development, and commercialization of boron compounds. Areas of interest range from materials to biomedical applications. The company is developing methods for the large-scale production of ammonia-borane, H_3NBH_3 (AB). AB is a very attractive solid source material for hydrogen, containing 19.6 wt% with a volumetric energy density of about 4.96 kW/L, far surpassing the 2.36 kW/L for liquid hydrogen. At BoroScience Canada, we have a dual use for AB, thereby providing additional incentive for large-scale production. AB can also be used for the production of borazine and polyborazylene, materials that are attracting increased attention for potential application. The company is also involved in the synthesis of boron hydride cluster compounds for the electronics industry—for example, the use of boron hydride cluster compounds in ion implantation processes in the fabrication of semiconductor devices. Another area being developed is the application of boron analogs of important biomolecules such as amino acids, peptides, nucleic acids, etc. for potential use as pharmaceuticals and in biotechnology [10].

OP06

"Multi-Functional Three-Coordinate Organoboranes and Their Applications in OLEDs and Optical Sensors" by S. N. Wang (Queen's University, Canada), W. L. Jia, Y. Jessa, D. R. Bai, T. McCormick, M. Moran, S. Brown, Y. Y. Yuan, and Z. H. Lu.

Abstract: New three-coordinate compounds that contain a variety of functional groups has been achieved. The functional groups include chelate groups, luminescent chromophores, and hole transport groups. Their applications in organic light-emitting diodes (OLEDs) and optical sensors have been investigated. Depending on the nature of the functional groups, this class of molecules can act as electron transport materials and blue emitters or hole transport/hole injection materials in OLEDs. Highly efficient OLEDs based on these molecules have been fabricated. This class of molecules was found to be effective sensors for certain chlorinated aromatic molecules. Metal ion–functionalized three-coordinate boron compounds were found to display a high sensitivity in optical sensors, which is attributed to the extended structure of the coordination compounds. The details on syntheses, electronic structures, supramolecular assembly, and luminescent properties of the new three-coordinate boron compounds will be presented [11].



OP07

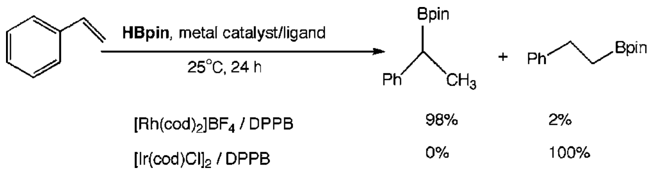
"The Bioorganometallic and Coordination Chemistry of Carboranes" by J. F. Valliant (McMaster University, Canada), O. O. Sogbein, A. S. King, R. Chankalal, and A. C. Green.

Abstract: Carboranes are versatile synthons that have been used in a wide variety of unique ligands, organometallic complexes, and medicinal compounds. Part of the attraction to carboranes is that they can be derived through both the cluster carbon and boron atoms with a variety of different functionalities. Our group has taken advantage of the versatility and the unique physical properties of carboranes to prepare novel organometallic-radiometal complexes and sterically hindered and robust pnictogen ligands. The former area involves utilizing functionalized carboranes as synthons for preparing organometallic radiopharmaceuticals based on ^{99m}Tc. A procedure for preparing Tc(I) (and Re[I]) carborane complexes in water under conditions that can be used to prepare radiopharmaceuticals containing sensitive targeting agents was developed. Prior to this work, the majority of metallocarboranes were prepared under anhydrous and highly basic reaction conditions. The second area in which we employed carboranes is in the preparation of sterically hindered phosphine and arsine ligands. Electron-rich hindered pnictogen ligands are routinely used to isolate unique coordination complexes and as co-ligands in Pd-catalyzed cross-coupling reactions. The use of such ligands is impaired by their rapid oxidation upon exposure to air and moisture. Using carboranes, a series of ligands that are both sterically hindered and resistant to oxidation was prepared. We have recently demonstrated that these ligands can be used to promote Suzuki cross-coupling reactions, including those involving aryl-chlorides and deactivated boronic acids. These new advances in the chemistry of carboranes, along with examples of their potential applications, will be presented [12].

OP08

"Asymmetric Hydroboration with Pinacol Borane: Deuterium Labelling and Mechanistic Studies" by C. M. Crudden (Queen's University, Canada), Y. B. Hleba, and D. Edwards.

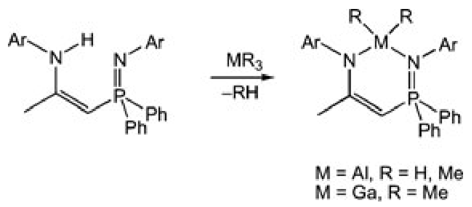
Abstract: Hydroboration of alkenes with pinacol borane is explored as a method to prepare enantiomerically pure 2-aryl propanoic acids. In addition, a CO-free hydroformylation reaction can be affected by a sequence of hydroboration/homologation. In an attempt to determine the dramatic switch in selectivity observed when changing catalysts from Rh to Ir, we have performed deuterium labelling and kinetic studies. These studies suggest that the difference in reactivity lies in the reversibility of the metal hydride insertion in the case of catalysis with iridium [13].



OP09

"Neutral and Cationic Group 13-Alkyl and Hydride Complexes" by D. W. Stephan (University of Windsor, Canada).

Abstract: Aluminum and Ga alkyl and hydride complexes of the phosphinimine-amine ligand (i-$\text{Pr}_2\text{C}_6\text{H}_3\text{N}$)C(Me)CHPPh$_2$($\text{NC}_6\text{H}_3$-$i$-$\text{Pr}_2$) and the *N*-imidoyl amidine ligand i-$\text{Pr}_2\text{C}_6\text{H}_3\text{N}$(C(Me)(NC6H3-$i$-$\text{Pr}_2$)$_2$ were prepared and characterized. The reactivity affording zwitterionic and cationic derivatives via reactions of these species with boranes are discussed. In addition, the kinetics of the deprotonation of the Al-alkyl, *N*-imidoyl amidine ligand to give the related amide–imine ligand complex were studied in detail. The results of these reactivity studies are presented and the implications considered [14].



OP10

"Chiral Borate Counter Anions: The Influence of Ion Pairing on Metal Catalysis" by B. A. Arndtsen (McGill University, Canada), D. B. Llewellyn, and D. Adamson.

Abstract: Weakly coordinating boron-based counterions have come to be of growing importance in the field of transition metal catalysis. The association of these anions to metal complexes provides a method to generate active catalysts that are relatively unhindered by anion coordination. However, there is a growing body of evidence that indicates even noncoordinating anions can modulate reactivity of metal catalysts through weak, ion-pairing interactions in solution. This talk will describe our studies on this phenomenon through the synthesis of new chiral borate counterions incorporating both the binapthol- and peptide-based chiral units on boron, and their use in metal catalysis. While structural studies suggest these boranions are associated to metal cations only through ion-pairing interactions in solution, their chirality is found to induce enantioselectivity in several Cu cation–catalyzed reactions. The generation of a library of peptide-based anions has been used to probe the influence of the borate counteranion structure on selectivity. The results of these studies, as well as insights into the ion-pairing contact between the anion and metal cation during catalysis, will be discussed [15].

OP11

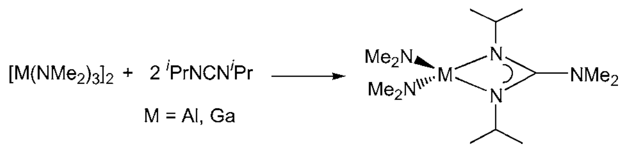
"Synthesis and Thermal Decomposition Studies of a Series of Indium-Phosphine Adducts" by G. G. Briand (Mount Allison University, Canada), R. J. Davidson and A. Decken.

Abstract: Trialkyl indium compounds have been of interest in recent years as reactants for the preparation of III-IV semiconductor materials. Although 1:1 adducts with tertiary phosphines have been studied as potential single source precursors to indium phosphide (InP), there have been no systematic studies examining the effect of substituent variation on the physical properties (e.g., volatility) of In-phosphine adducts. Reports on the high-yield preparation of a variety of homoleptic indium trisorganothiolates $(\text{RS})_3\text{In}$ support the fact that these compounds are ideal candidates for such studies. However, the vast majority of these materials have not been structurally characterized, because of the limited solubility in organic solvents and presumed polymeric structures. High melting points and low volatilities are also expected, although little data has been reported. The Lewis acidic nature of these materials allows the isolation of 1:1 and 1:2 adducts for the reaction with excess amine ligand. Furthermore, extensive studies into phosphine adducts of the In(III) halides have yielded similar complexes. The monomeric structure and relatively low melting point of these adducts suggest the potential for the preparation of volatile indium thiolate–phosphine complexes. In this context, we will present the facile synthesis of the series of 1:1 indium thiolate–phosphine adducts $(4\text{-RC}_6\text{H}_4\text{S})\text{In-PR}'_3$, which show low melting points and increased solubility compared to the corresponding indium thiolate reactants. The effect of the thiolate and phosphine substituents on the spectroscopic, structural, and thermal decomposition characteristics of these compounds will be discussed [16].

OP12

"Influence of Ligand Design on Volatility and Thermolysis: Tuning Aluminium and Gallium Chelate Compounds for Vapour Deposition Applications" by S. T. Barry (Carleton University, Canada), A. P. Kenney, and Z. D. Wang.

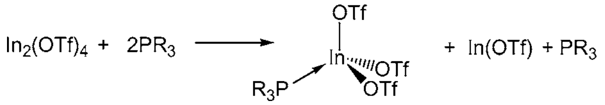
Abstract: Thin films of Group 13–containing oxides and nitrides continue to be important in vapor deposition methods like chemical vapor deposition (CVD) and atomic layer deposition (ALD). Guanidinate compounds of the Group 13 metals are extremely versatile with respect to modification, allowing optimization of key precursor characteristics like thermal robustness, volatility, and melting point. These characteristics are controlled through both the ligand's formulation and the coordination geometry of the metal center. General synthetic routes to guanidinates of the general formula $[\text{Me}_2\text{NC(N}^i\text{Pr)}_2]_x\text{Al(NMe}_2)_{3-x}$ ($x = 1, 2, 3$) will be discussed (including carbodiimide insertion and ligand exchange), as well as the control of melting point and volatility through ligand design. Thermal decomposition mechanisms will be presented, and the dangers of carbodiimide deinsertion will be discussed [17].



OP13

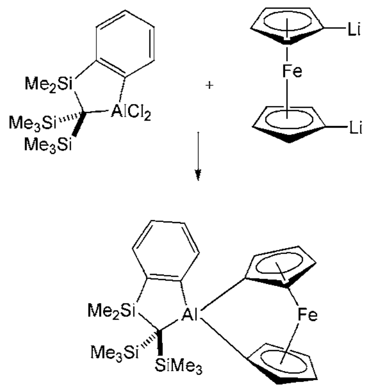
"The Surprising Reactivity of Low Oxidation State Group 13 Reagents" by C. L. B. Macdonald (University of Windsor, Canada).

Abstract: Our new discoveries concerning the chemistry of compounds containing the Group 13 elements in usually low oxidation states will be detailed. In particular, our synthesis of the unusually soluble salt In(I) trifluoromethanesulfonate has allowed us to begin to explore the chemistry of such species with much more control than was previously possible. For example, we have been able to study the unprecedented coordination chemistry of such reagents, the oxidation and reduction chemistry of these compounds, and the use of such reagents for the formation of organometallic derivatives. The structural features and reactivity of these and related compounds are explained using DFT calculations and the potential isolation of the lighter analogs of these reagents will be discussed [18].



OP14

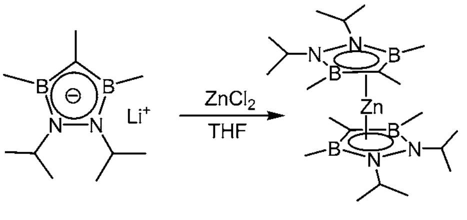
"[1]Ferrocenophanes with Bridging Heavier Group 13 Elements" by J. A. Schachner, C. L. Lund, J. Müller (University of Saskatchewan, Canada), and J. W. Quail.



Abstract: In 1975 Osborne and Whiteley described the first [1]ferrocenophane, a strained organometallic compound that contains Si in the bridging position [19a]. Three decades later, Manners et al. discovered that ring-opening polymerization of [1]silaferrocenophanes provides access to poly(ferrocenylsilanes) with high molecular weights [19b]. Today, [1]ferrocenophanes with different main-group elements in the bridging position are known; however, examples with heavier Group 13 elements were unknown until recently. Synthesis, characterization, and properties of the first [1]ferrocenophanes with heavier Group 13 elements in the bridging position will be presented and discussed [19c–e].

OP15

"Lithiocene and Zincocene Incorporating 1,2-Diaza-3,5-diborolidine, a Novel Cyclopentadienyl Analog" by H. V. Ly (University of Calgary, Canada), T. D. K. Forster, D. Maley, M. Parvez, and R. Roesler.



Abstract: Cyclopentadienyl (Cp) is one of the most important organic ligands in organometallic chemistry. Its metal complexes, the metallocenes, have found numerous applications in catalysis and the science of materials. The quest for tuning the electronic properties of Cp led to the isolation of numerous heterocyclic analogs obtained by the replacement of two ring carbons, C_2 with the isolobal pairs (B, N), (B, O), and (B, S). Phosphorus heterocycles incorporating up to three phosphorus atoms are also extremely versatile ligands that have enabled the stabilization of unusual coordination environments for many transition metals. To our knowledge, not more than three carbon atoms have been replaced to date by heteroatoms in heterocyclic analogs of Cp. In this report, we will discuss the synthesis of lithiocene and zincocene incorporating 1,2-diaza-3,5-diborolidine, a novel Cp analog where four ring carbons have been substituted with B and N. The lithium salt **1** displays a polymeric structure with μ,η^4,η^3 coordination of the cyclic ligand. The zinc complex **2** is the first symmetric zincocene and contains η^3 coordinating ligands. The compounds have been fully characterized by NMR, MS, and X-ray crystallography. The coordination chemistry of the ligand is being further investigated [20].

OP16

"New Univalent Indium(I) Salts: Convenient Reagents for Low Oxidation State Indium Chemistry" by C. G. Andrews (University of Windsor, Canada), C. L. B. Macdonald, and A. M. Corrente.

Abstract: Protonolysis of pentamethylcyclopentadienyl (Cp*) ligands by protic, nonoxidizing acids is a relatively new and versatile method for the preparation of new and otherwise inaccessible main group salts. This method allows for a varied selection of anions to complement the liberated cation, which can alter the properties and reactivities of the resulting salts. The protonolysis of Cp*In by triflic acid (HOTf) yields the unusually soluble In(I) salt InOTf. Protonolysis using various other acids such as HBF_4, methanesulfonic acid, $HB(C_6F_5)_4$, HCl in ether, benzoic acid and acetic acid have all been shown to successfully cleave the Cp* ring off the indium(I) center. The high solubility of InOTf in toluene allows for the in-depth investigation of many aspects of univalent indium chemistry that were previously inaccessible. Reaction with electron-deficient metallocenes has afforded the isolation of two unprecedented mixed-valent indium salts, $[CpIn_2][Cp_7In_2]$ and $In_3[In(OTf)_6]$. In addition, we are currently investigating the Lewis acidity and basicity of indium(I), its ability to form clusters and nanoparticles, and its potential for use in organic synthesis. It is anticipated that analogous salts of Ga(I) and possibly Al(I) may be accessible through the use of protonolysis of Cp*Ga and Cp*Al [18].

OP17

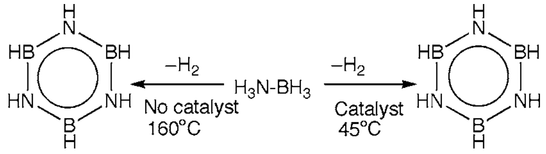
"Studies of Novel Metalloborane Complexes" by K. Kandiah (University of New Brunswick, Canada) and G. S. McGrady.

Abstract: Recently, a novel type of metalloborane has been prepared, in which condensation of two hydride–borohydride molecules produces a BH_6 moiety supported between two metal centers. For example, $[Fe(H_2O)_6](BF_4)_2$ with triphos [$Me(CH_2PPh_3)_3$: "P_3"] and an excess of $NaBH_4$ in THF–EtOH gives the known complex $[P_3Fe(H)_2$–$BH_4)]$ (**1**). However, if the reaction is allowed to stand for more than 15 days at room temperature, the novel cationic complex $[P_3Fe(\mu$ -$\eta^4{:}\eta^4$-$BH_6)FeP_3)]$ (**2**$^+$) is formed. This cation has been structurally and spectroscopically characterized, and the X-ray crystal structure of complex (**2**$^+$) reveals a central octahedral BH_6 moiety [21]. We intend to present the results of a single crystal neutron diffraction study of (**2**$^+$), along with details of our attempts to synthesize and characterize analogous complexes of Ni. We are also exploring whether the $B_3H_8^-$ ligand can display a similar chemistry to that revealed for BH_4^- in the conversion of (**1**) into (**2**$^+$) [21].

OP18

"Catalytic Dehydrocoupling of Amine–Borane Adducts: Synthesis, Mechanism and Applications" by C. A. Jaska (University of Calgary, Canada), T. J. Clark, and I. Manners.

Abstract: The use of metal-catalyzed routes in the formation of inorganic bonds is still relatively unexplored despite recent advances. Primary and secondary AB adducts ($RR'NH$–BH_3) have been found to undergo catalytic dehydrocoupling using a variety of transition metal precatalysts under mild conditions to afford either dimeric aminoboranes $[RR'NH–BH_2]_2$ or borazine derivatives $[RN–BH]_3$ [22]. Recent studies have suggested that the mechanism of dehydrocoupling involves the in situ formation of a heterogeneous catalyst from a homogeneous precatalyst. This is in contrast to the catalytic dehydrocoupling of the analogous phosphine–borane adduct systems, which involve a homogeneous mechanism [22]. In addition, the discovery of BH_3–THF as a selective poison of heterogeneously catalyzed reactions such as dehydrocoupling will also be presented.



OP19

"Competing Mechanisms in Aluminum Amidinate Synthesis and Reactivity" by A. L. Brazeau (Carleton University, Canada), Z. Wang, C. Rowley, and S. T. Barry.

Abstract: Aluminum amidinate compounds show promise as precursors for thin films' vapor deposition techniques. Ligand exchange is a useful synthetic approach to access intermediate five-coordinate geometries in Al compounds of the family $[RC(N^iPr)_2]_xAlR_{3-x}$ (where $x = 1 - 3$; $R = H$, Me, Et): an amidinate ligand is transferred to another species in exchange for a monodentate ligand (i.e., Cl, Me, H, NMe_2). The ability to exchange ligands and produce four- and five-coordinate Al complexes provides a synthetic route to these species in high yield. A comparison of carbodiimide insertion versus ligand exchange mechanisms will be discussed. Thermal reactivity related to these mechanisms, as well as other promising properties of Al amidinates as volatile precursors, will also be presented [17].

POSTER CONTRIBUTIONS

P01

"Synthesis and Transition Metal Complexes of a Rigid Lewis Acid/Lewis Base Hybrid Ligand" by D. J. H. Emslie (McMaster University, Canada) and J. M. Blackwell.

P02

"Sterically Demanding Ligands with Intramolecular Donor Capabilites. Organometallic Compounds of the Heavier Group 13 Elements" by C. L. Lund, J. Müller (University of Saskatchewan, Canada), and J. W. Quail.

P03

"The First [1]Ferrocenophanes Containing Heavier Group 13 Elements" by J. A. Schachner (University of Saskatchewan, Canada), C. L. Lund, J. W. Quail, and J. Müller.

P04

"The Synthesis and Characterisation of Poly(cyclodiborazane) Derivatives Incorporating Bis(alkylthio)maleonitrile Derivatives" by M. R. Pineau, D. M. Nelson, S. Backiel, B. Bajrami, C. Welch, A. D. Green, M. J. G. Lesley (Southern Connecticut State University, USA), A. D. Asandei, M. Zeller, and A. D. Hunter.

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