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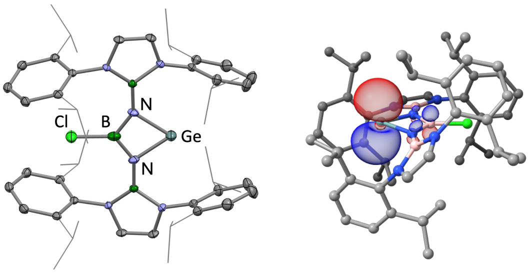
### 264. Synthesis of a diamido-germylene from an inorganic cumulene

**J. Tang, A. E. Crumpton, M. Dietz, S. Aldridge**

***Submitted***



The advent of boron-containing cumulenes as carbodiimide analogues allows for the one-pot synthesis of low-valent main-group species stabilized by a dianionic bis(borylamido) ligand chelate. We report here the synthesis of germylene complexes accessed via the reaction of $GeCl_2$·dioxane with K[$(HCDippN)_2$BNBNB$(NDippCH)_2$] (K[(boryl)NBN(boryl)], **1**). The four-membered N-heterocyclic germylene [ClB{(boryl)N}$_2$]Ge (**2-Cl**) so generated reacts further with $IMe_4$ to yield the Ge-bound adduct [ClB{(boryl)N}$_2$]Ge·$IMe_4$ (**3-Cl**). Reaction with trimethylsilyl azide ($Me_3SiN_3$) then affords the related azido-functionalized system [$(N_3)$B{(boryl)N}$_2$]Ge·$IMe_4$ (**3-N$_3$**). DFT and NBO analyses of **2-Cl** reveal a greater partial positive charge at Ge vs. B (+1.37 *vs.* +0.90 e); taken together with a LUMO which has predominant Ge $p_z$ character and the relative unimportance of Ge–N $\pi$ bonding (WBIs: Ge–N 0.44/0.46; B–N: 0.93, 0.94) these data rationalize the uptake of $IMe_4$ at germanium, rather than boron in a molecule offering two Lewis acidic centres (i.e. **3-Cl**/**3-N$_3$**).

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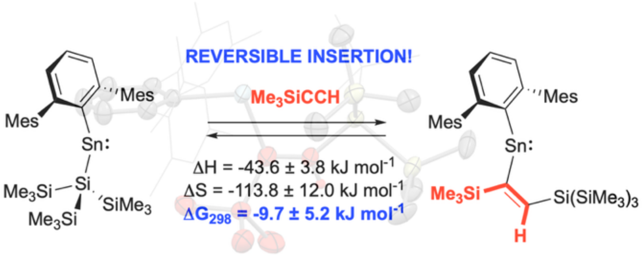
### 263. Reversible and irreversible regioselective alkyne insertion into a silyl-substituted stannylene

**A. J. Murray, L. L. Wales, A. E. Crumpton, M. Dietz, M. A. Ellwanger, A. Heilmann, J. J. C. Struijs, S. Aldridge**

***Submitted***



A range of aryl- and alkyl- substituted alkynes have been shown to insert regio-selectively into the Sn–Si bond of the electron-rich aryl(silyl)stannylene, $Ar^{Mes}SnSi(SiMe_3)_3$ ($Ar^{Mes}$ = 2,6-$Mes_2C_6H_3$, Mes = 2,4,6-$Me_3C_6H_2$) to generate a series of vinyl-stannylene products. In all cases, the product features a *syn* arrangement of Sn and Si-containing groups about the resulting carbon-carbon double bond; in the case of unsymmetrical alkynes, the more sterically bulky group is exclusively incorporated in the 1-position (i.e. proximal to Sn). Remarkably, insertion is shown to occur reversibly in the cases of 3-hexyne and trimethylsilylacetylene. The thermodynamic parameters associated with these processes have been determined by variable temperature NMR spectroscopy, and the activation barriers associated with the key mechanistic steps elucidated by quantum mechanical methods.

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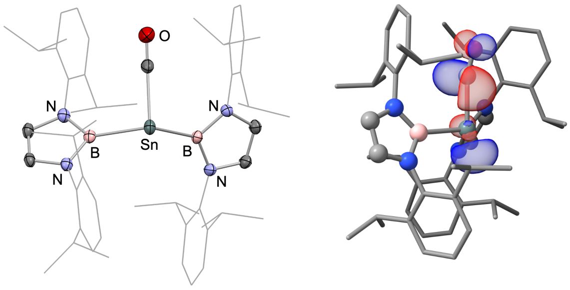
### 262. A crystalline main group metal carbonyl complex and its isomerization to a carbene-stabilized metal atom

**M. Dietz, A. V. Protchenko, A. E. Crumpton, S. Karwasara, M. M. D. Roy, J. Stewart-Moreno, C. Timmel, S. Aldridge**
***Science*, 2025, in press.**



We report an isolable, crystalline main group metal carbonyl complex and its isomerization to a species featuring a single metal atom stabilized by a single carbene ligand. In contrast to transition elements, *s*- and *p*-block metal compounds that coordinate CO at/close to ambient conditions are unknown. Here we show that a well-defined ('bottle-able') *p*-block metal complex can coordinate CO reversibly, to give an adduct which can be characterized by X-ray crystallography. (Boryl)$_2$Sn·CO (where Boryl = B(NDippCH)$_2$) rearranges at temperatures above 0 °C to generate the stannavinylidene, (Boryl)(OBoryl)C=Sn, *i.e.* a complex between the triplet carbene (Boryl)(OBoryl)C and 'naked' monatomic Sn(0) in its electronic ground state. A complex of this type, featuring the smallest fragment of an elemental metal supported by a single carbene donor, is unprecedented

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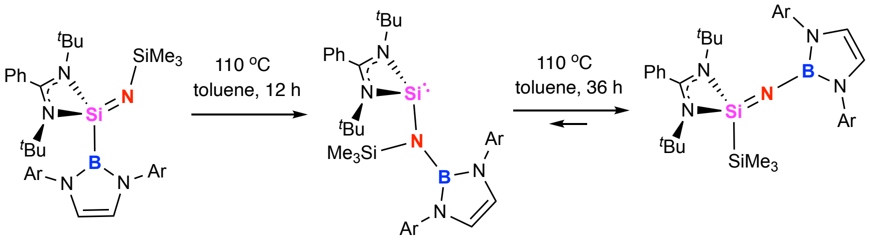
### 261. Isomerization and insertion chemistry of imidosilanes enabled by reversible Si(IV)/Si(II) redox shuttling

**J. Tang, Y. Wang, A. E. Crumpton, C. McManus, S. Aldridge**
***Angew. Chem. Int. Ed.*, 2025, in press (DOI: 10.1002/anie.202505872)**



Spontaneous redox shuttling at silicon is very rare, primarily reflecting the thermodynamic challenges associated with reduction processes for lighter *p*-block elements. Here we show that the reactions of boryl-substituted silylene {PhC($^t$BuN)$_2$}Si{B(NDippCH)$_2$} with an organo-azide proceed through a Si(IV)-Si(II)-Si(IV) series of redox processes involving both oxidative and reductive ligand migration steps. Each of the isomeric compounds related through this reaction manifold is isolable (and can be structurally characterized by X-ray crystallography), with the overall free energy profile being close to thermo-neutral. Broader studies within group 14 imply that this redox shuttling is unique to silicon, and that reductive ligand migration also plays a role in O-atom insertion chemistry.

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### 260. Main group–transition metal cooperativity

**J. Abbenseth, S. Aldridge**
***Z. Anorg. Allg. Chem.*, 2025, 651, e202500020 (invited guest editorial, DOI: 10.1002/zaac.202500020)**

Guest editorial for a special issue of *Z. Anorg. Allg. Chem.* focussing on d/p-block metal-metal cooperativity.

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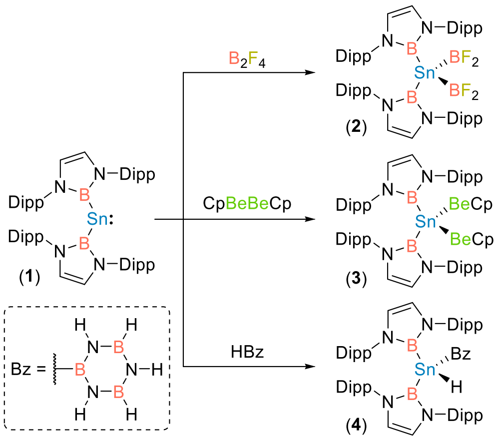
### 259. Breaking bonds at tin(II): reductive or oxidative addition?

**M. Dietz, J. T. Boronski, A. M. Swarbrook, S. Aldridge**

***Angew. Chem. Int. Ed.*, 2025, 64, e202503050 (DOI: 10.1002/anie.202503050)**



Here, the addition of H–H, Be–Be, B–B, and B–H bonds to $Sn^{II}$ is studied by experimental and theoretical means. We report the first examples of B–B and Be–Be bond additions to a main group element centre, along with the first example of borazine B–H bond addition to any element of the Periodic Table. Quantum chemical calculations suggest that the charge of the Sn centre may actually decrease in the formally ‘oxidative’ bond additions studied here, indicating that these reactions could be best described as ‘reductive’ processes.

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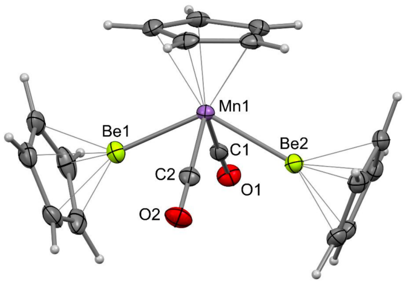
### 258. Methane beryllation catalysed by a base metal complex

**J. T. Boronski, A. E. Crumpton, J. J. C. Struijs, S. Aldridge**

***J. Am. Chem. Soc.*, 2025, 147, 10073–10077 (DOI: 10.1021/jacs.5c02179)**



The homogeneous catalytic functionalization of methane is extremely challenging due to the relative non-polarity and high C–H bond strength of this hydrocarbon. Here, using catalytic quantities (10 mol%) of $CpMn(CO)_3$ or $Cp^*Re(CO)_3$, the conversion of methane and benzene C–H bonds to C–Be and H–Be bonds by CpBeBeCp has been achieved under photochemical conditions. Possible intermediates in the beryllation reactions – trans-bis(beryllyl)-manganese and -rhenium complexes – were also isolated. Quantum chemical calculations indicate that the inherent properties of the beryllyl ligands – which are powerfully σ-donating and feature highly Lewis acidic beryllium centres – are decisive in enabling methane functionalization by these systems.

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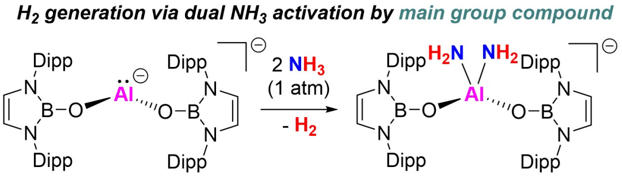
### 257. Dehydrogenative dual ammonia activation and transfer by an N-Heterocyclic boryloxy aluminyl compound

**D. Sarkar, P. Vasko, L. Ying, J. J. C. Struijs, L. P. Griffin, S. Aldridge**

***Angew. Chem. Int. Ed.*, 2025, 64, e202502326 (DOI: 10.1002/anie.202502326)**



The reactivity of an N-heterocyclic boryloxy (NHBO) ligated aluminyl compound has been harnessed for main-group-mediated dehydrogenative dual activation of ammonia. The Al(I) system K[{(HCDippN)$_2$BO}$_2$Al] reacts with excess $NH_3$ to give the Al(III) bis(amide) K[{(HCDippN)$_2$BO}$_2$Al(NH$_2$)$_2$] and in the process generates $H_2$. The initial stage of the reaction proceeds via formal N–H oxidative addition at Al(I) (via a coordination/proton shuttling sequence) to give an aluminium(III) primary amido hydride. Subsequent protonolysis of the strongly hydridic Al–H bond selectively yields the corresponding aluminium bis(amide) and $H_2$. This step occurs without competing protolytic ligand loss – exploiting the limited basicity of the supporting [(boryl)O]$^-$ donors. In terms of amide transfer reactivity, the utility of K[{(HCDippN)$_2$BO}$_2$Al(NH$_2$)$_2$] in delivering one or both equivalents of [NH$_2$]$^-$ to electrophilic substrates (HBpin, $CO_2$ and $Ph_2CO$) has been demonstrated.

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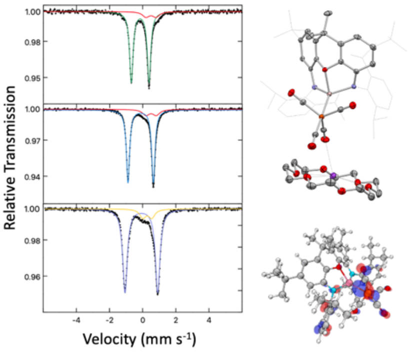
### 256. Synthesis, and structural and spectroscopic analysis of iron-trielyl complexes

**L. P. Griffin, A. K. Bauer, A. E. Crumpton, M. A. Ellwanger, A. Heilmann, A. Weisner, M. L. Neidig, S. Aldridge**

***Chem.-Eur. J.*, 2025, 31, e202404451 (DOI: 10.1002/chem.202404451)**



The reactivity of group 13 anions of the form [(NON)E]$^-$ (NON = 4,5-bis(2,6-diisopropylanilido)-2,7-di-*tert*-butyl-9,9-dimethyl-xanthene, E = Al, Ga, In) towards Fe(CO)$_5$ has been investigated. In the case of the aluminyl system, both reaction outcome and product structure are highly sensitive to the availability of the potassium counterion; sequestration by 18-crown-6 is necessary to yield a species featuring a direct, unsupported Al–Fe bond. 2.2.2-Cryptand, by contrast, yields a species featuring bridging carbonyl ligands, while the use of no sequestering agent at all leads to isocarbonyl bridging to aluminium. Owing to their lower oxophilicity, the heavier congeners gallium and indium more straightforwardly deliver Fe–E bonded adducts (E = Ga, In). The series of trielyl iron complexes has been interrogated by structural and computational analyses, as well as by IR and Mössbauer spectroscopies, revealing a consistent shift in bond polarity and electron richness at iron as group 13 is descended. This in turn is consistent with the diminishing donor strength of the trielyl ligand with increasing atomic number.

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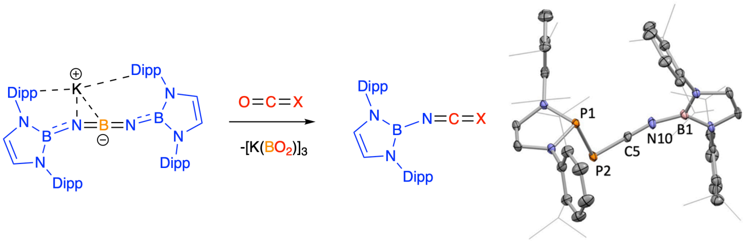
### 255. Metathesis chemistry of inorganic cumulenes driven by B–O bond formation

**J. Tang, C. Hu, A. E. Crumpton, D. Sarkar, L. P. Griffin, J. M. Goicoechea, S. Aldridge**

***Chem. Sci.*, 2025, 16, 2231-2237 (DOI: 10.1039/D4SC07487D)**



The reaction chemistry of an unprecedented ‘inorganic cumulene’ - featuring a five-atom BNBNB chain - towards C=O (and related) multiple bonds is disclosed. In marked contrast to related all-carbon systems, the intrinsic polarity of the BNBNB chain enables metathesis chemistry with electrophilic heteroallenes (such as $CO_2$) and with organic carbonyl compounds. Metathesis leads to $\{(HCDippN)_2\}BN$ transfer chemistry via consecutive [2+2] cyclo-addition/cyclo-reversion steps. Transfer of the imide unit to [CO], [CS], $[PP\{(NDippCH_2)_2\}]$ and [C(H)Ph] moieties generates (boryl)N=C=X systems (X = O, S, $PP\{(NDippCH_2)_2\}$, C(H)Ph), driven thermodynamically by B–O bond formation. An isolable complex of stoichiometry K[(boryl)NB(O)OC(H)Ph], formed via [2+2] cycloaddition to $[(boryl)N{=}B{=}O]^-$ can be shown to be an intermediate in the formation of (boryl)N=C(H)Ph, and provides corroborating evidence for a DFT-calculated mechanism proceeding via consecutive bora-Wittig steps.

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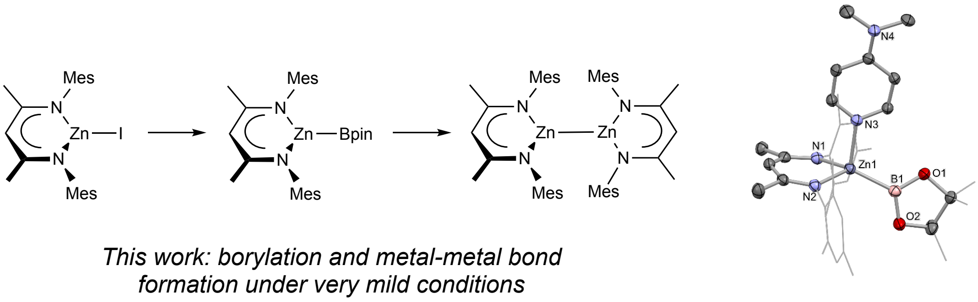
### 254. Zinc borylation and reduction by a diborane(4) species via B-O bond formation

**L. P. Griffin, S. Aldridge**

***Chem. Sci.*, 2024, 15, 19577-19582 (DOI: 10.1039/D4SC06389A)**



*This work: borylation and metal-metal bond formation under very mild conditions*

We report a convenient synthesis of the zinc-boryl complex $(Nacnac^{Mes})ZnBpin$ under mild conditions via formal disproportionation of bis(pinacolato)diboron(4), aided thermodynamically by B–O bond formation. This species can be isolated both base-free and as the DMAP adduct $(Nacnac^{Mes})Zn(DMAP)Bpin$ and crystallographically characterised in the latter form. Onward reactivity of the base free zinc boryl complex with $CO_2$ occurs reductively, yielding further B–O bonds as well as CO gas. The strength of this driving force can then be harnessed in the reaction between $(Nacnac^{Mes})ZnBpin$ and a Zn–O bonded species $(Nacnac^{Mes})ZnOB\{(NDippCH)_2\}$, which yields the metal-metal bonded dimer $[(Nacnac^{Mes})Zn]_2$, the overall formation of which utilizes a diboron(4) species as the stoichiometric reductant of Zn(II) to Zn(I).

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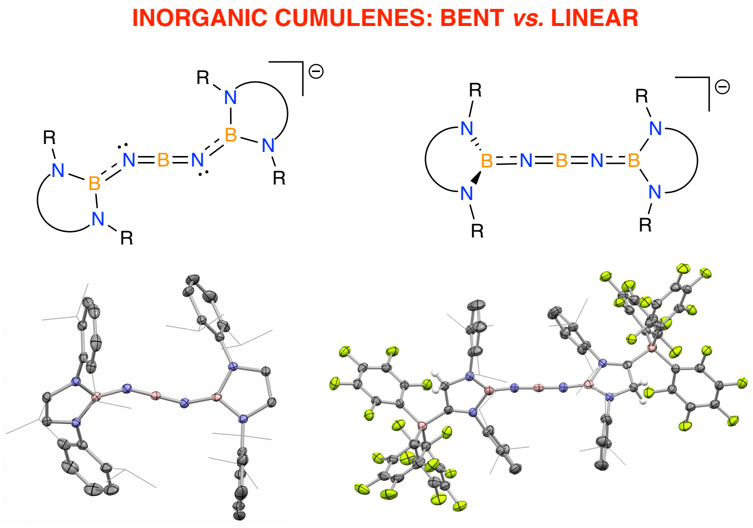
### 253. Syntheses, geometric and electronic structures of inorganic cumulenes

**J. Tang, C. Hu, A. E. Crumpton, D. Sarkar, L. P. Griffin, M. Dietz, J. M. Goicoechea, S. Aldridge**

***J. Am. Chem. Soc.*, 2024, 146, 30778-30783 (DOI: 10.1021/jacs.4c13231)**


INORGANIC CUMULENES: BENT *vs.* LINEAR

Molecular chains of 2-coordinate carbon atoms (cumulenes) have long been targeted, due to interest in the electronic structure and applications of extended π systems, and their relationship to the carbon allotrope, carbyne. While formal (isoelectronic) B=N for C=C substitution has been employed in 2-D materials for the modulation of opto-electronic properties, unsaturated one-dimensional 'all-inorganic' chains are unknown. Here, we report a high-yielding synthetic approach to a hetero-cumulene containing a five-atom BNBNB chain. Geometrically, this system is bent at the 2-/4-positions, as predicted for (hitherto unknown) isoelectronic NHC-terminated [4]cumulenes. Natural resonance theory calculations reveal significant contributions from four essentially equivalent B=N(:)–B≡N–B resonance forms featuring a lone pair at N (consistent with N-centred nucleophilicity). Molecular modification to generate a linear system described best by a B=N=B=N=B resonance structure can be accomplished by chemical transformation of the capping groups (using $B(C_5F_5)_3$) to enhance their π-acidity and conjugate the N-centred lone pairs.

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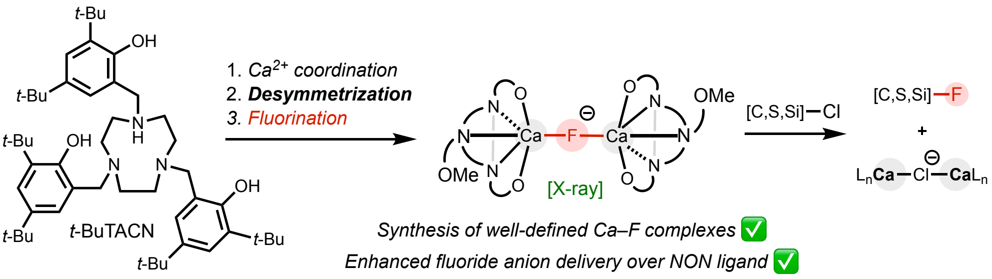
### 252. Nucleophilic fluoride anion delivery from triazacyclononane-supported molecular Ca–F complexes

**O Apolinar, J. J. C. Struijs, D. Sarkar, V. Gouverneur, S. Aldridge**

***Angew. Chem. Int. Ed.* 2024, 63, e202414790 (DOI: 10.1002/anie.202414790).**



*Synthesis of well-defined Ca–F complexes* ✅

*Enhanced fluoride anion delivery over NON ligand* ✅

Here we report the use of a multidentate bis(phenoxide) ligand based on a 1,4,7-triazacyclononane (TACN) scaffold for the formation of well-defined Ca–F complexes and demonstrate their capabilities in fluoride delivery. Key to this synthesis is a desymmetrization step carried out on the TACN ligand within the Ca coordination sphere. A series of stable anionic dinuclear calcium fluoride complexes has then been accessed and characterized by NMR spectroscopy (critically by $^{19}F$ NMR) and X-ray crystallography. Nucleophilic fluoride delivery can be used to generate C–F, Si–F and S–F bonds, with a notable advance over amide-derived ligand scaffolds being the reduced extent of side reactions derived from competing attack on the electrophile by the less nucleophilic O-donor anionic ligand set.

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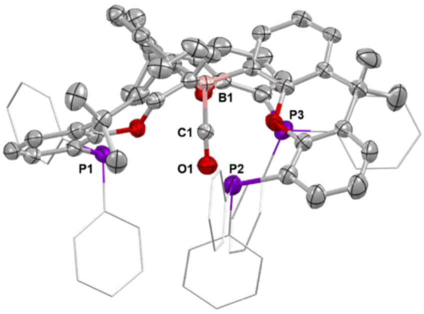
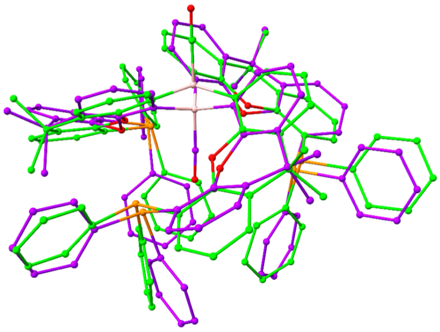
## 251. Leveraging non-covalent interactions for the binding of CO by a weakly Lewis acidic borane

**A. E. Crumpton, C. McManus, S. Aldridge**

***Angew. Chem. Int. Ed.*, 2025, 64, e202501774 (DOI: 10.1002/anie.202501774)**





Literature examples of boron carbonyl complexes exploit very high Lewis acidity, a low oxidation state boron centre and/or extensive ligand back-donation in order to capture and retain CO. By contrast, here we report a boron carbonyl complex featuring a very weakly Lewis acidic borane characterized by an acceptor number (13.6), which is only marginally higher than that reported for $B(NMe_2)_3$. Encapsulation of the CO guest within a cage-like binding pocket augments the donor-acceptor motif through non-covalent (primarily dispersion) interactions.

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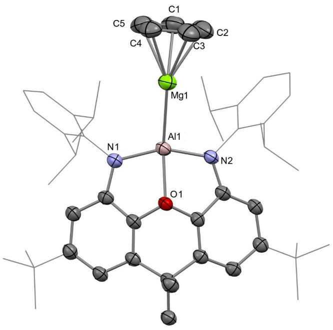
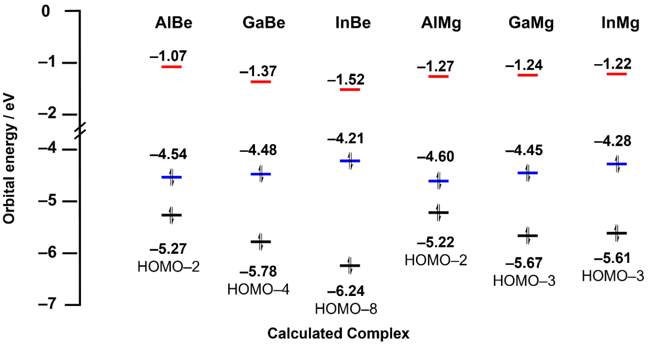
## 250. On the nature and limits of Alkaline Earth–Triel bonding

**J. T. Boronski, A. E. Crumpton, A. F. Roper, S. Aldridge**

***Chem. Sci.*, 2024, 15, 15377-15384 (DOI: 10.1039/D4SC03832K)**





The synthesis of a series of isostructural organometallic complexes featuring Ae–Tr bonds (Ae = Be, Mg; Tr = Al, Ga, In) has been investigated, and their electronic structures probed by quantum chemical calculations. This systematic study allows for comparison not only of the metal-metal bonding chemistries of the two lightest alkaline earth (Ae) elements, beryllium and magnesium, but also of the three triel (Tr) elements, aluminium, gallium, and indium. NBO and QTAIM analyses reveal (intuitively) that Be–Tr bonding is more covalent than Mg–Tr bonding; more strikingly, these calculations predict that the beryllium-indyl complex – featuring the first structurally characterised Be–In bond – should act as a source of nucleophilic beryllium. This has been confirmed experimentally by its reactivity towards methyl iodide, which yields the Be–Me functionality. By extension, the electrophilic character of the beryllium centre in the beryllium-gallyl complex contrasts with the umpoled, nucleophilic behaviour of the beryllium centre in both the -indyl and (previously communicated) -aluminyl complexes.

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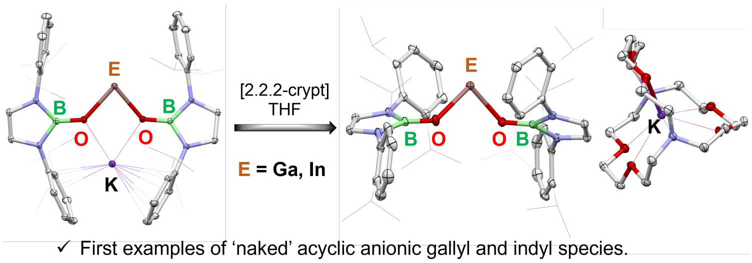
## 249. Synthesis, isolation, and reactivity studies of ‘naked’ acyclic gallyl and indyl anions

**D. Sarkar, P. Vasko, T. Gluharev, L. P. Griffin, C. Bogle, J. Struijs, J. Tang, A. F. Roper, A. E. Crumpton, S. Aldridge**
***Angew. Chem. Int. Ed.,* 2024, 63, e202407427 (DOI: [10.1002/anie.202407427](https://doi.org/10.1002/anie.202407427))**



✓ First examples of ‘naked’ acyclic anionic gallyl and indyl species.
✓ Demonstration of nucleophilicity through both metal and oxygen centres.

By exploiting the electronic capabilities of the N-heterocyclic boryloxy (NHBO) ligand, we have synthesized ‘naked’ acyclic gallyl $[Ga\{OB(NDippCH)_2\}_2]^-$ and indyl $[In\{OB(NDippCH)_2\}_2]^-$ anions (as their $[K(2.2.2\text{-crypt})]^+$ salts) through $K^+$ abstraction from $[KGa\{OB(NDippCH)_2\}_2]$ and $[KIn\{OB(NDippCH)_2\}_2]$ using 2.2.2-crypt. These systems represent the first O-ligated gallyl/indyl systems, are ultimately accessed from cyclopentadienyl $Ga^I/In^I$ precursors by substitution chemistry, and display nucleophilic reactivity which is strongly influenced by the presence (or otherwise) of the $K^+$ counterion.

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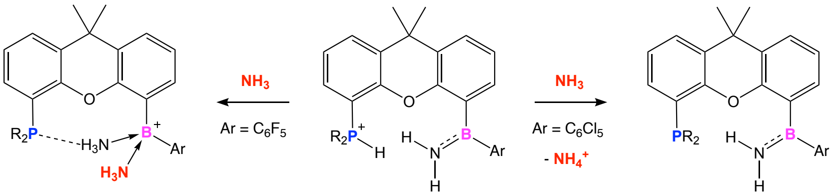
## 248. Modulating hydrogen shuttling in ammonia by neutral and cationic boron-containing Frustrated Lewis Pairs (FLPs)

**A. E. Crumpton, A. Heilmann, S. Aldridge**
***Angew. Chem. Int. Ed.,* 2024, 63, e202406440 (DOI: [10.1002/anie.202406440](https://doi.org/10.1002/anie.202406440))**

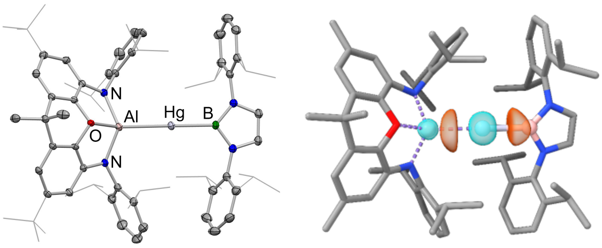


Xanthene-backbone FLPs featuring secondary borane functions $–B(Ar^X)H$ ($Ar^X = C_6F_5$ or $C_6Cl_5$) have been targeted through reactions of the dihydroboranes $Me_2S{\cdot}BAr^XH_2$ with $[4,5\text{-xanth}(PR_2)Li]_2$ (R = Ph, $^i$Pr), and investigated in the synthesis of related cationic systems via hydride abstraction. The reactivity of these systems with $NH_3$ have been probed, with a view to probing the potential for proton shuttling via N–H bond ‘activation.’ In the case of 4-coordinate boron systems (cationic or change neutral), the N–H linkage remains intact, supported by a NH···P hydrogen bond which is worth up to 17 kcal $mol^{-1}$ thermodynamically, and enabled by planarization of the flexible xanthene scaffold. For cationic 3-coordinate systems, N-to-P proton transfer is viable, driven by the ability of the boron centre to stabilise the $[NH_2]^-$ conjugate base through N-to-B $\pi$ bonding. This proton transfer can be shown to reversible in the presence of excess $NH_3$, depending on the nature of the B-bound $Ar^X$ group. It is viable in the case of $C_6F_5$ substituents, but is prevented by the more sterically encumbering and secondary donor-stabilising capabilities of the $C_6Cl_5$ substituent.

### 247. Mercury-group 13 metal covalent bonds: a systematic comparison of aluminyl, gallyl and indyl metallo-ligands

**L. P. Griffin, M. A. Ellwanger, A. E. Crumpton, M. M. D. Roy, A. Heilmann, S. Aldridge**

***Angew. Chem. Int. Ed.*, 2024, 63, e202404527 (DOI: 10.1002/anie.202404527)**



We present a systematic appraisal of group 13 metalloligands of the type $[(NON)E]^-$ (E = Al, Ga and In) through a comparison of structural and spectroscopic parameters associated with the *trans* L or X ligands in linear $d^{10}$ complexes of the types LM{E(NON)} and XM'{E(NON)}. These studies are facilitated by convenient syntheses (from the In(I) precursor, InCp) of the potassium indyl species $[\{K(NON)In\}\cdot KCp]_n$ (**1**) and $[(18\text{-crown-}6)_2K_2Cp]\,[(NON)In]$ (**1'**), and lead to the first structural characterisation of Ag–In and Hg–E (E = Al, In) covalent bonds. The resulting structural, spectroscopic and quantum chemical probes of Ag/Hg complexes are consistent with markedly stronger □-donor capabilities of the aluminyl ligand, $[(NON)Al]^-$, over its gallium and Indium counterparts.

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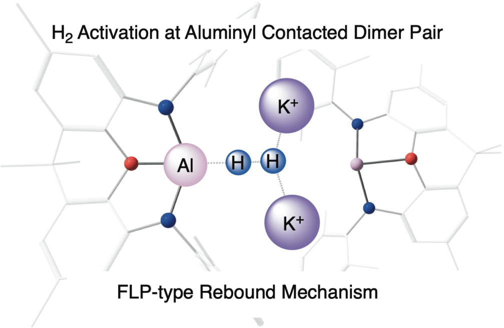
### 246. Hydride rebound: an FLP-type cooperative mechanism for $H_2$ activation by a potassium aluminyl compound

**K. M. Byrne, J. Hicks, L. P. Griffin, S. Aldridge, T. Krämer**

***Chem.-Eur. J.* 2025, 31, e202500095 (DOI: 10.1002/chem.202500095)**



Combining experiment and theory, the mechanisms of $H_2$ activation by the potassium-bridged aluminyl dimer $K_2[Al(NON)]_2$ (NON = 4,5-bis(2,6-diisopropylanilido)-2,7-di-tertbutyl-9,9-dimethylxanthene) and its monomeric $K^+$-sequestered counterpart have been investigated. These systems show diverging reactivity towards the activation of dihydrogen, with the dimeric species undergoing formal oxidative addition of $H_2$ at each Al centre under ambient conditions, and the monomer proving to be inert to dihydrogen addition. Noting that this $K^+$ dependence is inconsistent with classical models of single centre reactivity for carbene-like Al(I) species, these observations are rationalized by the action of a frustrated Lewis pair (FLP)-type mechanism in the dimer. The potassium ions play explicit roles in stabilizing a nascent $\mu_2$-bridging hydride, formed by heterolytic H–H bond cleavage (with accompanying protonation of the aluminium-centred lone pair). K-to-Al hydride "rebound" into the vacant aluminium-centred p-orbital then completes the net addition of $H_2$ via sequential $H^+/H^-$ transfer. The experimentally determined kinetic isotope effect ($k_H/k_D$ = 2.6) reflects a high degree of bond activation in the transition state (as predicted quantum chemically).

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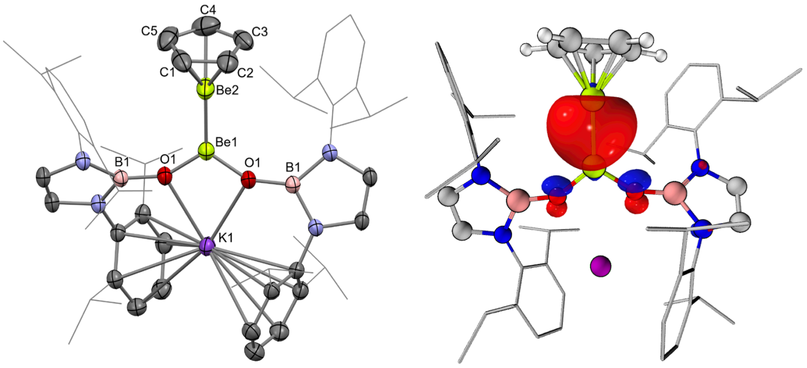
### 245. Metathesis at $[\mathrm{Be{-}Be}]^{2+}$: a route to nucleophilic beryllyl complex

**J. T. Boronski, A. E. Crumpton, A. F. Roper, S. Aldridge**

***Nature Chem.*, 2024, 16, 1295-1300 (DOI: 10.1038/s41557-024-01534-9)**



The ligand metathesis chemistry of diberyllocene (**1**; CpBeBeCp) – a stable complex with a Be–Be bond – has been investigated. These studies yield two new complexes with Be–Be bonds: Cp*BeBeCp (**2**) and $[\mathrm{K\{(HCDippN)_2BO\}_2}]$BeBeCp (**3**; Dipp = 2,6-diisopropylphenyl). Quantum chemical calculations reveal that the unsymmetrical coordination environment at the beryllium centres in **2** and **3** leads to a polarization of the Be–Be. The bond polarization in **3** is of sufficient magnitude that the complex is best considered a mixed-valence $\mathrm{Be^0/Be^{II}}$ complex. In support of this formulation, it is demonstrated that **3** can transfer the "beryllyl" anion, $[\mathrm{CpBe}]^-$, to an organic substrate, by analogy with the reactivity of $sp^2$-$sp^3$ diboranes

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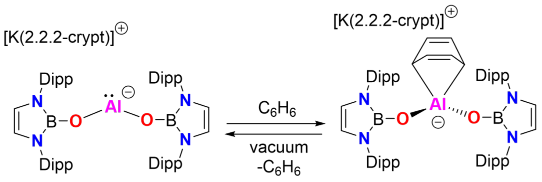
### 244. Reversible [4+1] cycloaddition of arenes via a 'naked' acyclic aluminyl compound

**D. Sarkar, P. Vasko, A. F. Roper, A. E. Crumpton, M. M. D. Roy, L. P. Griffin, C. Bogle, S. Aldridge**

***J. Am. Chem. Soc.*, 2024, 146, 11792–11800 (DOI: 10.1021/jacs.4c00376)**



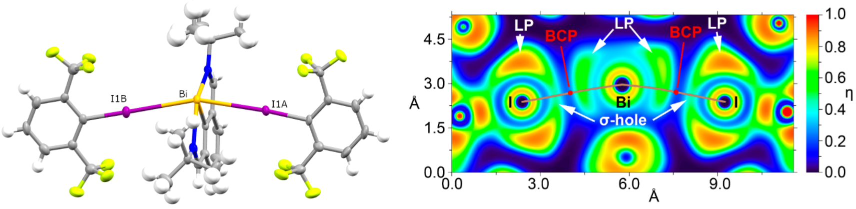
- ✓ First example of a 'naked' acyclic aluminyl complex.
- ✓ Reversible [4+1] cycloaddition of benzene at a single metal center.
- ✓ Counter-cation tuneable regioselectivity in polycyclic arene cycloaddition.

The large steric profile of the N-heterocyclic boryloxy ligand, $\mathrm{-OB(NDippCH)_2}$, and its ability to stabilise the metal-centred HOMO, are exploited in the synthesis of the first example of a 'naked' acyclic aluminyl complex, $[\mathrm{K(2.2.2\text{-}crypt)}][\mathrm{Al\{OB(NDippCH)_2\}_2}]$. This system, which is formed by substitution at $\mathrm{Al^I}$ (rather than reduction of $\mathrm{Al^{III}}$), represents the first O-ligated aluminyl compound, and is shown to be capable of hitherto unprecedented *reversible* single-site [4+1] cycloaddition of benzene. In addition, the regioselectivity of the related cycloaddition of polycyclic arenes can be shown to be tuneable by modulating the availability of the $\mathrm{K^+}$ counter-cation.

## 243. Evidence for Bi(I) as the heaviest halogen bond acceptor

**L. Griffin, T.-M. Streit, R. Sievers, S. Aldridge, R. M. Gomila, A. Frontera, M. Malischewski**

***J. Am. Chem. Soc.*, 2024, 146, 29877–29882 (DOI: 10.1021/jacs.4c11901).**



Reaction of a bismuthinidene (RBi) with two equivalents of a highly fluorinated aryl iodide at low temperature allows the crystallographic identification of an unstable species, RBi·2(IAr) that can be regarded as an intermediate of an oxidative addition reaction. Both C-I bonds are orientated towards the filled 6p orbital of bismuth (Bi-I distances 3.44 - 3.52 Å), leading to elongation the C-I distances. DFT calculations confirm that the bismuth center is acting as an electron donor, establishing two strong and directional halogen bonds. As such, this study presents the first structural proof of bismuth, (and more generally of heavy organo-pnictogen compounds in oxidation state +1), acting as halogen bond acceptors.

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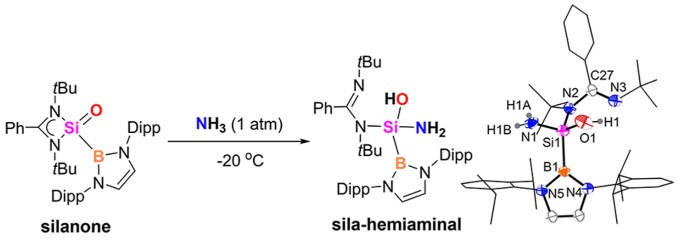
## 242. Boryl ancillary ligands: influencing stability and reactivity of amidinato-silanone and germanone systems in ammonia activation

**Y. Wang, A. E. Crumpton, M. A. Ellwanger, C. McManus, S. Aldridge**

***Angew. Chem. Int Ed.*, 2024, 63, e202402795 (DOI: 10.1002/anie.202402795)**



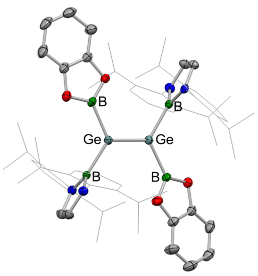
- ✓ Stable boryl-substituted amidinato-silanone and germanone
- ✓ Isolable sila-hemiaminal
- ✓ Unique $NH_3$ activation mechanism

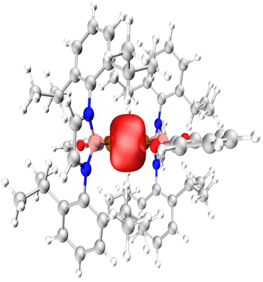
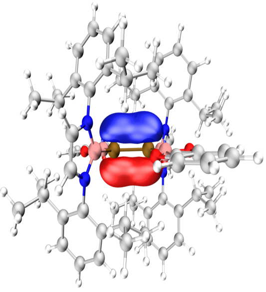
Here we present a room-temperature stable boryl-substituted amidinato-silanone (boryl){PhC(*t*BuN)$_2$}Si=O (**1**-Si, boryl = (HCDippN)$_2$B), formed from the corresponding silylene under a $N_2O$ atmosphere. **1**-Si reacts cleanly with $NH_3$ in 1,2-fashion to give the isolable sila-hemiaminal complex (boryl){PhC(*t*BuN)$_2$}Si(OH)(NH$_2$), **2**. Quantum chemical calculations show that the formation of **2** is crucially dependent on the nature of the ancillary ligand scaffold. It is facilitated thermodynamically by the hemi-lability of the amidinate ligand (which allows for the formation of an energetically critical intramolecular N···HO hydrogen bond within the product) and is enabled mechanistically by a process in which the silanone initially acts in umpolung fashion *as a base* (rather than an acid), due to the strongly electron-releasing and sterically bulky nature of the ancillary boryl ligand.

### 241. A planar per-borylated digermene

**X. Zheng, A. E. Crumpton, M. A. Ellwanger, S. Aldridge**

***Dalton Trans.*, 2023, 52, 16591-16595 (DOI: 10.1039/D3DT03416J)**



A tetraboryl digermene synthesized by the reaction between a dianionic digermanide nucleophile and a boron halide electrophile is dimeric both in the solid state and in hydrocarbon solution. It features both a planar 'alkene-like' geometry for the $Ge_2B_4$ core, and an exceptionally short Ge=Ge double bond. These structural features are consistent with the known electronic properties of the boryl group, and with lowest energy (*in silico)* fragmentation into two triplet bis(boryl)germylene fragments.

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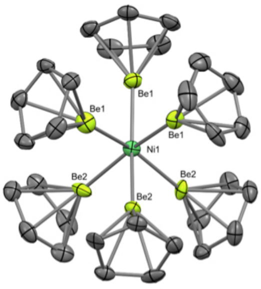
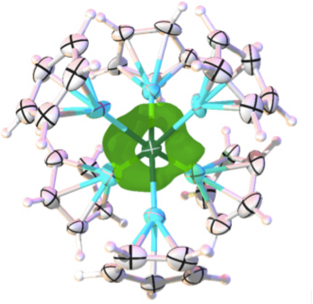
### 240. A Crystalliine $NiX_6$ Complex

**J. T. Boronski, A. E. Crumpton, S. Aldridge**

***J. Am. Chem. Soc.*, 2024, 146, 35208–35215 (DOI: 10.1021/jacs.4c12125)**





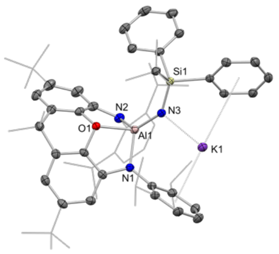
High-valent nickel species are implicated as intermediates in industrially relevant chemical transformations and in the catalytic cycles of metalloenzymes. Although a small number of tetravalent nickel complexes have been crystallographically characterized, higher valence states have not been identified. Here, a stable hexavalent nickel complex, $Ni(BeCp)_6$ (Cp = cyclopentadienyl anion), is reported, generated by the oxidative addition of three Be–Be bonds at nickel(0). This 16-electron species is diamagnetic and exhibits $C_{3v}$ symmetry, on account of the lifting of Ni 4p-orbital degeneracy in this molecular geometry. Single-crystal x-ray diffraction and quantum chemical calculations both reveal a toroidal band of electron density perpendicular to the $C_3$ axis of the complex, which may be attributed to delocalised, multi-center σ-aromatic $NiBe_6$ bonding.

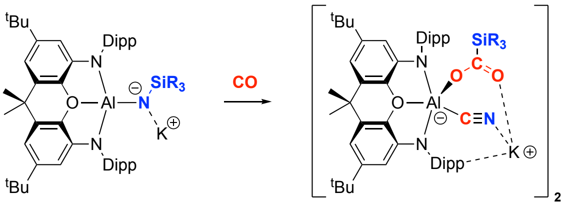
### 239. Aluminium and gallium silylimides as nitride sources

**A. Heilmann, A.M. Saddington, J.M. Goicoechea, S. Aldridge**

***Chem.-Eur. J.*, 2023, 29, e202302512 (DOI: 10.1002/chem.202302512)**

**Also available in preprint form at ChemRxiv (DOI: 10.26434/chemrxiv-2023-mc2jv)**





Terminal aluminium and gallium imides of the type K[(NON)M(NR)] bearing heteroatom substituents at R have been synthesised via reactions of anionic aluminium(I) and gallium(I) reagents with silyl and boryl azides. These systems vary significantly in their lability in solution: the N(Si$^i$Pr$_3$) and N(Boryl) complexes are very labile, on account of the high basicity at nitrogen. Phenylsilylimido derivatives provide greater stabilization through the $\pi$-acceptor capabilities of the SiR$_3$ group. K[(NON)AlN(Si$^t$BuPh$_2$)] offers a workable compromise between stability and solubility, and has been completely characterized by spectroscopic, analytical and crystallographic methods. The silylimide species examined feature minimal $\pi$-bonding between the imide ligand and aluminium/gallium, with the HOMO and HOMO-1 orbitals effectively comprising orthogonal lone pairs centred at N. Reactivity-wise, both aluminium and gallium silylimides can act as viable sources of nitride, $[N]^{3-}$, with systems derived from either metal reacting with CO to afford cyanide complexes. By contrast, only the gallium system K[(NON)Ga{N(SiPh$_3$)}] is capable of effecting a similar transformation with N$_2$O to yield azide, $N_3^-$, via formal oxide/nitride metathesis. The aluminium systems instead generate RN$_3$ via transfer of the imide fragment $[RN]^{2-}$.

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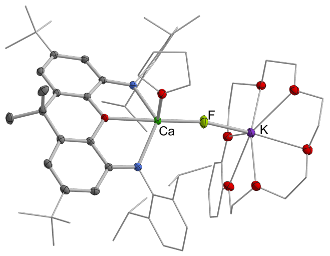
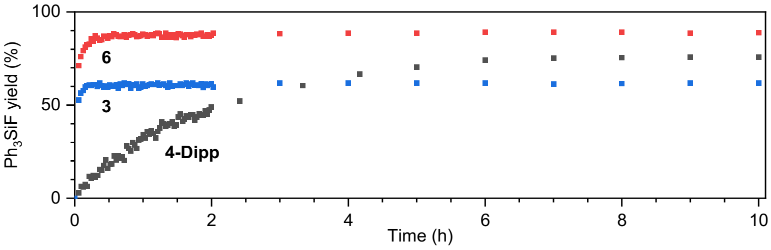
### 238. Enabling nucleophilic reactivity in molecular calcium fluoride complexes

**J. J. C. Struijs, M.A. Ellwanger, A.E. Crumpton, V. Gouverneur, S Aldridge**

***Nature Chem.*, 2024, 16, 1473-1480 (DOI: 10.1038/s41557-024-01524-x).**





Calcium fluoride is the ultimate source of all fluorochemicals. Current synthetic approaches rely on the use of HF, generated from naturally occurring fluorspar and sulfuric acid. Methods for constructing E–F bonds directly from CaF$_2$ have long been frustrated by its high lattice energy, low solubility, and impaired fluoride ion nucleophilicity. Little fundamental understanding of the reactivity of Ca–F moieties is available to guide methodology development; well-defined molecular species containing Ca–F bonds are extremely rare, and existing examples are strongly aggregated and evidence no nucleophilic fluoride delivery. By contrast, we show that by targeting anionic systems of the type $[L_n(X)_2CaF]^-$, monomeric calcium fluoride complexes containing single Ca–F bonds can be synthesized, including via routes involving fluoride abstraction from existing C–F bonds. Comparative structural and spectroscopic studies of mono- and dinuclear systems allow us to define structure-activity relationships for E–F bond formation from molecular calcium fluorides.

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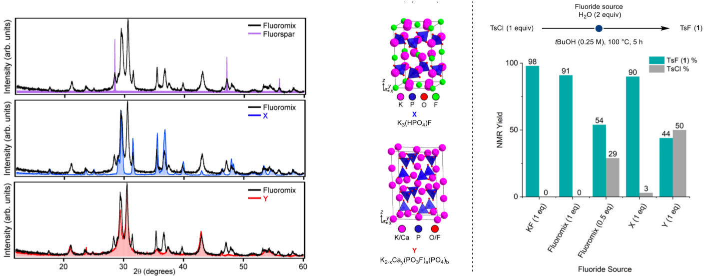
### 237. Fluorochemicals from fluorspar with a process bypassing the production of hydrogen fluoride

**C. Patel, E. André-Joyaux, J.A. Leitch, X. Martinez De Irujo-Labalde, F. Ibba, J. Struijs, M. Ellwanger, R. Paton, D.L. Browne, G. Pupo, S. Aldridge, M.A. Hayward, V. Gouverneur**

***Science*, 2023, 381, 302-306 (DOI: 10.1126/science.adi1557)**



All fluorochemicals are derived from hydrogen fluoride (HF), a highly toxic and corrosive gas produced by reacting acid grade fluorspar (> 97% $CaF_2$) with sulfuric acid under harsh reaction conditions. The use of fluorspar to produce fluorochemicals *via* a process by-passing HF is an unsolved problem due to the prohibitive insolubility of $CaF_2$. Inspired by calcium phosphate biomineralization, we herein disclose a solution consisting of treating acid grade fluorspar with $K_2HPO_4$ under mechanochemical conditions. The process affords new solid matter composed of crystalline $K_3(HPO_4)_F$ and $K_{2-x}Ca_y(PO_3F)_a(PO_4)_b$, found suitable for forging S–F and C–F bonds. This operationally simple protocol using activated fluorspar as a fluorinating reagent represents a paradigm shift in fluorination chemistry with the potential to change standard practices in academia and industry

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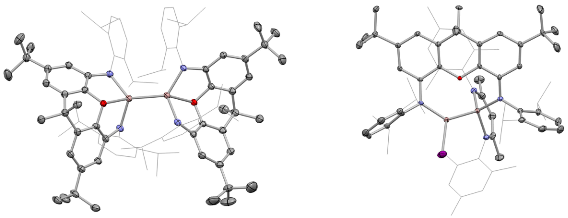
### 236. Ga-C and Ga-Ga bond formation using a NON-ligated gallyl nucleophile

**M. Edwards, J. Hicks, C. McManus, J.M. Goicoechea, S. Aldridge**

***Polyhedron*, 2023, 242, 116520 (DOI: 10.1016/j.poly.2023.116520; invited contribution for special issue on main group metal-metal bonds)**



**SYMMETRICAL AND UNSYMMETRICAL DIGALLANES(4)**

We report an improved synthesis of the NON-donor stabilized potassium gallyl dimer $[K\{Ga(NON)\}]_2$ (NON = 4,5-bis(2,6-diisopropylanilido)-2,7-di-*tert*-butyl-9,9-dimethyl-xanthene) from (NON)GaI and potassium naphthalenide that avoids issues associated with over-reduction of the metal centre. The use of $[K\{Ga(NON)\}]_2$ in the synthesis of Ga–E bonds has been explored through its reactions with a range of electrophiles. The reaction with (NON)GaI to give $\{Ga(NON)\}_2$ via Ga–Ga bond formation mirrors the behaviour of the corresponding aluminyl compound, while Ga–C bond formation via nucleophilic attack on *n*-bromopentane to give (NON)Ga(n-pentyl) avoids the retention of KBr often encountered in the formation of (more Lewis acidic) $Al^{III}$ compounds. Attempted formation of a Mg-Ga bond, e.g. via the reaction of $[K\{Ga(NON)\}]_2$ with $(Nacnac^{Mes})MgI(OEt_2)$, generates the unsymmetrical digallane(4), $(Nacnac^{Mes})Ga(\mu_2\text{-}N,N'\text{-}NON)GaI$, consistent with enhanced lability of Ga (over Al) within the NON-ligand scaffold.

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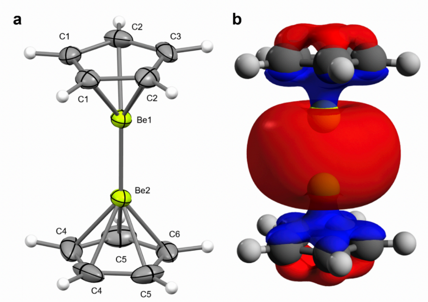
### 235. Diberyllocene: a stable compound of Be(I) with a Be-Be bond

**J.T. Boronski, A.E. Crumpton, L.L. Wales, S. Aldridge**

***Science*, 2023, 380, 1147-1149 (DOI: 10.1126/science.adh4419)**



The first example of a stable compound with a beryllium-beryllium bond – the lightest metal-metal bonding combination – is reported. This complex, diberyllocene (CpBeBeCp; Cp = cyclopentadienyl anion), has long been predicted to be stable, and has been the subject of numerous synthetic and quantum chemical investigations over the past five decades. Diberyllocene has finally been prepared by the reduction of beryllocene ($BeCp_2$) with a magnesium reductant and its structure in the solid state has been determined crystallographically. The reactivity of diberyllocene has been probed – the complex can act as a two-electron reductant and employed for the preparation of beryllium-metal bonds. Quantum chemical calculations indicate that there are parallels between the electronic structure of diberyllocene and the simple homodiatomic species diberyllium ($Be_2$).

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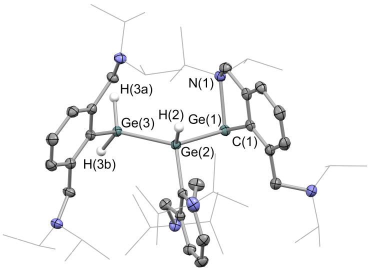
### 234. Redox flexibility in a germanium hydride manifold: hydrogen shuttling via oxidative addition and reductive elimination

**A. Caise, J. Hicks, A. Heilmann, S. Aldridge**

***Chem. Commun.*, 2023, 59, 7251-7254 (DOI: 10.1039/D3CC01411H)**



We report the synthesis of a trimetallic mixed-valence Ge(I)/Ge(II)/Ge(III) trihydride, the structure of which represents a novel motif among systems of the type $(XMH)_n$ (M = group 14 metal). $(Ar^{NiPr2})GeGe(Ar^{NiPr2})(H)Ge(Ar^{NiPr2})(H)_2$ can act as a source of both the Ge(II) and Ge(IV) hydrides $[(Ar^{NiPr2})GeH]$ and $[(Ar^{NiPr2})GeH_3]$ (in reactions with $CO_2$ and $[Ph_3C][B(C_6F_5)_4]$, respectively) via Ge–H reductive elimination from the central metal centre involving two possible regiochemistries.

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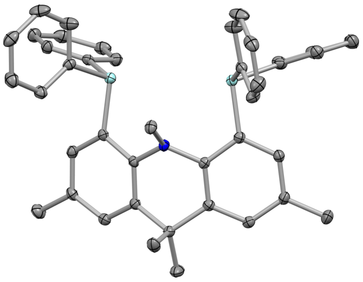
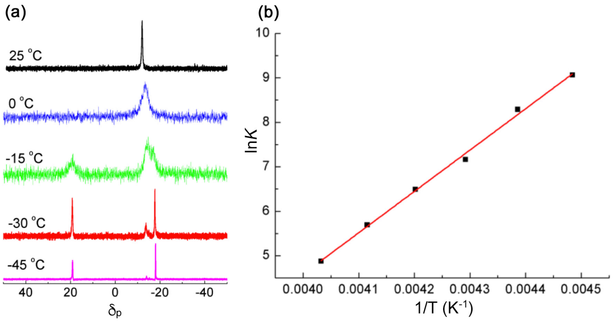
### 233. Torsional control of frustrated Lewis pair behaviour involving PNP-type phosphines

**Y. Guo, I. Zulkifly, J. Sodermann, A. V. Protchenko, E. Kolychev, M. Á. Fuentes, S. Aldridge**

***Z. Anorg. Allg. Chem.*, 2023, e202300016 (DOI: 10.1002/zaac.202300016; invited special issue for 70th birthday of Doug Stephan)**





A range of PNP-type phosphines featuring a pair of *ortho*-functionalized $ArPPh_2$ moieties linked via a central NMe unit has been synthesized. These comprise the acyclic system *bis*(2-diphenylphosphino-phenyl)methylamine, together with related systems centred around 5-, 6- and 7-membered heterocycles. Structurally, contraction of the backbone tether causes the phosphine centres to be projected further apart, and to be more constrained torsionally to the plane containing the NMe unit. In terms of potential frustrated Lewis pair (FLP) reactivity, conformationally more flexible systems based on an acyclic linker or a cyclic 7-membered core, are capable of achieving P–B bond formation and generating a classical Lewis adduct with $B(C_6F_5)_3$. The less flexible carbazole-derived compound (featuring a five membered heterocyclic core) gives rise to an FLP at room temperature, and an equilibrium mixture of frustrated and classical Lewis pairs at lower temperatures. Most interestingly, the PNP system based on a central six-membered acridine ring - which gives rise to the shortest contacts in the solid state between phosphorus and the N-bound methyl group - undergoes C–H activation in the presence of $B(C_6F_5)_3$, resulting in the formation of B–H and P–C bonds.

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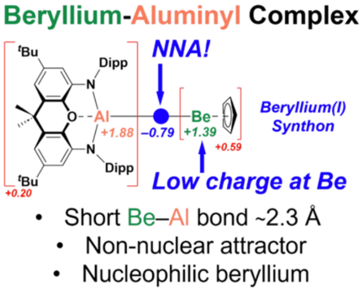
### 232. Inducing nucleophilic reactivity at beryllium with an aluminyl ligand

**J. T. Boronski, L. R. Thomas-Hargreaves, M. A. Ellwanger, A. E. Crumpton, J. Hicks, D. F. Bekis, M. R. Buchner, S. Aldridge**

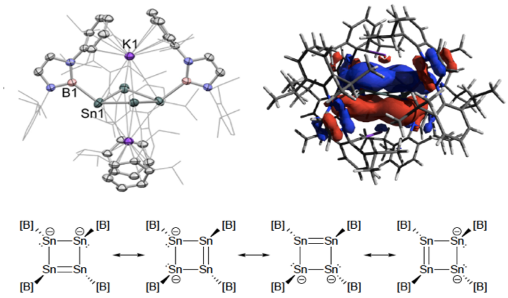
***J. Am. Chem. Soc.*, 2023, 145, 4408-4413 (DOI: 10.1021/jacs.3c00480)**



The reactions of anionic aluminium or gallium nucleophiles [K{E(NON)}]$_2$ (NON = 4,5-bis(2,6- diisopropylanilido)-2,7-di-tert-butyl-9,9-dimethylxanthene) with $BeCp_2$ lead to the formation of compounds containing Be–Al or Be–Ga bonds, (NON)EBeCp (E = Al or Ga, **4**). The Be–Al bond in the beryllium-aluminyl complex (2.310(4) Å) is much shorter than that found in the small number of previous examples (2.368(2) – 2.432(6) Å) and quantum chemical calculations suggest the existence of a non-nuclear attractor (NNA) for the Be–Al interaction. This represents the first example of a NNA for a heteroatomic interaction in an isolated molecular complex. As a result of this unusual electronic structure and the similarity in the Pauling electronegativities of beryllium and aluminium, the charge at beryllium center (+1.39) is calculated to be less positive than that of the aluminium centre (+1.88). This calculated charge distribution suggests the possibility for nucleophilic behaviour at beryllium and correlates with the observed reactivity of the beryllium-aluminyl complex with *N,N'*-diisopropylcarbodiimide – the electrophilic carbon center of the carbodiimide undergoes nucleophilic attack by beryllium, yielding a beryllium-diaminocarbene complex.

### 231. Synthesis of homo-metallic heavier analogues of cyclobutene and the cyclobutadiene dianion

**X. Zheng, A. E. Crumpton, A. V. Protchenko, M. Ellwanger, A. Heilmann, S. Aldridge**
***Chem.-Eur. J.*, 2023, 29, e202300006 (DOI: 10.1002/chem.202300006)**
**Also available in preprint form at ChemRxiv (DOI: 10.26434/chemrxiv-2022-4nqlv)**



The reduction of the boryl-substituted $Sn^{II}$ bromide $\{(HCDippN)_2B\}Sn(IPrMe)Br$ with 1.5 equivalents of potassium graphite leads to the generation of the cyclic tetratin tetraboryl system $K_2[Sn_4\{B(NDippCH)_2\}_4]$, a homo-metallic heavier analogue of the cyclobutadiene dianion. This system is non-aromatic as determined by Nucleus Independent Chemical Shift Calculations (NICS(0) = −0.28, NICS(1) = −3.17), with the primary contributing resonance structures shown by Natural Resonance Theory (NRT) to involve a Sn=Sn double bond and 1,2-localized negative charges. Abstraction of the $K^+$ cations or oxidation lead to contraction or cleavage of the $Sn_4$ unit, respectively, while protonation generates the neutral dihydride *cis*-1,2-$Sn_4\{B(NDippCH)_2\}_4H_2$ (a heavier homologue of cyclobutene) in a manner consistent with the predicted charge distribution in the $[Sn_4\{B(NDippCH)_2\}_4]^{2-}$ dianion.

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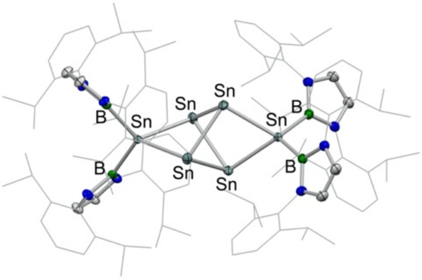
### 230. Disproportionation and ligand lability in low oxidation state boryl-tin chemistry

**X. Zheng, A. E. Crumpton, A. V. Protchenko, A. Heilmann, M. Ellwanger, S. Aldridge**
***Chem.-Eur. J.*, 2023, 29, e202203395 (DOI: 10.1002/chem.202203395)**
**Also available in preprint form at ChemRxiv (DOI: 10.26434/chemrxiv-2022-zk61r)**



Boryltin compounds in the +1 or 0 oxidation states can be synthesized from NHC-stabilized tin(II) bromide (boryl)Sn(NHC)Br by the use of strong reducing agents. The formation of (boryl)SnSn(IPrMe)(boryl) (**2**) and $K_2[Sn_2(boryl)_2]$, (**3**) using Mg(I) and K reducing agents mirrors related germanium chemistry. Carbene abstraction from **2** using $BPh_3$, and two-electron oxidation of **3** both result in the formation of a 2:1 mixture of the Sn(II) compound $Sn(boryl)_2$, and the hexatin cluster, $Sn_6(boryl)_4$ (**4**). A viable mechanism for this rearrangement is shown by quantum chemical studies to involve a vinylidene intermediate which undergoes facile atom transfer to generate $Sn(boryl)_2$ and trinuclear $[Sn_3(boryl)_2]$. The latter then dimerizes to give the observed hexametallic product **4**, with independent studies also showing that similar trigermanium species aggregate in analogous fashion.

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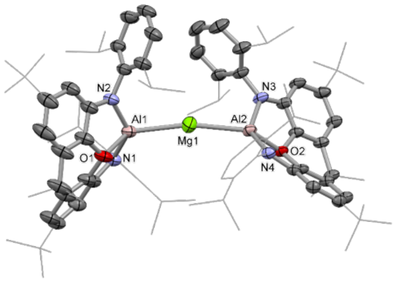
### 229. Bis(aluminyl)magnesium: a source of nucleophilic or radical aluminium-centred reactivity

**L. P. Griffin, M. Ellwanger, J. Clarke, A. F. Roper, A. Heilmann, S. Aldridge**

***Angew. Chem. Int. Ed.* 2024, 63, e202405053 (DOI: 10.1002/anie.202405053)**
**Also available in preprint form at ChemRxiv (DOI: 10.26434/chemrxiv-2022-s63x6)**



The homoleptic magnesium bis(aluminyl) compound Mg[Al(NON)]$_2$ (NON = 4,5-bis(2,6-diisopropylanilido)-2,7-di-tert-butyl-9,9-dimethylxanthene) can be accessed from K$_2$[Al(NON)]$_2$ and MgI$_2$ and shown to possess a non-linear geometry (∠Al–Mg–Al = 164.8(1)°) primarily due to the influence of dispersion interactions. This compound acts a four-electron reservoir in the reductive defluorination of SF$_6$, and reacts thermally with polar substrates such as MeI via nucleophilic attack through aluminium, consistent with the QT-AIM charges calculated for the metal centres and a *formal* description as a Al(I)–Mg(II)–Al(I) trimetallic. Under photolytic activation, the reaction with 1,5-cyclo-octadiene leads to the stereoselective generation of transannular cycloaddition products consistent with radical chemistry, emphasizing the covalent nature of the Mg–Al bonds and a description as a Al(II)–Mg(0)–Al(II) synthon.

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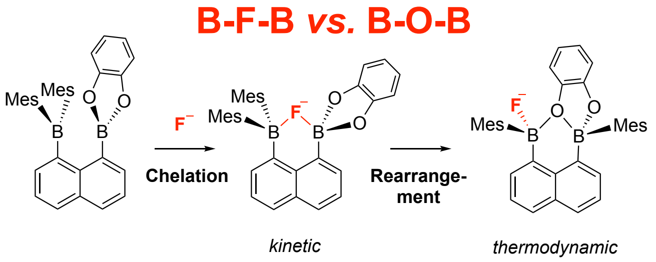
### 228. Boronic ester functionalised 1,8-diboryl-naphthalene scaffolds: fluoride *versus* oxide chelation

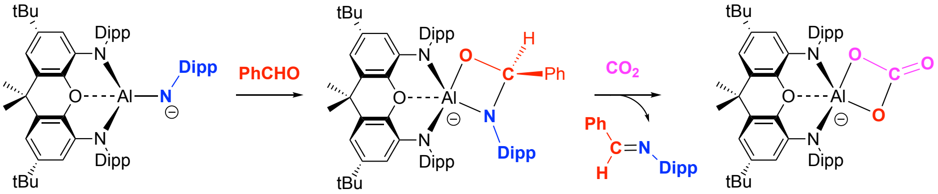
**A. C. Booth, P. Vasko, M. Á. Fuentes, B. Cornelissen, S. Faulkner, S. Aldridge**

***Dalton Trans.*, 2022, 51, 15783-15791 (DOI: 10.1039/D2DT02888C)**



1,8-bis(boronic ester) derivatives of naphthalene present an attractive target as receptors for the fluoride ion via B–F–B chelation, but are synthetically challenging to access due to the competing formation of a very stable anhydride containing a B–O–B motif. Unsymmetrical systems of the type 1,8-$C_{10}H_6${B(OR)$_2$}(BR'$_2$) can be synthesized for the first time for (OR)$_2$ = 1,2-$O_2C_6H_4$ (*i.e.* Cat) and R' = Mes. This system is shown to be competent for the uptake of F$^-$, making use of a chelating mode of action and the formation of a bridging B–F–B motif between the two boron centres. However, both experimental and quantum chemical studies indicate that the $\mu_2$-F adduct is the kinetic product of fluoride uptake, with an alternative structural motif featuring a terminal B–F bond and a B–O–B bridge using one of the catechol oxygens being (marginally) more favourable thermodynamically.

**227. A terminal aluminium imide as a transfer agent for the $[NR]^{2-}$ function via metathesis chemistry**
**A. Heilmann, P. Vasko, J. Hicks, J. M. Goicoechea, S. Aldridge**
***Chem.-Eur. J.,* 2023, 29, e202300018 (DOI: [10.1002/chem.202300018](https://doi.org/10.1002/chem.202300018))**
**Also available in preprint form at ChemRxiv (DOI: [10.26434/chemrxiv-2022-q2zxh](https://doi.org/10.26434/chemrxiv-2022-q2zxh))**



The reactions of a terminal aluminium imide with a range of oxygen-containing substrates have been probed with a view to developing its use as a transfer agent for the $[NR]^{2-}$ fragment. We demonstrate transfer of the imide moiety to $[N_2]$, [CO] and [Ph(H)C] units driven thermodynamically by Al-O bond formation. $N_2O$ reacts rapidly to generate the organoazide $DippN_3$, while $CO_2$ (under dilute reaction conditions) yields the isocyanate, DippNCO. Mechanistic studies identify a carbamate complex $K_2[(NON)Al\{\kappa^2\text{-}(N,O)\text{-}N(Dipp)CO_2\}]_2$ (formed via [2+2] cycloaddition) as an intermediate in the formation of DippNCO. In the case of benzaldehyde, a [2+2] cycloaddition process generates a metallacyclic hemiaminal complex, $K_n[(NON)Al\{(N(Dipp)C(Ph)(H)O\}]_n$. Extrusion of the imine, PhC(H)NDipp via cyclo-reversion is disfavoured thermally. However, addition of $CO_2$ allows the imine to be released, driven by the formation of the thermodynamically more stable aluminium carbonate co-product, $K_2[(NON)Al(CO_3)]_2$.

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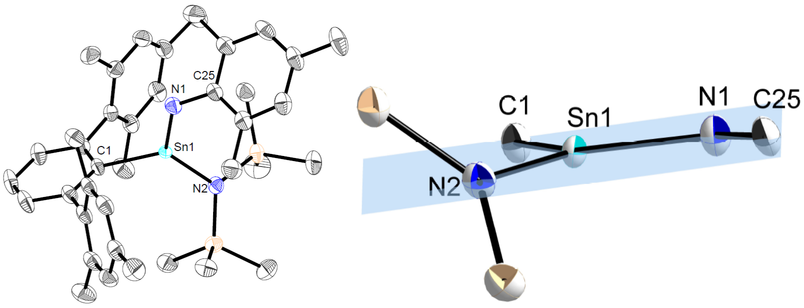
**226. Taming heavier group 14 imine analogues: accessing Sn=N double bonds and their cycloaddition/metathesis chemistry**
**M. Fischer, M. M. D. Roy, L. L. Wales, A. F. Roper, M. A. Ellwanger, C. McManus, A. Heilmann, S. Aldridge**
***Angew. Chem. Int. Ed.*, 2022, 61, e202211616 (DOI: [10.1002/anie.202211616](https://doi.org/10.1002/anie.202211616)).**

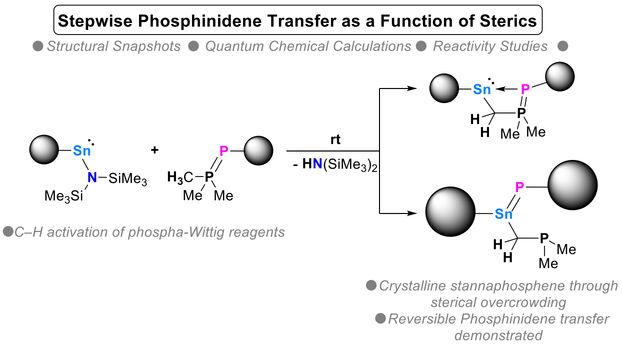


A systematic study of stable stannaimines has been carried out by combining a range of heteroleptic stannylenes with organoazides. Mixed terphenyl-/hypersilyl-substituted stannylenes give access to the putative tin nitrogen double bonds, but formation is directly followed by 1,2-silyl migration to give stannylenes featuring bulky amido ligands. By contrast, the use of a mixed σ-donor/π-donor ligand set proved successful for the isolation of three new stannaimines which can be handled at room temperature. Stannaimines with mesityl substitution at the nitrogen atom are shown to be capable of activating a broad range of substrates under ambient conditions leading to 1,2-addition reactions, [2+2] and [4+2] cycloaddition reactions and rare examples of main group multiple bond metathesis chemistry.

## 225. Structural snapshots in reversible phosphinidene transfer: synthetic, structural and reaction chemistry of a Sn=P double bond

**M. Fischer, M.M.D. Roy, L.L. Wales, M.A. Ellwanger, A. Heilmann, S. Aldridge**

***J. Am. Chem. Soc.*, 2022, 144, 8908-8913 (DOI: 10.1021/jacs.2c03302)**



The reaction of amido-substituted stannylenes with phospha-Wittig reagents ($R_3PPR$) results in release of $HN(SiMe_3)_2$ and tethering of the resulting -$CH_2PMe_2PR$ fragment to the tin centre to give P-donor stabilised stannylenes featuring four-membered *Sn*,*C*,*P*,*P* heterocycles. Through systematic increase in steric loading, the structures of these systems in the solid state can be tuned, leading to successive P-P bond lengthening and Sn-P contraction, and in the most encumbered case, to complete P-to-Sn transfer of the phosphinidene fragment. The resulting stannaphosphene features a polar Sn=P double bond as determined by structural and computational studies. The reversibility of phosphinidene transfer can be established by solution phase measurements and reactivity studies.

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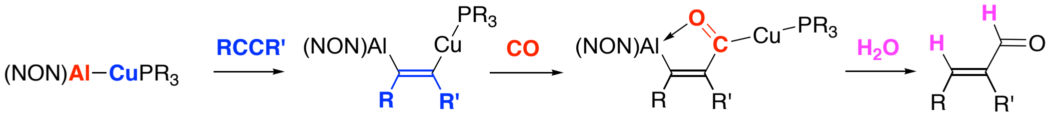
## 224. Alkyne insertion into Cu-Al bonds and selective functionalisation to form copper acyl compounds

**C. McManus, A. E. Crumpton, S. Aldridge**

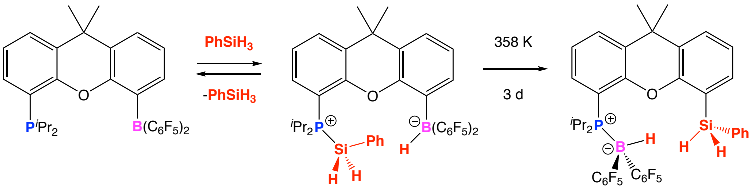
***Chem Commun.*, 2022, 58, 8274-8277 (DOI: 10.1039/D2CC02578G)**

**Also available in preprint form at ChemRxiv (DOI: 10.26434/chemrxiv-2022-90lb7)**



We report on the insertion of alkynes into heterometallic M–M' bonds, producing (aluminylalkenyl)copper compounds which possess differential reactivity at the two derived M–C functions. Uniquely, this system is capable of controlling access to isolable *syn* or *anti* dimetallated alkenes, by employing either kinetic or thermo-dynamic control. Variation of reaction time also allows regiocontrol to be exerted over the insertion of unsymmetrical alkynes. Subsequent derivatization with CO is both stereoselective (to *syn* systems) and regioselective (to Cu–C bonds), leading to the formation of the first structurally characterized examples of copper acyl compounds - aided by the cooperative reactivity of the proximal aluminium centre.

**223. Reactions of a dimethylxanthene-derived frustrated Lewis pair with silanes and stannanes**
**I. Zulkifly, A.V. Protchenko, M.Á. Fuentes, J. Hicks, S. Aldridge**
***Z. Anorg. Allg. Chem.*, 2022, 648, e202200110 (DOI: 10.1002/zaac.202200110; invited special issue for 60th birthday of Prof. C. Jones)**



The reactivity towards Si–H and Sn–H bonds of a dimethylxanthene-based frustrated Lewis pair featuring -$P^iPr_2$ and -$B(C_6F_5)_2$ functions is reported. In the case of $PhSiH_3$, the silylphosphonium borohydride $\mathbf{1}^{iPr}(SiH_2Ph)(H)$ is formed by Si–H bond activation across the P/B manifold. On heating, it undergoes a metathesis process leading to installation of the –$SiH_2Ph$ function at the 5-position of the xanthene scaffold, with accompanying migration of the boryl group (as Piers' borane, $HB(C_6F_5)_2$) to the phosphine. Similar chemistry is observed with $SiH_4$ (although occurring much more readily), and such processes are thought to be mechanistically similar to related rearrangements occurring with the boranes HBpin and HBcat. By contrast, the activation of the weaker Sn–H bonds found in stannanes occurs more readily, even for bulkier substrates, and the stannyl-phosphonium borohydrides $\mathbf{1}^{iPr}(Sn^nBu_3)(H)$ and $\mathbf{1}^{iPr}(SnPh_3)(H)$ are obtained from the room temperature reactions with $^nBu_3SnH$ and $Ph_3SnH$, respectively.

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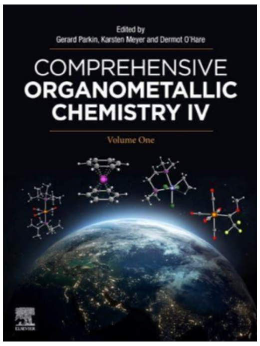
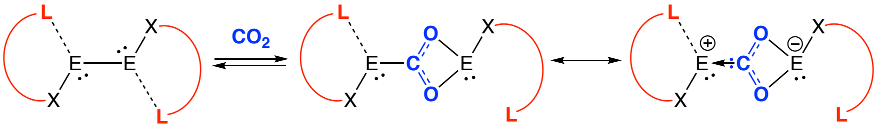
**222. Main Group Compounds: Introduction**
**S. Aldridge**
***Comprehensive Organometallic Chemistry IV*, Elsevier, 2022 (DOI: 10.1016/B978-0-12-820206-7.00175-X)**
(book chapter as volume editor)



### 221. Reversible uptake of $CO_2$ by pincer ligand supported dimetallynes

**A. Caise, L.P. Griffin, C. McManus, A. Heilmann, S. Aldridge**

***Angew. Chem. Int. Ed.*, 2022, 61, e202117496 (DOI: 10.1002/anie.202117496)**



We report on the reversible uptake of carbon dioxide by dimetallynes featuring ancillary hemi-labile pincer ligands. Insertion into the Ge–Ge/Sn–Sn bonds yields species containing an E($CO_2$)E unit, with the mode of ligation of the $CO_2$ fragment determined crystallographically being found to be dependent on the identity of the group 14 element. The thermodynamics of $CO_2$ uptake/loss can be established through VT-NMR ($\Delta H° = +24.6(2.3)$ kJ mol$^{-1}$, $\Delta S° = +64.9(3.8)$ J mol$^{-1}$ K$^{-1}$, $\Delta G°_{298} = +5.3(1.9)$ kJ mol$^{-1}$ for the loss of $CO_2$ in the Ge case), and the chemical consequences of reversibility demonstrated by thermodynamically-controlled exchange reactions.

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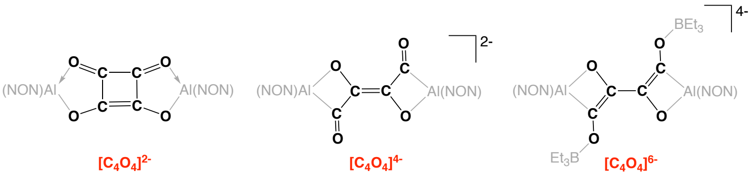
### 220. Coordination and homologation of CO at Al(I): mechanism and chain growth, branching, isomerization and reduction

**A. Heilmann, M.M.D. Roy, A.E. Crumpton, L.P. Griffin, J. Hicks, J.M. Goicoechea, S. Aldridge**

***J. Am. Chem. Soc.*, 2022, 144, 12942-12953 (DOI: 10.1021/jacs.2c05228)**

**Also available in preprint form at ChemRxiv, DOI: 10.26434/chemrxiv-2022-rv7h5)**

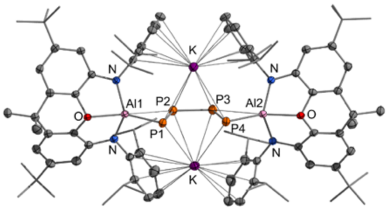


The homologation of CO via C–C bond formation is central to the heterogeneous Fischer Tropsch Process for the production of hydrocarbon fuels from carbon monoxide and hydrogen. The product distribution is known to be strongly dependent on the ratio of reductant ($H_2$) to CO, and the composition of the gaseous feedstock is therefore of critical commercial importance. Here we show that 4- or 6-electron reduction of CO can be accomplished by the use of anionic aluminium(I) ('aluminyl') compounds. The coupling of four molecules of CO to yield the topologically linear $[C_4O_4]^{4-}$ and $[C_4O_4]^{6-}$ chains shows that conversion of C–O to C–C bonds is dependent on reductant availability.

### 219. Generation of a pi-bonded isomer of $[P_4]^{4-}$ by aluminyl reduction of white phosphorus and its ammonolysis to $PH_3$

**M.M.D. Roy, A. Heilmann, M. Ellwanger, S. Aldridge**

***Angew. Chem. Int. Ed.*, 2021, 60, 26550-26554 (DOI: 10.1002/anie.202112515)**



By employing the highly reducing aluminyl complex $[K\{(NON)Al\}]_2$, we demonstrate the controlled formation of $P_4^{2-}$ and $P_4^{4-}$ complexes from white phosphorus, and chemically reversible inter-conversion between them. The tetra-anion features a unique planar π-bonded structure, with the incorporation of the $K^+$ cations offering additional stabilization of the unsaturated isomer of the $P_4^{4-}$fragment. This complex is extremely reactive, acting as a source of $P^{3-}$: exposure to ammonia leads to the release of phosphine ($PH_3$) under mild conditions (room temperature and pressure), which contrast with those used for the direct combination of $P_4$ and $NH_3$ (>5 kba, >250°C).

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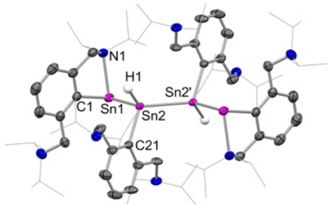
### 218. Controlling oxidative addition and reductive elimination at Sn(I) via hemi-lability

**A. Caise, A.E. Crumpton, P. Vasko, J. Hicks, C. McManus, N.H. Rees, S. Aldridge**

***Angew. Chem. Int. Ed.*, 2021, 61, e202114926 (DOI: 10.1002/anie.202114926)**

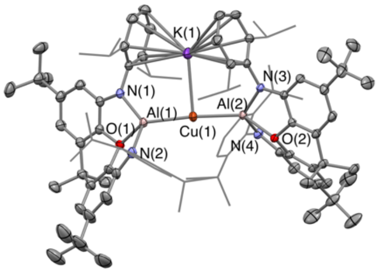


We report on the synthesis of a distannyne supported by a pincer ligand bearing pendant amine donors that is capable of reversibly activating E–H bonds at one or both of the tin centres through dissociation of the hemi-labile N–Sn donor/acceptor interactions. This chemistry can be exploited to sequentially (and reversibly) assemble mixed-valence chains of tin atoms of the type ArSn{Sn(Ar)H}$_n$SnAr ($n$ = 1, 2). The experimentally observed (decreasing) propensity towards chain growth with increasing chain length can be rationalized both thermodynamically and kinetically by the electron-withdrawing properties of the –Sn(Ar)H– backbone units generated via oxidative addition.

### 217. Coinage metal aluminyl complexes: probing regiochemistry and mechanism in the insertion and reduction of carbon dioxide

**C. McManus, J. Hicks, X. Cui, L. Zhao, G. Frenking, J.M. Goicoechea, S. Aldridge**

***Chem. Sci.*, 2021, 12, 13458-13468 (DOI: 10.1039/D1SC04676D)**



The synthesis of coinage metal aluminyl complexes is reported via salt metathesis between an aluminyl nucleophile and group 11 electrophiles. This approach allows access to both bimetallic (1:1) systems, ($^{t}$Bu$_3$P)MAl(NON) (M = Cu, Ag, Au) and a 2:1 di(aluminyl)cuprate system, K[Cu{Al(NON)}$_2$]. The bimetallic complexes readily insert heteroallenes into the unsupported M–Al bonds to give systems containing a M(CE$_2$)Al bridging unit (E = O, NR). Although the products of carbodiimide insertion are stable to further reaction, their CO$_2$ analogues have the potential to react further. ($^{t}$Bu$_3$P)Ag(CO)$_2$Al(NON) reacts slowly with CO$_2$ to give the corresponding carbonate complex (and CO), while the copper system proceeds rapidly to the carbonate even at low temperatures. Experimental and quantum chemical investigations of the mechanism are consistent with rate-determining extrusion of CO from the initially-formed M(CO)$_2$Al fragment to give a bimetallic oxide that rapidly assimilates a second molecule of CO$_2$.

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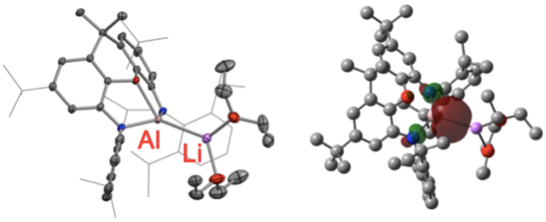
### 216. Probing the extremes of covalency in M–Al bonds: lithium and zinc aluminyl compounds

**M.M.D. Roy, J. Hicks, P. Vasko, A. Heilmann, A.-M. Baston, J.M. Goicoechea, S. Aldridge**

***Angew. Chem. Int. Ed.*, 2021, 60, 22031-22036 (DOI: 10.1002/anie.202109416)**



Synthetic routes to Li, Mg and Zn aluminyl complexes are reported, allowing for the first structural characterization of an unsupported Li-Al bond. Crystallographic and quantum chemical studies are consistent with the presence of a highly polar Li–Al interaction, characterized by a low bond order and relatively little charge transfer from Al to Li. Comparison with Mg and Zn aluminyl systems reveals changes to both the M–Al bond and the (NON)Al fragment consistent with greater covalent character, with the latter complex being shown to react with CO$_2$ via a pathway that implies that the *zinc* centre acts as the nucleophilic partner.

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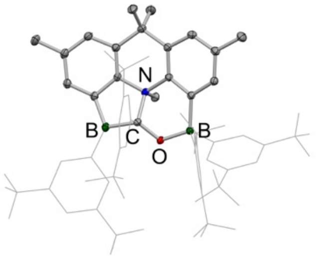
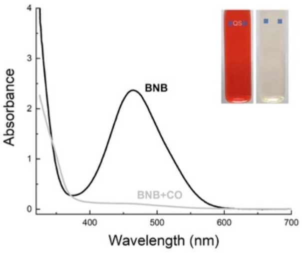
### 215. Colorimetric metal-free detection of carbon monoxide: reversible CO uptake by a BNB frustrated Lewis pair

**X. Zheng, I. Zulkifly, A. Heilmann, C. McManus, S. Aldridge**

***Angew. Chem. Int. Ed.*, 2021, 60, 16416-16419 ([DOI: 10.1002/anie.202106413](https://doi.org/10.1002/anie.202106413))**





We report two BNB-type frustrated Lewis pairs which feature an acceptor/donor/acceptor functionalized cavity, and which differ in the nature of the B-bound fluoroaryl group ($C_6F_5$ vs. $C_6H_3(CF_3)_2$-3,5, $Ar^f$). These receptor systems are capable of capturing gaseous CO, and in the case of the $-BAr^f_2$ system this can be shown to occur in reversible fashion. For both systems, the binding event is accompanied by migration of one of the aryl substituents to the electrophilic carbon of the CO guest. Experiments utilizing an additional equivalent of $P^tBu_3$ allow the initially-formed (non-migrated) CO adduct to be identified and trapped (via demethylation), while also establishing the reversibility of the B-to-C migration process. When partnered with the less Lewis acidic $-BAr^f_2$ substituent, this reversibility allows for release of the captured CO in the temperature range 40-70 °C, and the possibility for CO sensing, making use of the associated colourless to orange/red colour change.

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### 214. Frustrated Lewis pairs for CO detection and sensing

**X. Zheng, I. Zulkifly, S. Aldridge**

**Patent application: GB2106765.7, filed 12 May 2021 (granted February 2022)**

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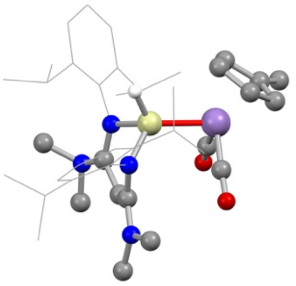
### 213. N-nacnac stabilized tetrylenes: access to silicon hydride systems *via* migration processes

**D.C.H. Do, E. Kolychev, J. Hicks, S. Aldridge**

***Z. Anorg. Allg. Chem.*, 2021, 647, 1679-1684 (invited special issue for 80th birthday of Prof. H. Schnöckel, DOI: [10.1002/zaac.202100142](https://doi.org/10.1002/zaac.202100142))**



Chloride metathesis between the 'N-nacnac' stabilised chlorosilylene ($\mathbf{L}^{\mathbf{Dipp}}$)SiCl ($\mathbf{L}^{\mathrm{Dipp}}$ = HC{($Me_2N$)CDippN}$_2$) and Na[$C_5H_5$] is accompanied by a C-to-Si hydrogen migration process, generating the hydridosilicon(IV) species ($\mathbf{L}^{\mathbf{Dipp}}$)Si(H)($C_5H_4$), By contrast, a Si(II) hydride species can be generated from ($\mathbf{L}^{\mathbf{Dipp}}$)SiCl via reaction with K[($\eta^5$-$C_5H_4$Me)Mn(CO)$_2$H], which acts as both hydride source and coordinative trap for ($\mathbf{L}^{\mathbf{Dipp}}$)SiH through the silylene complex ($\eta^5$-$C_5H_4$Me)Mn(CO)$_2${Si(H)$\mathbf{L}^{\mathbf{Dipp}}$} (shown).

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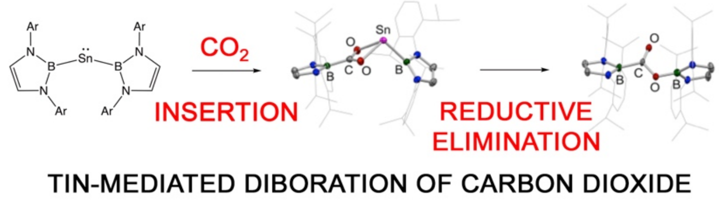
### 212. Reactions of a diborylstannylene with $CO_2$ and $N_2O$: diboration of carbon dioxide by a main group bis(boryl) complex

**A.V. Protchenko, M.Á. Fuentes, J. Hicks, C. McManus, S. Aldridge**

***Dalton Trans.*, 2021, 50, 9059-9067 (DOI: 10.1039/D1DT01216A).**



The reactions of the boryl-substituted stannylene $Sn\{B(NDippCH)_2\}_2$ with $CO_2$ have been investigated and shown to proceed via pathways involving insertion into the Sn–B bond(s). In the first instance this leads to formation of the (boryl)tin(II) borylcarboxylate complex $Sn\{B(NDippCH)_2\}\{O_2CB(NDippCH)_2\}$ (**2**), which has been structurally characterized and shown to feature a $\kappa^2$ mode of coordination of the $[(HCDippN)_2BCO_2]^-$ ligand at the metal centre. **2** undergoes B–O reductive elimination in hexane solution (in the absence of further $CO_2$) to give the boryl (borylcarboxylate) ester $(HCDippN)_2BO_2CB(NDippCH)_2$ (**3**) i.e. the product of formal diboration of carbon dioxide. Alternatively, **2** can assimilate a second equivalent of $CO_2$ to give the homoleptic bis(borylcarboxylate) $Sn\{O_2CB(NDippCH)_2\}_2$ (**4**), which can be prepared via an alternate route from $SnBr_2$ and the potassium salt of $[(HCDippN)_2BCO_2]^-$, and structurally characterized as its DMAP adduct.

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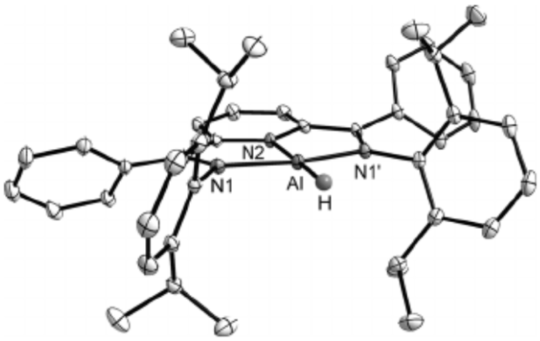
### 211. Molecular main group metal hydrides

**M.M.D. Roy, A. Omana, A. Wilson, M.S. Hill, S. Aldridge, E. Rivard**

***Chem. Rev.*, 2021, 121, 12784-12965 (DOI: 10.1021/acs.chemrev.1c00278).**



A comprehensive review of the chemistry of main group hydride compounds focusing on the literature since the publication of the last major review on the area in 2001. This review, written in collaboration with the Rivard and Hill groups (in Edmonton and Bath, respectively) covers hydride compounds of the metals of groups 1, 2, 12, 13, 14, 15 and 16 and emphasizes new synthetic developments and applications of main group hydride compounds in catalysis.

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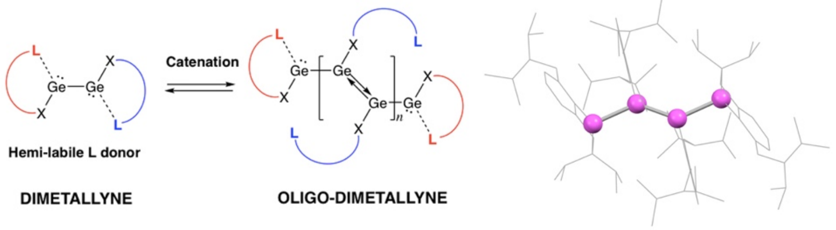
### 210. Controlling catenation in Ge(I) chemistry through hemi-lability

**A. Caise, L.P. Griffin, A. Heilmann, C. McManus, J. Campos, S. Aldridge**

***Angew. Chem. Int. Ed.*, 2021, 60, 15606-15612 (DOI: 10.1002/anie.202104643)**



A new approach for the rational construction of chains of group 14 metal atoms linked by unsupported metal-metal bonds is reported, which exploits hemi-labile ancillary ligands to generate unsaturated metal sites. The formation of catenated species can be controlled by the use of (acidic or basic) 'protecting groups' and through variation of the supporting ligand scaffold. The resulting oligo-dimetallyne chains feature alternating single and double metal-metal bonds.

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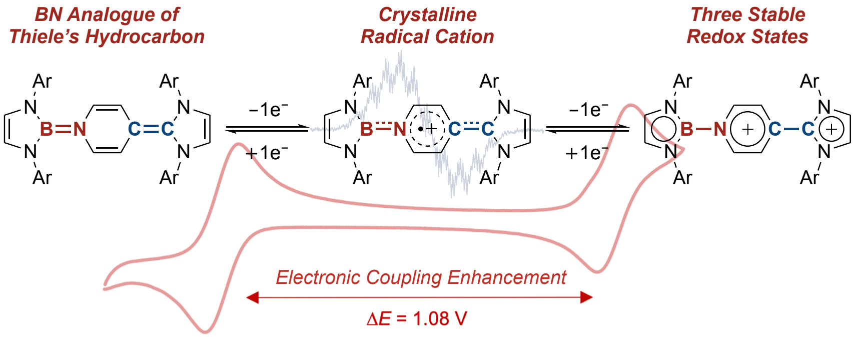
### 209. An unsymmetrical BN analogue of Thiele’s hydrocarbon: access to crystalline organoboron radical cations and dications

**Y.K. Loh, P. Vasko, C. McManus, A. Heilmann, W.K. Myers, S. Aldridge**

***Nature Commun.*, 2021, 12, 7052 (DOI: 10.1038/s41467-021-27104-y)**

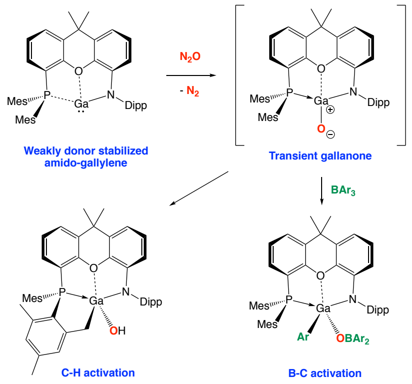


Thiele’s hydrocarbon has attracted tremendous attention as an open-shell platform for new organic materials, however little is known about its redox behavior. Here, we employ a mixed BN/carbene approach to access an unsymmetrical organoboron analogue (**1**) stabilized by isoelectronic N-heterocyclic boryl and N-heterocyclic carbene substituents. We show that the B=N motif of **1** renders an electronic coupling enhancement which confers increased stability on the radical cation, allowing for the first isolation of a crystalline boron-containing radical cation $\mathbf{1}^{\bullet+}$ derived from Thiele’s hydrocarbon. Further single-electron oxidation affords borenium dication $\mathbf{1}^{2+}$, thereby establishing a new cationic organoboron redox system fully characterized by X-ray crystallography, NMR/EPR, CV, UV-vis and (TD-)DFT in all three redox states.

### 208. A xanthene-based mono-anionic PON ligand: exploiting a bulky, electronically unsymmetrical donor in Main Group chemistry

**X. Zheng, A. Heilmann, C. McManus, S. Aldridge**

***Chem.-Eur. J.,*** **2021, 27, 3159-3165 ([DOI: 10.1002/chem.202004741](https://doi.org/10.1002/chem.202004741))**



The application of a sterically demanding mono-anionic PON ligand in gallium chemistry has been probed, revealing a highly unsymmetrical donor profile towards Ga(I) and structural features reminiscent of one-coordinate gallium amides. Oxidation at the metal leads to a marked increase in the donor capabilities of the phosphine donor, although the transient gallanone formed by O-atom transfer still undergoes facile C-H activation across the Ga-O bond.

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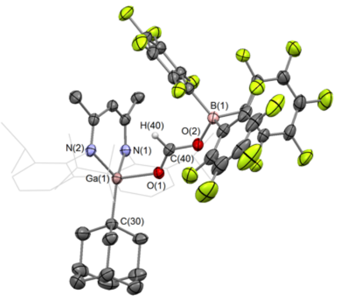
### 207. Partnering a three-coordinate gallium cation with a hydroborate counter-ion for the catalytic hydrosilylation of $CO_2$

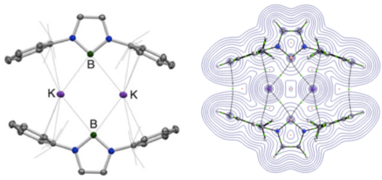
**A. Caise, J. Hicks, M.Á. Fuentes, J. M. Goicoechea, S. Aldridge**

***Chem.-Eur. J.,*** **2021, 27, 2138-2148 ([DOI: 10.1002/chem.202004408](https://doi.org/10.1002/chem.202004408))**



The addition of an equivalent of $B(C_6F_5)_3$ to ($^{Dipp}$Nacnac)Ga(Ad)H leads to the formation of a tractable 3-coordinate cationic gallane, partnered with a hydroborate anion, [($^{Dipp}$1)Ga(Ad)][$HB(C_6F_5)_3$]. This complex catalyses the reduction of carbon dioxide to the formaldehyde oxidation level at 60°C, selectively yielding $H_2C(OSiEt_3)_2$. When the catalysis is undertaken in the presence of excess $B(C_6F_5)_3$, an appreciable enhancement in activity of the system is observed, with a corresponding reduction in selectivity, yielding a product distribution including $H_2C(OSiEt_3)_2$, $CH_4$ and $O(SiEt_3)_2$.

**206. Approaching a ‘naked’ boryl anion: amide metathesis as a route to calcium, strontium and potassium boryl complexes**
**A.V. Protchenko, P. Vasko, M.Á. Fuentes, J. Hicks, D. Vidovic, S. Aldridge**
***Angew. Chem. Int. Ed.*, 2021, 60, 2064-2068 (DOI: 10.1002/anie.202011839)**



Amide metathesis has been used to generate the first structurally characterized boryl complexes of potassium, calcium and strontium. The solvent-free borylpotassium dimer $[K\{B(NDippCH)_2\}]_2$ is stable in the solid state at room temperature for extended periods (48 h) and possesses a dimeric structure in which the $K^+$ cations interact weakly with both the ipso-carbons of the flanking Dipp groups and the boron centres of the diazaborolyl heterocycles ($d$(K···B) > 3.1 Å). These structural features, together with Atoms in Molecules (QTAIM) calculations imply that the boron-containing fragment closely approaches a limiting description as a ‘free’ boryl anion in the condensed phase.

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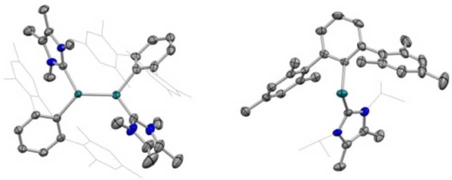
**205. Synthesis, structure and reactivity of terphenyl-substituted germylium-ylidene cations**
**R.J. Mangan, A.R. Davies, J. Hicks, C.P. Sindlinger, A.L. Thompson, S. Aldridge**
***Polyhedron,* 2021, 196, 115006, (invited special issue on ‘Dative Carbon Donors’ DOI: 10.1016/j.poly.2020.115006)**



Terphenyl-substituted germylium-ylidene cations of composition $[(NHC)(Ar)Ge]^+$ are reported, exploiting a range of aryl and NHC substituent combinations. The smallest combination ($IMe_4$ and $Ar^{Mes}$) results in a dicationic dimer, $[(IMe_4)(Ar^{Mes})Ge{=}Ge(Ar^{Mes})(IMe_4)]^{2+}$; increased steric loading favours monomeric cations stabilized in the solid state to varying degrees by 2$^{o}$ interactions with the peripheral arene pi systems or C-H bonds.

### 204. Acid-Base free Main Group carbonyl analogues

**Y.K. Loh, S. Aldridge**

***Angew. Chem. Int. Ed.*, 2021, 60, 8626-8648 (DOI: 10.1002/anie.202008174)**

Carbonyl compounds ($R_2C{=}O$) are cornerstones of organic chemistry. In sharp contrast, main group analogues ($R_2E{=}O$) derived from *p*-block elements from groups 13-15, have long been considered to be elusive species. A new era was marked by the recent isolation of acid-base (i.e. acid *and* base) free main group carbonyl analogues, ranging from a lighter boracarbonyl to the heavier silacarbonyls, phosphacarbonyls and a germacarbonyl. Most importantly, the rich chemistry of these unperturbed main group carbonyl compounds has begun to emerge, spanning the vista from classical organic carbonyl-type reactions to transition metal-like oxide ion transfer chemistry.

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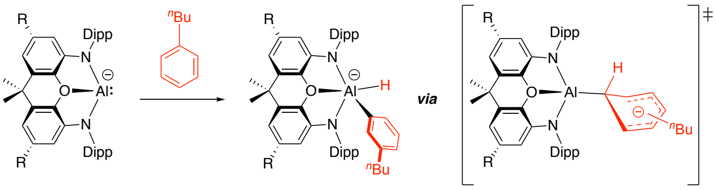
### 203. Arene C-H activation at aluminium(I): *meta* selectivity driven by the electronics of $S_NAr$ chemistry

**J. Hicks, P. Vasko, A. Heilmann, J.M. Goicoechea, S. Aldridge**

***Angew. Chem. Int. Ed.*, 2020, 59, 20376-20380 (DOI: 10.1002/anie.202008557)**



EXCLUSIVE *META* SELECTIVITY

The reactivity of the electron-rich anionic Al(I) (‘aluminyl’) compound $K_2[(NON)Al]_2$ towards mono- and disubstituted arenes is reported. C-H activation chemistry with *n*-butylbenzene gives exclusively the product of activation at the arene *meta* position. Mechanistically, this transformation proceeds in a single step via a Meisenheimer-type transition state. Selectivity is therefore based on similar electronic factors to classical $S_NAr$ chemistry, which implies the destabilization of transition states featuring electron-donating groups in either the *ortho* or the *para* positions.

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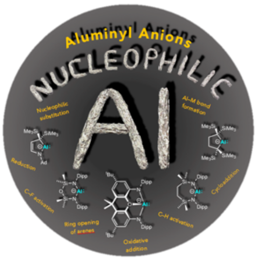
### 202. The aluminyl anion: a new generation of aluminium nucleophile

**J. Hicks, P. Vasko, J.M. Goicoechea, S. Aldridge**

***Angew. Chem. Int. Ed.,* 2021, 60, 1702-1711 (DOI: 10.1002/anie.202007530)**

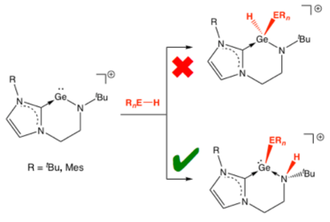


Trivalent aluminium compounds are well known for their reactivity as Lewis acids/electrophiles, a feature that is exploited in many pharmaceutical, industrial and laboratory-based reactions. Recently, a series of isolable aluminium(I) anions (‘aluminyls’) have been reported, which offer an alternative to this textbook description: these reagents behave as aluminium nucleophiles. This mini-review covers the synthesis, structure and reactivity of aluminyl species reported to date, together with their associated metal complexes. The frontier orbitals of each of these species have been investigated using a common methodology to allow for a like-for-like comparison of their electronic structure and a means of rationalizing (sometimes unprecedented) patterns of reactivity.

### 201. Cooperative N-H bond activation by amido-Ge(II) cations

**X. Zhou, P. Vasko, J. Hicks, M. Á. Fuentes, A. Heilmann, E. L. Kolychev, S. Aldridge**

***Dalton Trans.*, 2020, 49, 9495-9504 ([DOI: 10.1039/D0DT01960G](https://doi.org/10.1039/D0DT01960G))**



**Cooperative (1,2-) E-H bond activation**

Two-coordinate germylium-ylidene cations, $[R(NHC)Ge:]^+$, featuring tethered amido substituents at R have been synthesized and structurally characterized. Narrow N-Ge-C angles are consistent with wide HOMO-LUMO gaps (> 400 kJ mol$^{-1}$) and inactivity in single site oxidative E-H bond activation. The strongly Lewis acidic germanium cation and proximal amide function, however, allow for facile cleavage of protic E-H bonds in (1,2-) fashion across the Ge-N unit.

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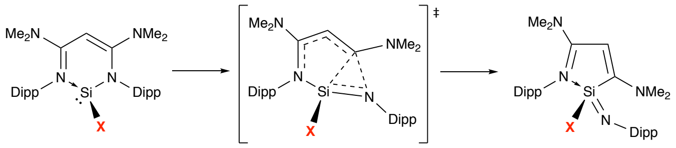
### 200. Probing the non-innocent nature of an amino-functionalised β-diketiminate ligand in silylene/imino-silane systems

**D.C.H. Do, P. Vasko, M.Á. Fuentes, J. Hicks, S. Aldridge**

***Dalton Trans.,* 2020, 49, 8701-8709 ([DOI: 10.1039/D0DT01447H](https://doi.org/10.1039/D0DT01447H))**



$\Delta G^\ddagger$: Cl > $PR_2$ > H > $SiR_3$

**SILYLENE-TO-IMINOSILANE RING CONTRACTION**

Electron-rich β-diketiminate ligands, featuring amino groups at the backbone β positions ("N-nacnac" ligands) have been employed in the synthesis of a range of silylene ($Si^{II}$) complexes of the type (N-nacnac)SiX (where X = H, Cl, $N(SiMe_3)_2$, $P(SiMe_3)_2$ and $Si(SiMe_3)_3$). A combination of experimental and quantum chemical approaches reveals that in all cases rearrangement to give an aza-butadienyl $Si^{IV}$ imide featuring a contracted five-membered heterocycle is thermodynamically favourable (and experimentally viable). Kinetically, this process is driven by electron releasing and sterically unencumbered silicon-bound substituents.

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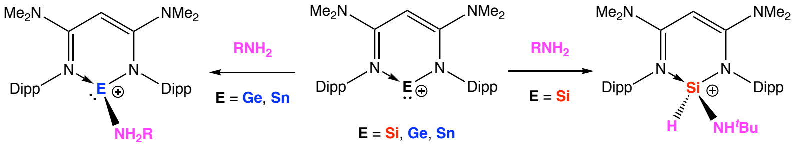
### 199. N-H cleavage vs. Werner complex formation: reactivity of cationic Group 14 tetrelenes towards amines

**D.C.H. Do, A.V. Protchenko, M.Á. Fuentes, J. Hicks, P. Vasko, S. Aldridge**

***Chem. Commun.,* 2020, 56, 4684-4687 ([DOI: 10.1039/D0CC00875C](https://doi.org/10.1039/D0CC00875C))**



**WERNER COMPLEX *vs.* N-H OXIDATIVE ADDITION**

β-Diketiminate ligands featuring backbone $NMe_2$ groups have been exploited to access a series of two-coordinate cations of the type $[(N\text{-nacnac})E]^+$ (E = Si, Ge, Sn), whose reactivity towards N-H bonds has been investigated. While the heavier group 14 systems react via simple adduct formation, N-H oxidative addition occurs for E = Si consistent with differences in $E^{II}/E^{IV}$ redox potentials. The structurally characterized Ge/Sn adducts can be viewed as models for the corresponding (transient) Si systems $[(N\text{-nacnac})Si\cdot(NH_2R)]^+$ (R = H, $^tBu$) - which are potential intermediates in the formation of $[(N\text{-nacnac})Si(H)(NHR)]^+$ via a proton-shuttling mechanism.

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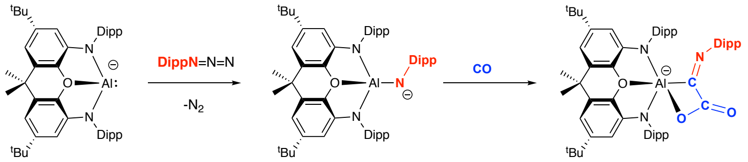
### 198. Carbon monoxide activation by a molecular aluminium imide: C-O Bond cleavage and C-C bond formation

**A. Heilmann, J. Hicks, P. Vasko, J.M. Goicoechea, S. Aldridge**

***Angew. Chem. Int. Ed.*, 2020, 59, 4897-4901 (DOI: 10.1002/anie.201916073)**



C-O CLEAVAGE AND C-C COUPLING BY A DISCRETE ALUMINIUM IMIDE ANION

Anionic molecular imide complexes of aluminium are accessible via a rational synthetic approach involving the reactions of organo azides with a potassium aluminyl reagent. In the case of $K_2[(NON)Al(NDipp)]_2$ structural characterization by X-ray crystallography reveals a short Al-N distance, due primarily to the low coordinate nature of the nitrogen centre. The Al-N unit is highly polar, and capable of the activation of relatively inert chemical bonds, such as those found in $H_2$ and CO. In the latter case, uptake of two molecules of the substrate leads to C-C coupling and $C\equiv O$ bond cleavage.

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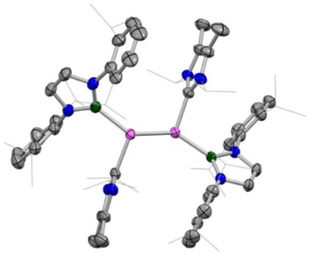
### 197. Activation of protic, hydridic and apolar E-H bonds by a boryl-substituted Ge(II) cation

**R.J. Mangan, A. Rit, C.P. Sindlinger, R. Tirfoin, J. Campos, J. Hicks, K.E. Christensen, H. Niu, S. Aldridge**

***Chem.-Eur. J.*, 2020, 26, 306-315 (DOI: 10.1002/chem.201904171)**



Chloride abstraction from the boryl/NHC stabilized Ge(II) precursor $(IPrMe)GeCl\{B(NDippCH)_2\}$ yields $[(IPrMe)\{(HCNDipp)_2B\}Ge{=}Ge\{B(NDippCH)_2\}(IPrMe)]^{2+}$ which can be viewed as an imidazolium-functionalized digermene, and is cleaved in the presence of donor solvents to give monomeric adducts of the type $[Ge\{B(NDippCH)_2\}(IPrMe)(L)]^+$. The thf adduct is sufficiently labile that it can act as a convenient source of monomeric $[Ge\{B(NDippCH)_2\}(IPrMe)]^+$, which undergoes oxidative bond activation chemistry with silanes, dihydrogen, and ammonia, in line with the very small HOMO-LUMO gap for this system (132 kJ mol$^{-1}$).

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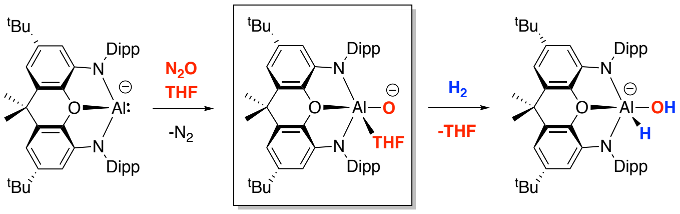
### 196. Trapping and reactivity of a molecular aluminium oxide ion

**J. Hicks, A. Heilmann, P. Vasko, J.M. Goicoechea, S. Aldridge**

***Angew. Chem. Int. Ed.*, 2019, 58, 17265-17268 (DOI: 10.1002/anie.201910509)**



DISCRETE ALUMINIUM OXIDE ANION

Reactions of the potassium aluminyl complex $K_2[(NON)Al]_2$ with $CO_2$, PhNCO and $N_2O$ all proceed via a common aluminium oxide intermediate. This highly reactive species can be trapped by coordination of a THF molecule as the anionic oxide complex $[(NON)AlO(THF)]^-$, which features discrete Al-O bonds and dimerizes in the solid state via weak O···K interactions. This oxide reacts with a range of small molecules including $N_2O$ to give a hyponitrite ($[N_2O_2]^{2-}$) complex and $H_2$, the latter offering an unequivocal example of heterolytic E-H bond cleavage across a main group M-O bond.

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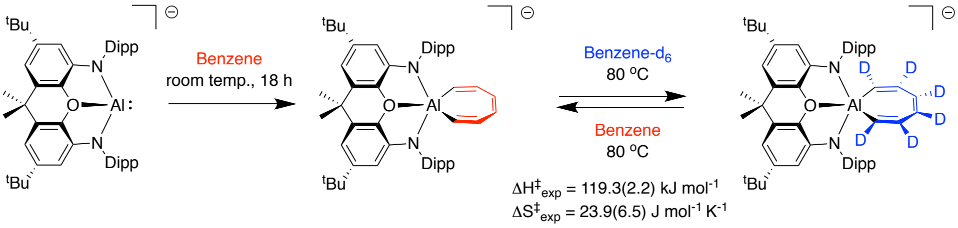
### 195. Reversible, room-temperature C-C bond activation of benzene by an isolable metal complex

**J. Hicks, P. Vasko, J.M. Goicoechea, S. Aldridge**

***J. Am. Chem. Soc.*, 2019, 141, 11000-11003 (DOI: 10.1021/jacs.9b05925)**



The activation of C-C bonds in aromatic hydrocarbons such as benzene, C-C cleavage is thermodynamically disfavoured and is brought about only by transient highly reactive species generated *in situ*. Here we show that the oxidative addition of the C-C bond in benzene by an isolated metal complex is not only possible, but occurs at room temperature and reversibly at a single aluminium centre in [(NON)Al]$^-$ (where NON = 4,5-bis(2,6-diisopropylanilido)-2,7-di-*tert*-butyl-9,9-dimethylxanthene). Selectivity over C-H bond activation is achieved kinetically and allows for the generation of functionalized acyclic products from benzene.

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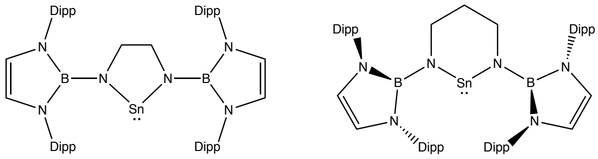
### 194. Synthetic, structural and reaction chemistry of *N*-heterocyclic germylene and stannylene compounds featuring *N*-boryl substituents

**L. Kristinsdóttir, N. Oldroyd, R. Grabiner, A. Knights, A. Heilmann, A.V. Protchenko, H. Niu, E.L. Kolychev, J. Campos, S. Aldridge**

***Dalton Trans.*, 2019, 48, 11951-11960 (DOI: 10.1039/C9DT02449B)**



The synthesis of N-heterocyclic germylenes and stannylenes featuring diazaborolyl groups, {(HCNDipp)$_2$B}, as both of the N-bound substituents, is investigated in order to generate strongly electron-donating and sterically imposing tetrelenes. The reactivity of germylene systems towards oxygen atom transfer agents has been examined, with 2:1 reaction stoichiometries being observed for both Me$_3$NO and pyridine *N*-oxide, leading to the formation of products derived from the activation of C-H bonds by a transient first-formed germanone complex.

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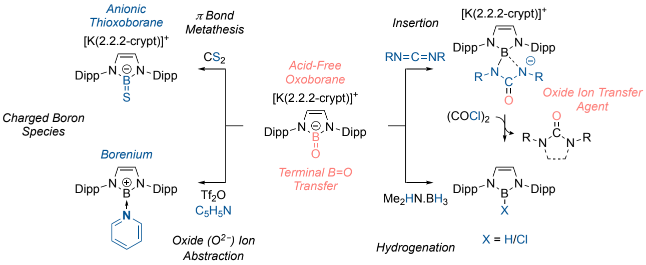
### 193. An acid-free anionic oxoborane isoelectronic with carbonyl: facile access and transfer of a terminal B=O double bond

**Y.K. Loh, K. Porteous, M.Á. Fuentes, D.C.H. Do, J. Hicks, S. Aldridge**

***J. Am. Chem. Soc.*, 2019, 141, 8073-8077 (DOI: 10.1021/jacs.9b03600)**

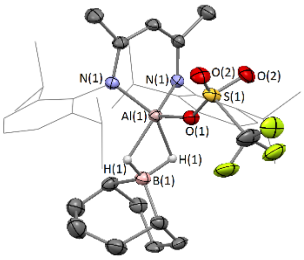


The first acid-free anionic oxoborane, [K(2.2.2-crypt)][(HCDippN)$_2$BO] (**1**), which is isoelectronic with classical carbonyl compounds can be accessed from its borinic acid by a simple deprotonation/sequestration sequence. Crystallographic and DFT analyses support the presence of a polarized terminal B=O double bond. Facile B=O bond cleavage can be achieved to access B–H and B–Cl bonds, and via a remarkable oxide (O$^{2-}$) ion abstraction to generate a borenium cation [(HCDippN)$_2$B(NC$_5$H$_5$)][OTf] (**4**). By extension, **1** can act as an oxide transfer agent to organic substrates, a synthetic role traditionally associated with transition metal compounds. Hence we show that B–O linkages, which are often considered to be thermodynamic sinks, can be activated under mild conditions towards bond cleavage and transfer, by exploiting the higher reactivity inherent in the B=O double bond.

### 192. Reversible borohydride formation from aluminium hydrides and H-9BBN: structural, thermodynamic and reactivity studies

**A. Caise, E. Kolychev, J. Hicks, M.Á. Fuentes, J.M. Goicoechea, S. Aldridge**

***Dalton Trans.,* 2019, 48, 10845-10852 ([DOI: 10.1039/C9DT00535H](https://doi.org/10.1039/C9DT00535H))**



A series of aluminium borohydrides of the type (Nacnac)Al(R){$H_2$(9-BBN)} has been synthesised offering variation in both the auxiliary R substituent and in the Nacnac backbone itself. A number of these complexes show unusual dissociation of the borane from the aluminium hydride in solution under ambient conditions. The lability of the borane is shown (by VT-NMR studies) to be influenced by the electronic character of *both* the R substituent and the Nacnac ligand itself, such that electron-withdrawing substituents lead to greater dissociation of the borane. This behaviour is shown to be highly influential on the ability of the corresponding borohydride complexes to reduce carbon dioxide in a stoichiometric manner.

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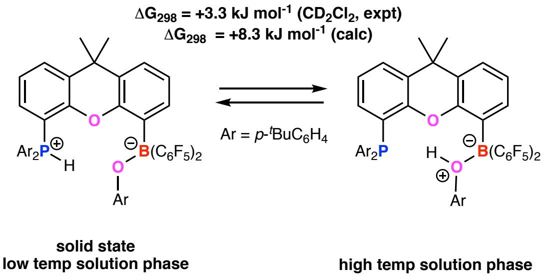
### 191. Reversible O-H bond activation by an intramolecular frustrated Lewis pair

**P. Vasko, M.Á. Fuentes, J. Hicks, S. Aldridge**

***Dalton Trans.*, 2019, 48, 2896-2899 ([DOI: 10.1039/C9DT00228F](https://doi.org/10.1039/C9DT00228F))**



The interactions of the O-H bonds in alcohols, water and phenol with dimethylxanthene-derived frustrated Lewis pairs (FLPs) have been probed. Within the constraints of this backbone framework, the preference for adduct formation or O-H bond cleavage to give the corresponding zwitterion is largely determined by p$K_a$ considerations. In the case of the $PPh_2/B(C_6F_5)_2$ system and $p$-$^tBuC_6H_4OH$, an equilibrium is established between the two isomeric forms which allows the thermodynamic parameters associated with zwitterion formation via O-H bond cleavage to be probed.

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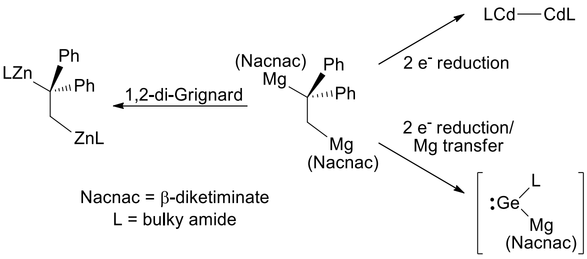
### 190. Acyclic 1,2-dimagnesioethanes/-ethene derived from magnesium(I) compounds: multipurpose reagents for organometallic synthesis

**D. Dange, A.R. Gair, D.D.L. Jones, M. Juckel, S. Aldridge, C. Jones**

***Chem. Sci.*, 2019, 10, 3208-3216 ([DOI: 10.1039/C9SC00200F](https://doi.org/10.1039/C9SC00200F))**



In collaborative work with the Jones group involving Part 2 student Andy Gair, the sometimes redox reversible 1,2-additions of magnesium(I) dimers across several alkenes and one alkyne is shown to yield 1,2-dimagnesioethanes and a 1,2-dimagnesioethene. Treatment of these with very bulky amido metal halide precursors afford novel products *via* three different modes of reactivity (see picture).

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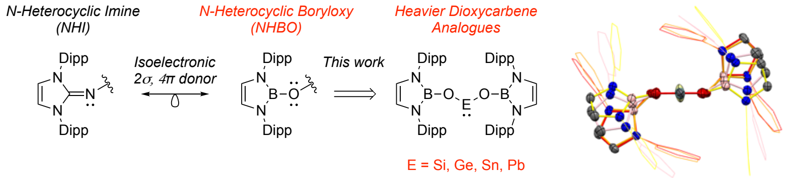
### 189. An *N*-heterocyclic boryloxy ligand isoelectronic with *N*-heterocyclic imines: access to an acyclic dioxysilylene and its heavier congeners

**Y.K. Loh, L. Ying, M.Á. Fuentes, D.C.H. Do, S. Aldridge**
***Angew. Chem., Int. Ed.*, 2019, 58, 4847-4851 (DOI: 10.1002/anie.201812058)**



Exploiting the isoelectronic relationship with *N*-heterocyclic imine (NHI), we introduce a new class of *N*-heterocyclic boryloxy (NHBO) ligand that is a strong O-donor. Employing the NHBO ligand, we present the first acyclic two-coordinate dioxysilylene and its heavier (Ge, Sn, Pb) congeners, which represents the first complete series of group 14 heavier dioxycarbene analogues

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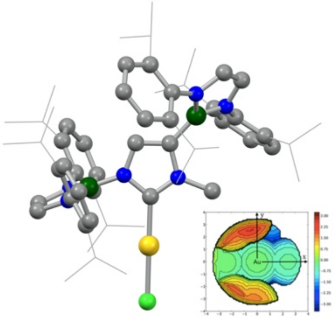
### 188. Borylated N-heterocyclic carbenes: rearrangement and chemical trapping

**L. Kristinsdóttir, P. Vasko, H. Niu, E.L. Kolychev, J. Campos, M.Á. Fuentes, J. Hicks, A.L. Thompson, S. Aldridge**
***Chem.-Eur. J.*, 2019, 25, 2556-2568 (DOI: 10.1002/chem.201804808)**



Attempts to access NHCs featuring the diazaborolyl group, $\{(HCNDipp)_2B\}$, as the N-bound substituent(s) are reported. These are characterized by facile N-to-C migration, although in the cases of imidazolium systems bearing one diazaborolyl and one Me substituent, the target carbenes can be characterized *in situ* by NMR measurements, and trapped by reactions with metal fragments and elemental selenium

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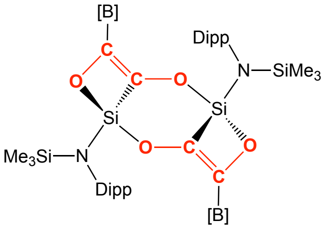
### 187. Reduction of carbon oxides by an acyclic silylene: reductive coupling of CO

**A.V. Protchenko, P. Vasko, D.C.H. Do, J. Hicks, M. Ángeles Fuentes, C. Jones, S. Aldridge**
***Angew. Chem., Int. Ed.*, 2019, 58, 1808-1812 (DOI: 10.1002/anie.201812675)**

**CO to $[C_2O_2]^{2-}$; $Si^{II}$ to $Si^{IV}$**



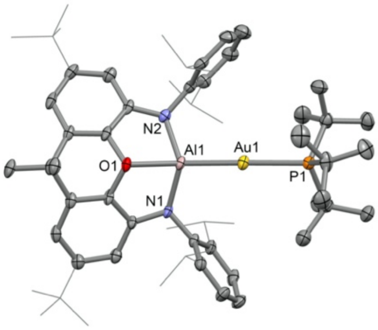
[B] = $B(NDippCH)_2$

The reactions of a boryl-substituted acyclic silylene with carbon dioxide and monoxide are reported. The former proceeds via oxygen atom abstraction (generating CO), and rearrangement of the putative silanone product via silyl group transfer. The latter is characterized by reductive coupling of CO to give an ethynediolate fragment which inserts into the Si-B bond. The net reaction of carbon dioxide with two equivalents of silylene can therefore be shown to bring about three-electron reduction of $CO_2$ to $[C_2O_2]^{2-}$.

### 186. A nucleophilic gold complex

**J. Hicks, A. Mansikkamäki, P. Vasko, J.M. Goicoechea, S. Aldridge**

***Nature Chem.*, 2019, 11, 237-241 (DOI: 10.1038/s41557-018-0198-1)**



The first 2-coordinate molecular auride (NON)AlAuP$^t$Bu$_3$ has been synthesized by the reaction of [K{Al(NON)}]$_2$ with $^t$Bu$_3$PAuI. QTAIM charge analysis supports its description as a molecular auride: the calculated charge at gold (–0.82) is in line with the relative electronegativities of the two metals (Au: 2.54; Al: 1.61 on the Pauling scale). Crucially, it is found to act as an unprecedented nucleophilic source of gold, reacting with diisopropylcarbodiimide and CO$_2$ to give the Au–C bonded insertion products of the type (NON)Al(X$_2$C)AuP$^t$Bu$_3$.

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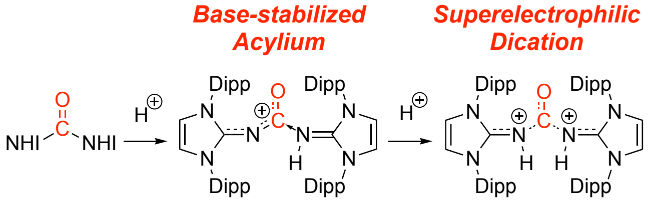
### 185. Successive protonation of an *N*-heterocyclic imine derived carbonyl: superelectrophilic dication versus masked acylium ion

**Y.K. Loh, M. Á. Fuentes, P. Vasko S. Aldridge**

***Angew. Chem., Int. Ed.*, 2018, 57, 16559-16563 (DOI: 10.1002/anie201810709)**



Superelectrophilic dications formed by the double protonation of heteroatom functionalized carbonyl compounds were introduced conceptually and studied *in situ* in the seminal work of Olah. By employing sterically demanding and strongly electron-releasing *N*-heterocyclic iminato substituents, the first such example, [(IDippNH)$_2$CO]$^{2+}$, has been structurally characterized.

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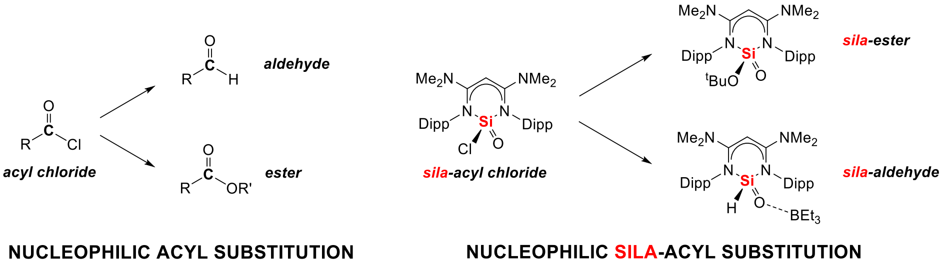
### 184. A β-diketiminate stabilized sila-acyl chloride: systematic access to base-stabilised silicon analogues of classical carbonyl compounds

**D.C.H. Do, A.V. Protchenko, M. Ángeles Fuentes, J. Hicks, E. Kolychev, P. Vasko, S. Aldridge**

***Angew. Chem., Int. Ed.*, 2018, 57, 13907-13911 (DOI: 10.1002/anie.201807543)**

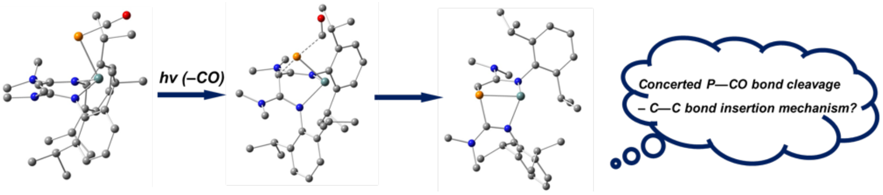


The first simple silicon analogue of an acyl chloride can be accessed by mild oxidation of a N-nacnac stabilized chlorosilylene. This sila-acyl chloride undergoes facile functional group exchange, to yield the corresponding sila-ester and sila-aldehyde, in a manner analogous to that seen in classical carbonyl chemistry. These transformations demonstrate a significant breakthrough by applying seemingly ubiquitous organic reaction pathways to the heavier group 14 elements.

### 183. N-nacnac stabilized tetrelenes: formation of an *N*,*P*-heterocyclic germylene via C—C bond insertion

**D.C.H. Do, A.V. Protchenko, P. Vasko, J. Campos, E.L. Kolychev, S. Aldridge**

***Z. Anorg. Allg. Chem.*, 2018, 644, 1238-1242 (invited special issue for 65th birthday of Prof W. Uhl; DOI: 10.1002/zaac.201800259)**



The complexation chemistry of N-nacnac-stabilized germylenes provides insight into electronic divergence from conventional Nacnac- supported systems. In the case of a PCO-substituted system, UV-induced decarbonylation affords an unusual bicyclic N,P-heterocyclic germylene. This is proposed to occur *via* a C—C bond insertion initiated by interaction of P with the remarkably nucleophilic γ-carbon of the ligand backbone.

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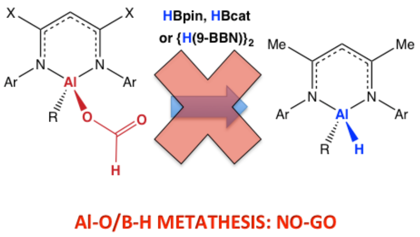
### 182. On the viability of catalytic turnover via Al-O/B-H metathesis: the reactivity of β-diketiminate aluminium hydrides towards $CO_2$ and boranes

**A. Caise, D. Jones, E.L. Kolychev, J. Hicks, J.M. Goicoechea, S. Aldridge**

***Chem.-Eur. J.*, 2018, 24, 13624-13635 (DOI: 10.1002/chem.201802603)**



Mononuclear beta-diketiminate stabilized aluminium hydrides have recently been implicated in a number of reduction processes of C=O bonds. Here we show that turnover in the borane reduction of $CO_2$ by a range of such complexes is rendered thermodynamically non-viable by the excessive strength of the Al-O bond.

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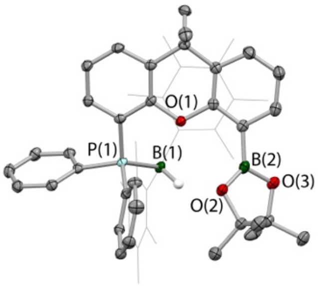
### 181. Reversible C-H activation, facile B-C/B-H metathesis and apparent hydroboration catalysis by a xanthene-based frustrated Lewis pair

**P. Vasko, I. Zulkifly, M. Á. Fuentes, Z. Mo, J. Hicks, P. Kamer, S. Aldridge**

***Chem.-Eur. J.*, 2018, 24, 10531-10540 (DOI: 10.1002/chem.201801871)**



A xanthene-based FLP can effect reversible cleavage of the C-H bond in phenylacetylene, PhCCH. This system also reacts with B-H bonds, such as those in HBpin and HBcat, although in a different fashion, proceeding via B-C/B-H exchange. This process leads to replacement of the $–B(C_6F_5)_2$ Lewis acid component by –Bpin/–Bcat and transfer of $HB(C_6F_5)_2$ to the phosphine Lewis base. Moreover it also proves to be at the heart of its ability to act as a catalyst for the hydroboration of alkynes by HBpin: the active species is derived from the $HB(C_6F_5)_2$ fragment generated in this exchange process.

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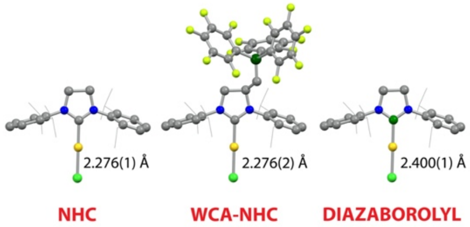
### 180. Experimental and quantum chemical studies of anionic analogues of N-heterocyclic carbenes

**H. Niu, R. Mangan, A.V. Protchenko, N. Phillips, W. Unkrig, C. Friedmann, E.L. Kolychev, R. Tirfoin, J. Hicks, S. Aldridge**

***Dalton Trans.*, 2018, 47, 7445-7455 (DOI: 10.1039/C8DT01661E)**



A combination of quantum chemical and synthetic/crystallographic methods have been employed to probe the electronic structures of two series of anionic ligands related to the well known N-heterocyclic carbene (NHC) class of donor: (a) complexes of NHC ligands which incorporate a pendant weakly coordinating anion component (WCA-NHCs) and (b) systems featuring isoelectronic (formally anionic) diazaborolyl ligands. Diazaborolyl donors (in which the negative charge is formally located at the boron donor atom) offer significantly stronger σ-donation and a very high *trans* influence.

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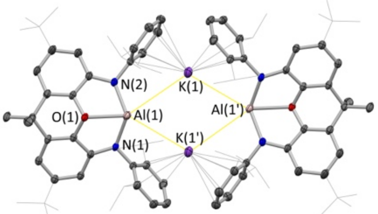
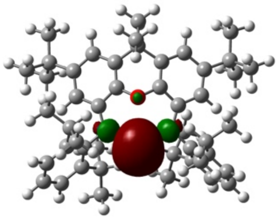
### 179. Synthesis, structural and reaction chemistry of a nucleophilic aluminyl anion

**J. Hicks, P. Vasko, J.M. Goicoechea, S. Aldridge**

***Nature*, 2018, 557, 92-95 (DOI: 10.1038/s41586-018-0037-y)**





Aluminium is the most abundant metal in the Earth's crust and is widely exploited in key industrial processes; $Al^{III}$ compounds are archetypal electrophiles. Here we show that anionic $Al^{I}$ compounds can act as nucleophiles. A dimethylxanthene-stabilized potassium aluminyl compound of the type $[\{(NON)Al\}K]_2$ can be synthesized by the potassium reduction of the corresponding (NON)AlI species, and shown to be a $K^+$ bridged dimer both in the solid state (by X-ray crystallography) and in arene solution (by DOSY NMR). It reacts in an unprecedented 'umpolung' fashion as an aluminium-centred nucleophile in the formation of Al-E covalent bonds (E = H, C, metal).

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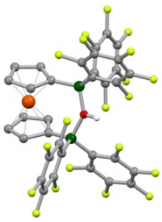
### 178. Frustrated Lewis pairs incorporating the bifunctional Lewis acid 1,1'-fc$\{B(C_6F_5)_2\}_2$: reactivity towards small molecules

**R. Tirfoin, J. Gilbert, M.J. Kelly, S. Aldridge**

***Dalton Trans.*, 2018, 47, 1588-1598 (DOI: 10.1039/C7DT04136E)**



Applications of the bifunctional ferrocene-diyl Lewis acid 1,1'-fc$\{B(C_6F_5)_2\}_2$ in FLP chemistry are described. The coordination (or otherwise) of a range of sterically encumbered C-, N- and P-centred Lewis bases has been investigated, with lutidine, tetramethylpiperidine, $PPh_3$, $P^tBu_3$ and the expanded ring carbene 6Dipp being found to be sterically incapable of coordinate bond formation. The chemistry of a range of these FLPs in the presence of $H_2O$, $NH_3$, $CO_2$ and cyclohexylisocyanate (CyNCO) has been investigated, with the patterns of reactivity identified including simple coordination chemistry, E-H bond cleavage and C-B insertion.

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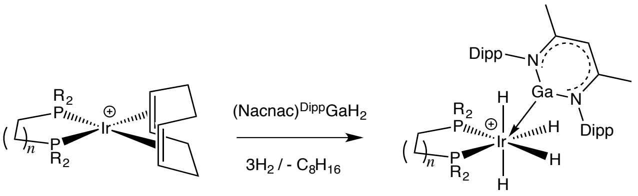
### 177. A gallium hydride as an oxidizing agent: direct synthesis of Ir(V) complexes via Ga-H bond activation

**A. Caise, J.A.B. Abdalla, R. Tirfoin, A.L. Thompson, A.J. Edwards, S. Aldridge**
***Chem.-Eur. J.,* 2017, 23, 16906-16913 (DOI: 10.1002/chem.201704372)**



**2**-dppp: *n* = 2, R = Ph
**2**-dcype: *n* = 1, R = Cy

Reactions of (Nacnac)$^{Dipp}$Ga$H_2$ with chelating Ir(I) bis(phosphine) precursors are shown to provide a simple route to Ir(V) complexes stabilized by strongly $\sigma$-donating hydrides and the carbene-like (Nacnac)$^{Dipp}$Ga donor. Characterization of these systems as 7-coordinate Ir(V) tetrahydride species is supported by single crystal X-ray/neutron diffraction, and by NMR $T_1$ measurements. Related systems featuring more sterically demanding (non-chelating) ancillary ligands, by contrast, are better described in terms of a bis(hydride) dihydrogen [Ir(H)$_2$(H$_2$)] formulation and a formal Ir(III) oxidation state.

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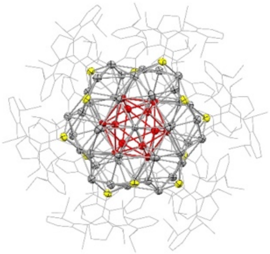
### 176. Electronic delocalization in two and three dimensions: differential aggregation in indium 'metalloid' clusters

**A.V. Protchenko, J. Urbano, J.A.B. Abdalla, J. Campos, D. Vidovic, A.D. Schwarz, M.P. Blake, P. Mountford, C. Jones, S. Aldridge**
***Angew. Chem. Int. Ed.,* 2017, 56, 15098-15102 (DOI: 10.1002/anie.201708496)**



Reduction of indium boryl precursors to give two- and three-dimensional M-M bonded networks is influenced by the choice of supporting ligand. While the unprecedented nanoscale cluster [In$_{68}$(boryl)$_{12}$]$^-$ (with an In$_{12}$@In$_{44}$@In$_{12}$(boryl)$_{12}$ concentric structure), can be isolated from the potassium reduction of a bis(boryl)indium(III) chloride precursor, analogous reduction of the corresponding (benzamidinate)In$^{III}$Br(boryl) system gives a near-planar (and weakly aromatic) tetranuclear [In$_4$(boryl)$_4$]$^{2-}$ system.

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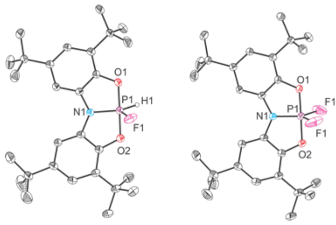
### 175. On the redox reactivity of a geometrically constrained phosphorus(III) compound

**T.P. Robinson, D. De Rosa, S. Aldridge, J.M. Goicoechea**
***Chem.-Eur. J.,* 2017, 23, 15455-15465 (DOI: 10.1002/chem.201703119)**

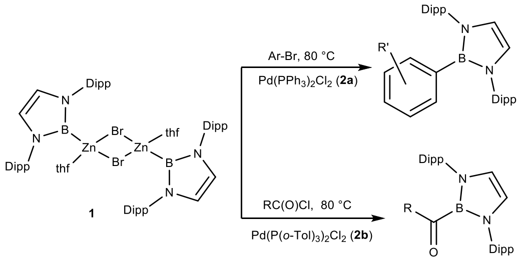


In the latest paper in collaboration with the Goicoechea group, the reactivity of a geometrically constrained phosphorus(III) complex bearing the *N*,*N*-bis(3,5-di-*tert*-butyl-2-phenolate)amide pincer ligand [designated P(ONO)], towards oxidants and reductants is explored.

### 174. A combined experimental/computational study of the mechanism of a palladium-catalyzed bora-Negishi reaction

**J. Campos, A. Nova, E.Kolychev, S. Aldridge**

***Chem.-Eur. J.,*** **2017, 23, 12655-12667 (DOI: 10.1002/chem.201702703)**



A full paper follow-up stemming from Jesus‘ recent communication on the development of a bora-Negishi coupling reaction, examines in depth the mechanism for Pd-catalysed C-B bond formation. A combination of experimental and quantum chemical approaches sheds light on the processes leading to reductive generation of the active Pd(0) species, oxidative addition of the substrate, transmetalation and ultimately product formation via reductive elimination. A common pathway involving pre-dissociation of a phosphine co-ligand is favoured both computationally and from an experimental perspective.

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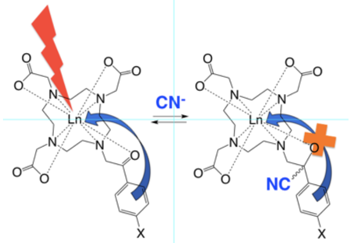
### 173. Lanthanide complexes that respond to changes in cyanide concentration in water

**J. Routledge, X. Zhang, M. Connolly, M. Tropiano, O.A. Blackburn, A.M. Kenwright, P.D. Beer, S. Aldridge, S. Faulkner**

***Angew. Chem. Int. Ed.,*** **2017, 56, 7783-7786 (DOI: 10.1002/anie.201702296)**



In collboration with the Faulkner group, cyanide ions have been shown to interact with lanthanide complexes of phenacylDO3A derivatives in aqueous solution, giving rise to changes in the luminescence and NMR spectra. These changes are the consequence of cyanohydrin formation, favoured by the coordination of the phenacyl carbonyl group to the lanthanide centre. These complexes display minimal affinity for fluoride. By contrast, lanthanide complexes with DOTAM derivatives display no affinity for cyanide in water, but respond to changes in fluoride concentration

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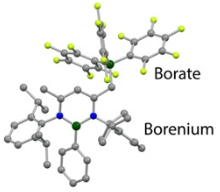
### 172. A zwitterionic hydrocarbon-soluble borenium borate based on a β-diketiminate backbone

**J.A.B. Abdalla, R.C. Tirfoin, H. Niu, S. Aldridge**

***Chem. Commun.*****, 2017, 53, 5981-5984 (DOI: 10.1039/c7cc03121a)**



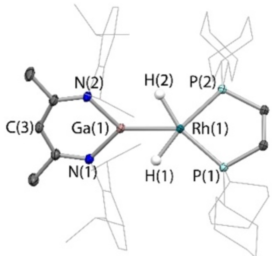
ZWITTERIONIC
LEWIS ACIDS

A synthetic route has been developed to access strongly Lewis acidic borenium cations (and heavier group 13 analogues) featuring a pendant weakly-coordinating borate function. The resulting hydrocarbon-soluble zwitterions display comparable Lewis acidity to $B(C_6F_5)_3$, despite featuring a pendant (non-fluorinated) aryl group and two flanking N-donors.

### 171. Structural snapshots of concerted double E-H bond activation at a transition metal centre

**J.A.B. Abdalla, A. Caise, C. Sindlinger, R. Tirfoin, A.L. Thompson, A.J. Edwards, S. Aldridge**

***Nature Chem.,* 2017, 9, 1256-1262 (DOI: 10.1038/nchem.2792)**



In this work from Joe Abdalla and Alexa Caise, in collaboration with Alison Edwards at ANSTO, we report on fundamental studies defining a new oxidative activation pathway. Combined experimental and computational approaches yield structural snapshots of the simultaneous activation of both bonds of an $EH_2$ unit at a single metal center. Systematic variation of the supporting ligands on the transition metal and single crystal X-ray/neutron diffraction are exploited in tandem to allow structural visualization of the activation process, from a $\kappa^2$ $\sigma$-complex showing little E-H bond activation, through species of intermediate geometry featuring stretched E-H and compressed M-H/M-E bonds, to a fully activated metal carbenoid dihydride.

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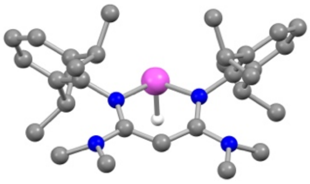
### 170. Highly electron rich β-diketiminato systems: Synthesis and coordination chemistry of amino functionalized 'Nnacnac' ligands

**D.C.H. Do, A. Keyser, A. V. Protchenko, B. Maitland, I. Pernik, H. Niu, E.L. Kolychev, A Rit, A. Stasch, C. Jones, S. Aldridge**

***Chem.-Eur. J.,* 2017, 23, 5830-5841 (DOI: 10.1002/chem.201700757)**



In collaboration with Cameron Jones' group at Monash, a series of highly electron rich amino-functionalized $[\text{Nnacnac}]^-$ ligands has been synthesized and the coordination chemistry of these systems probed. Two different synthetic strategies have been developed to give access to diimine pro-ligands of the type $\{RNC(NMe_2)\}_2CH_2$ (R = Ph, Mes, Dipp, ${}^tBu$) and a variety of metallation strategies developed. Subsequent coordination chemistry at tin(II) and ytterbium(II) centres reveals that the steric profile of the N-substituents exerts subtle influence over the electronic properties of these novel donors.

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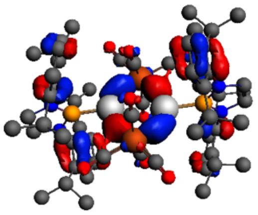
### 169. Boryl substituted group 13 metallylenes: complexes with an iron carbonyl fragment

**D. Dange, C.P. Sindlinger, S. Aldridge, C. Jones**

***Chem. Commun*., 2017, 53, 149-152 (DOI: 10.1039/C6CC08449D)**

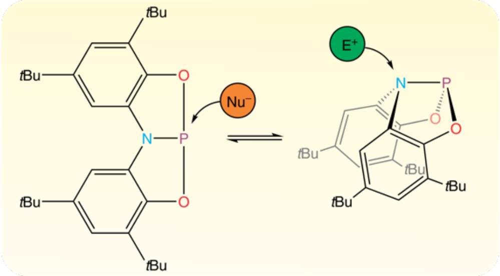


In the first of two papers looking at the controlled reduction of boryl-substituted group 13 halides in collaboration with the Jones group, the first examples of boryl substituted aluminylene and gallylene complexes are reported. $[(DAB)B(THF)Al\{Fe(CO)_3(\mu\text{-}CO)\}]_2$ and $[(DAB)BGa\{\mu\text{-}Fe(CO)_4\}]_2$ (DAB = $\{(C_6H_3Pr^i_2\text{-}2,6)NCH\}_2$) have been prepared by reduction of $MX_2(THF)\{B(DAB)\}$ (M = Al or Ga, X = Cl or Br) with $K_2[Fe(CO)_4]$.

### 168. On the ambiphilic reactivity of geometrically constrained phosphorus(III) and arsenic(III) compounds: Insights into their interaction with ionic substrates

**T.P. Robinson, S.-K. Lo, D. De Rosa, S. Aldridge, J.M. Goicoechea**

***Chem. Eur.-J.,* 2016, 22, 15712-15724 (DOI: 10.1002/chem.201603135)**



In a full-paper follow up to our earlier communication in *Angewandte Chemie*, the ambiphilic nature of geometrically constrained group 15 complexes bearing the *N*,*N*-bis(3,5-di-*tert*-butyl-2-phenolate)amide pincer ligand ($ONO^{3-}$) is explored in collaboration with Jose Goicoechea. Despite their differing reactivity towards nucleophilic substrates with polarized element–hydrogen bonds (e.g. $NH_3$), both the phosphorus(III), P(ONO), and arsenic(III), As(ONO) compounds exhibit similar reactivity towards charged nucleophiles and electrophiles.

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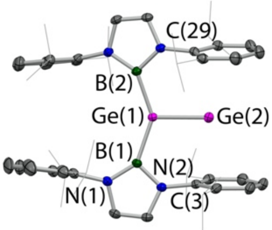
### 167. A stable heavier Group 14 analogue of vinylidene

**A. Rit, J. Campos, H. Niu, S. Aldridge**

***Nature Chem.,* 2016, 8, 1022-1026 (DOI: 10.1038/nchem.2597)**



Vinylidene ($H_2C=C$) is a member of the family of compounds of composition CH (and is isomeric with ethyne, $HC\equiv CH$) but remarkably, no structurally characterized compounds of the type $R_2E=E$ have been reported for any Group 14 element. By employing the sterically bulky and strongly donating boryl ligand $(HCDippN)_2B$, a simple monomeric digermavinylidene compound $(boryl)_2GeGe$ can be synthesized which is stable at room temperature. Structural and computational studies of $\{(HCDippN)_2B\}_2GeGe$ reveal a weak GeGe double bond (the $\pi$ component of which contributes to the HOMO), with a Ge-centred lone pair as the HOMO-1.

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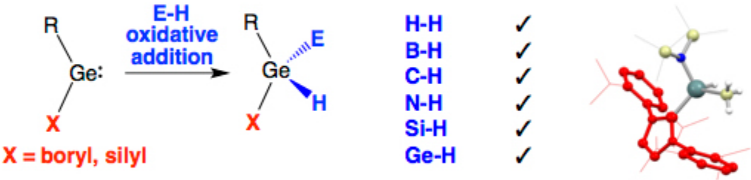
### 166. A systematic study of structure and E-H bond activation chemistry by sterically encumbered germylene complexes

**M. Usher, A.V. Protchenko, A. Rit, J. Campos, E.L. Kolychev, R. Tirfoin, S. Aldridge**

***Chem.-Eur. J.,* 2016, 22, 11685-11698 (DOI: 10.1002/chem.201601840)**



A systematic study of the effects of the $\alpha$-substituents on the geometric/electronic structure and reactivity of acyclic germylene complexes reveals that wide R(X)Ge: angles, narrow HOMO-LUMO gaps and high reactivity towards E-H activation are associated with systems bearing boryl or silyl groups at X.

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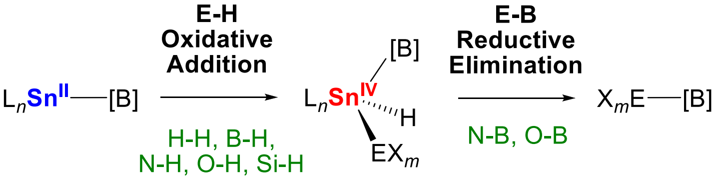
### 165. Enabling and probing oxidative addition and reductive elimination at a Group 14 metal center: cleavage and functionalization of E-H bonds by a *bis*(boryl)stannylene

**A.V. Protchenko, J.I. Bates, L.M.A. Saleh, M.P. Blake, A.D. Schwarz, E.L. Kolychev, A.L. Thompson, C. Jones, P. Mountford, S. Aldridge**

***J. Am. Chem. Soc.*, 2016, 138, 4555-4564 (DOI: 10.1021/jacs.6b00710)**



Redox-based bond cleavage/formation of ammonia is demonstrated for a single-site Main Group system at room temperature. From a mechanistic viewpoint, a two-step coordination/proton transfer process for N-H activation is shown to be viable through the isolation of species of the types Sn(boryl)$_2$·NH$_3$ and [Sn(boryl)$_2$(NH$_2$)]$^-$ and their onward conversion to the formal oxidative addition product Sn(boryl)$_2$(H)(NH$_2$).

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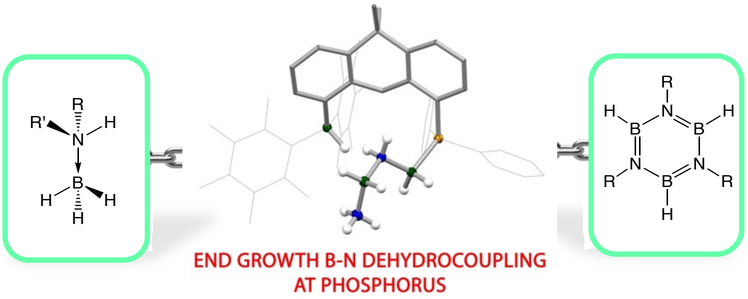
### 164. Catalytic B-N dehydrogenation using frustrated Lewis pairs: evidence for a chain-growth coupling mechanism

**Z. Mo, A. Rit, J. Campos, E.L. Kolychev, S. Aldridge**

***J. Am. Chem. Soc.*, 2016, 138, 3306-3309 (DOI: 10.1021/jacs.6b01170)**



The catalytic dehydrogenation of amine-boranes by a dimethylxanthene-derived FLP is described. Turnover is facilitated thermodynamically by the ready release of H$_2$ from the weakly basic PPh$_2$-containing system. Isolated intermediates provide evidence for a mechanism initiated by B-H activation, followed by end-growth BN coupling involving the terminal NH bond of the bound BN fragment and a BH bond of the borane monomer.

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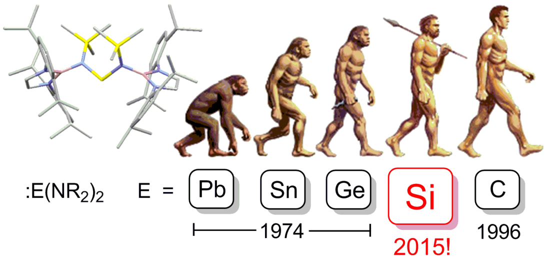
### 163. Stabilization of a two-coordinate, acyclic diaminosilylene (ADASi): completion of the series of isolable diaminotetrylenes,:E(NR$_2$)$_2$ (E = group 14 element)

**T.J. Hadlington, J.A.B. Abdalla, R. Tirfoin, S. Aldridge, C. Jones**

***Chem. Commun.*, 2016, 52, 1717-1720 (DOI: 10.1039/C5CC09673A)**



The latest paper from a long-standing collaboration with the group of Cameron Jones at Monash University, exploiting a new class of (boryl)amido ligand to stabilize a two-coordinate acyclic silylene. While examples of related compounds from the other Group 14 elements have been known for decades, a missing link is therefore finally realized.

### 162. Modern main group chemistry

**S. Aldridge, C. Jones**
***Chem. Soc. Rev.*, 2016, 45, 763-764 (editorial; DOI: 10.1039/C6CS90014C)**

Editorial introducing a special issue on Chemical Society Reviews on recent developments in main group chemistry.

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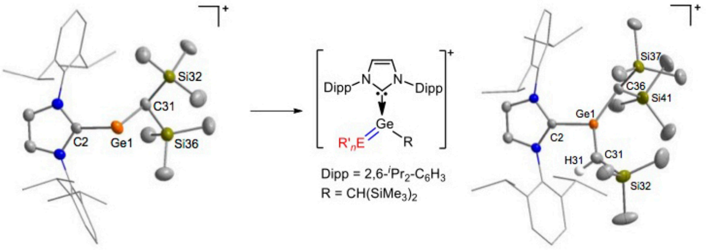
### 161. Exploiting electrostatics to generate unsaturation: oxidative Ge=E bond formation using a non π-donor stabilized $[R(L)Ge:]^+$ cation

**A. Rit, R. Tirfoin, S. Aldridge**
***Angew. Chem. Int. Ed.*, 2016, 55, 378-382 (DOI: 10.1002/anie.201508940)**



The 2-coordinate Ge cation $[(IDipp)\{(Me_3Si)_2CH\}Ge:]^+$ has been synthesized, which lacks π-donor stabilization and consequently has a very small HOMO-LUMO gap (187 kJ/mol). It undergoes facile oxidative bond-forming reactions, most notably allowing access to the first examples of Group 14 metal cations containing M=E multiple bonds (E = C, N).

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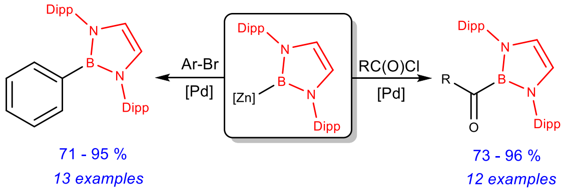
### 160. Catalytic borylation using an air-stable zinc boryl reagent: systematic access to elusive acylboranes

**J. Campos, S. Aldridge**
***Angew. Chem. Int. Ed.*, 2015, 54, 14159-14163 (DOI: 10.1002/anie.201507627)**



Here we describe for the first time the use of borylzinc reagents in Pd-catalyzed borylation chemistry – a C-B coupling protocol analogous to well-known Negishi chemistry. This approach is shown to enable the first systematic method for the preparation of acylboranes, whose conversion into synthetically useful acyltrifluoroboronates can be demonstrated.

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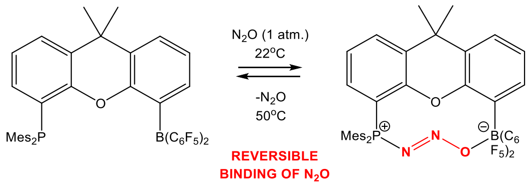
### 159. Facile reversibility by design: tuning small molecule capture and activation by single component frustrated Lewis pairs

**Z. Mo, E.L. Kolychev, A. Rit, J. Campos, H. Niu, S. Aldridge**
***J. Am. Chem. Soc.*, 2015, 137, 12227-12230 (DOI: 10.1021/jacs.5b08614)**



The single component dimethylxanthene based FLP $\{(C_6H_4)_2(O)CMe_2\}(PMes_2)(B(C_6F_5)_2)$ has been designed to effect reversible small molecule capture/activation, and (i) heterolytically cleaves $H_2$ to give an equilibrium mixture of FLP and activation product in solution at room temperature, and (ii) reversibly captures $N_2O$ (uptake at 20°C and 1 atm; release at 323 K).

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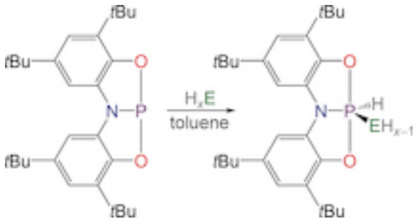
### 158. E–H bond activation of ammonia and water by a geometry-constrained phosphorus(III) compound

**T.P. Robinson, D.M. De Rosa, S. Aldridge, J.M. Goicoechea**

***Angew. Chem. Int. Ed.*, 2015, 54, 13758-13763 (DOI: 10.1002/anie.201506998)**



As part of a collaboration with Jose Goicoechea's group, a $P^{III}$ compound bearing a *N*,*N*-bis(3,5-di-*tert*-butyl-2-phenoxy)amide ligand has been shown to react with $NH_3$ and $H_2O$, activating the E-H bonds in both substrates by formal oxidative addition. In the case of water, both O-H bonds can be activated, splitting the molecule into its constituent elements - the first time that a compound based on Main Group elements has been show to sequentially activate water in this manner.

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### 157. Frustrated Lewis pairs

**Z. Mo, S. Aldridge**

**Patent application: GB1510312, filed 12 June 2015**

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### 156. Extension of conjugation: probing anion binding strength and reporter mechanisms in (phenyl)cyclopentadienyl and indenyl receptors

**R. Tirfoin, J.A.B. Abdalla, S. Aldridge**

***Dalton Trans.*, 2015, 44, 13049-13059 (DOI: 10.1039/C5DT01955A)**

Borane receptors featuring a rigidly conjugated indenyl-iron function give rise to enhanced anion binding affinities and ready colorimetric reporting – exemplified above by the selective green-to-pink colour change in the presence of sources of cyanide.

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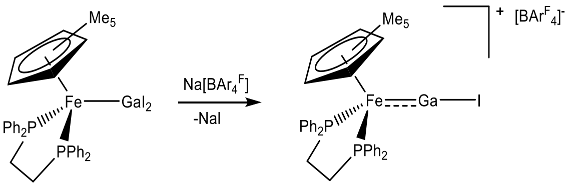
### 155. Group 13 Metal-Metal Bonds

**J.A.B. Abdalla, S. Aldridge**

***Molecular Metal-Metal Bonds. Compounds, Synthesis, Properties* Wiley, February 2015, p455-484 (book chapter, volume editor S. Liddle) (DOI: 10.1002/9783527673353.ch13)**

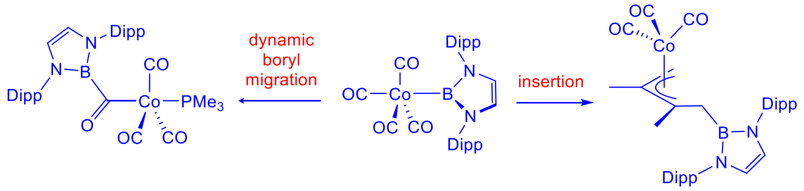


A book chapter examining metal-metal bonds featuring the Group 13 metals aluminium, gallium, indium and thallium, and focussing primarily on unsupported metal-metal bonds in discrete molecular systems, rather than multinuclear clusters described by delocalized schemes of bonding.

### 154. Cobalt boryl complexes: enabling and exploiting migratory insertion in base-metal mediated borylation

**R. Frank, J. Howell, J. Campos, R. Tirfoin, N. Phillips, S. Zahn, D.M.P. Mingos, S. Aldridge**

***Angew. Chem., Int. Ed.*, 2015, 54, 9586-9590 (DOI: 10.1002/anie.201504929)**



The insertion of CO into M–R bonds is a key fundamental step in organometallic chemistry but is hitherto unknown for boryl ligands. We demonstrate CO migratory insertion in Co boryl complexes, and show applications thereof in alkene functionalization – a well-known reaction for noble metals such as Rh or Pt.

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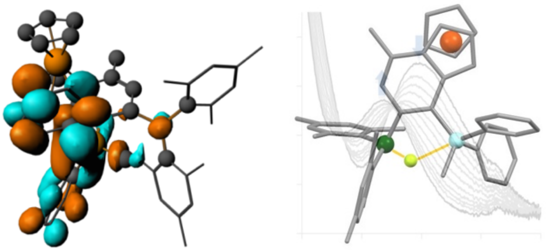
### 153. Bifunctional indenyl-derived receptors for fluoride chelation and detection

**R. Tirfoin, J.A.B. Abdalla, S. Aldridge**

***Chem.-Eur. J.*, 2015, 21, 11813-11824 (DOI: 10.1002/chem.201501547)**



Pre-organized anion receptors based on a CpFe(indenyl) scaffold and featuring *ortho* -BMes$_2$ and –PPh$_2$Me$^+$ groups display selectivity for F$^-$ over CN$^-$ via anion chelation. In the case of the 4-(MePh$_2$P)-5-(Mes$_2$B)-7-Me-indenyl derivative (see figure), F$^-$ uptake is signalled by a large cathodic shift in the Fe$^{II}$/Fe$^{III}$ potential and by a green-to-maroon colour change.

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### 152. Organometallic sensor device

**S. Aldridge, I.A. Fallis**

**Patent: US9023652, granted 5 May 2015**

This invention relates to detectors for fluorine-containing compounds and/or cyanide containing compounds, including HF or HCN gas, hydrofluoric acid in solution, selected chemical warfare agents, selected industrial chemicals which may be hydrolysed to release HF or HCN gas, compounds containing a cyanide group, and compounds that can release HF or HCN.

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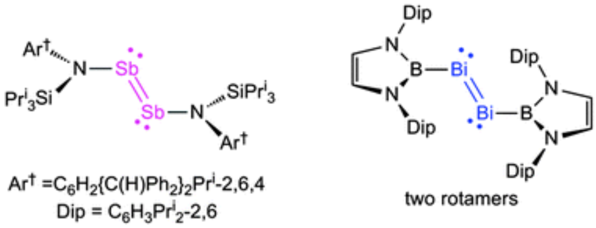
### 151. Utilisation of a lithium boryl as a reducing agent in low oxidation state group 15 chemistry: synthesis and characterization of an amido-distibene and a boryl-dibismuthene

**D. Dange, A. Davey, J.A.B. Abdalla, S. Aldridge, C. Jones**

***Chem. Commun.*, 2015, 51, 7128-7131 (DOI: 10.1039/C5CC01772F)**

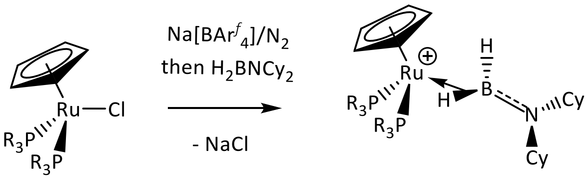


In collaboration with Cameron Jones' group, the first examples of an amido-distibene and a boryl dibismuthene (see picture) have been prepared by reaction of a lithium boryl complex with extremely bulky amido-group 15 dihalide precursor compounds.

### 150. Coordination and activation of E-H bonds (E = B, Al, Ga) at transition metal centres

**I.M. Riddlestone, J.A.B. Abdalla, S. Aldridge**

***Adv. Organomet. Chem.*, 2015, 63, 1-38 (DOI:10.1016/bs.adomc.2015.02.003)**



Developments in the coordination chemistry of B-H, Al-H and Ga-H bonds at transition metal centres are reviewed, with particular emphasis on factors influencing electronic/geometric structure and the extent/mode of bond activation.

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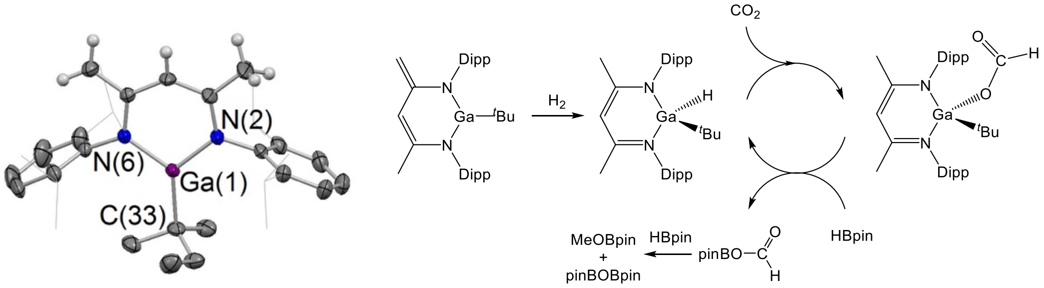
### 149. Cooperative bond activation and catalytic reduction of carbon dioxide at a Group 13 metal centre

**J.A.B. Abdalla, I.M. Riddlestone, R. Tirfoin, S Aldridge**

***Angew. Chem., Int. Ed.*, 2015, 54, 5098-5102 (DOI: 10.1002/anie.201500570)**



A single component ambiphilic Group 13 system has been developed capable of the co-operative activation of protic, hydridic and apolar H-X bonds. The hydride complex derived from the activation of $H_2$ catalyzes the selective transformation of $CO_2$ to a methanol derivative, representing the first example of a reduction process catalyzed by a molecular Ga-containing complex.

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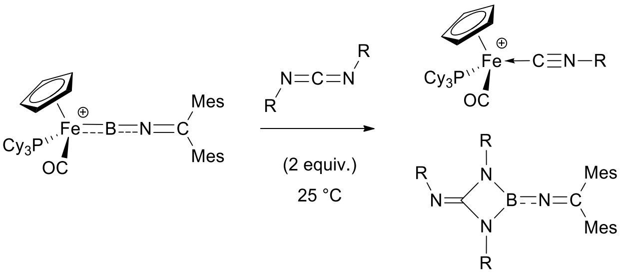
### 148. Iminoborylene complexes: evaluation of synthetic routes towards BN-allenylidenes and unexpected reactivity towards carbodiimides

**J. Niemeyer, M.J. Kelly, I.M. Riddlestone, D. Vidovic, S. Aldridge**

***Dalton Trans.*, 2015, 44, 11294-11305 (DOI: 10.1039/C5DT00131E)**

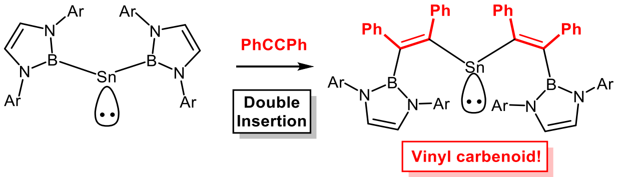


The iminoborylene complex $[CpFe(PCy_3)(CO)(BNCMes_2)]^+$ undergoes M=B metathesis reactivity with carbodiimides, resulting in Fe=B cleavage and the formation of isonitrile complexes.

### 147. Reactivity of boryl- and silyl-substituted carbenoids towards alkynes: insertion and cycloaddition chemistry

**A.V. Protchenko, M.P. Blake, A.D. Schwarz, C. Jones, P. Mountford, S. Aldridge**

***Organometallics,* 2015, 34, 2126-2129 (DOI: 10.1021/om501252m)**



Different modes of reactivity of alkynes towards acyclic tetrelenes are reported: reaction pathways are dependent not only on the Group 14 element, but also on the supporting ligand set. Systems featuring Sn-B or Ge-B bonds undergo insertion chemistry while a more strongly reducing $Si^{II}$ system undergoes [2+1] cycloaddition chemistry

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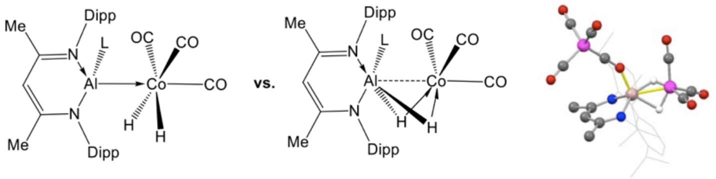
### 146. Coordination and activation of Al-H and Ga-H bonds

**J.A.B. Abdalla, I.M. Riddlestone, J. Turner, P.A. Kaufman, R. Tirfoin, N. Phillips, S. Aldridge**

***Chem.-Eur. J.*, 2014, 20, 17624-17634 (DOI: 10.1002/chem.201405018)**



The modes of interaction of two families of Group 13 hydrides (E = Al, Ga) have been investigated towards 14- and 16-electron transition metal fragments, revealing considerable diversity in terms of the patterns of reactivity uncovered. More electron-rich alanes/gallanes of the type $NHC·EH_3$ (E = Al or Ga) uniformly generate $\kappa^2$ $\sigma$-complexes. By contrast, □eta-diketiminato (‘Nacnac’) stabilized systems, $\{HC(MeCDippN)_2\}EH_2$, show much more diverse chemistry, including examples of hitherto unprecedented E-H bond activation.

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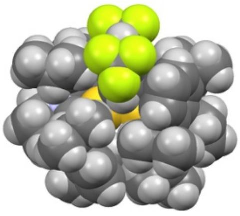
### 145. Expanded ring N-heterocyclic carbenes in the stabilization of highly electrophilic gold(I) cations

**N. Phillips, T. Dodson, R. Tirfoin, J.I. Bates, S. Aldridge**

***Chem.-Eur. J.*, 2014, 20, 16721-16731 (DOI: 10.1002/chem.201404939)**

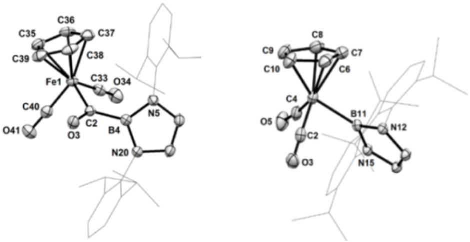


Highly electrophilic $Au^I$ complexes are synthesized featuring bulky expanded-ring NHCs. Electron rich hydrides (NHC)AuH are protonated to generate $[\{(NHC)Au\}_2(\mu\text{-}H)]^+$ (NHC = 6-Dipp or 7-Dipp), while activation by $B(C_6F_5)_3$ generates a labile species featuring the $[HB(C_6F_5)_3]^-$ fragment. Halide abstraction from (NHC)AuCl using $Na[BAr^f_4]$ generates $[\{(NHC)Au\}_2(□\text{-}Cl)]^+$ species which are still electrophilic enough at gold to abstract $Ar^f$ from $[BAr^f_4]^-$.

### 144. Circumventing redox chemistry: synthesis of transition metal boryl complexes from a boryl nucleophile by decarbonylation

**R. Frank, J. Howell, R. Tirfoin, D. Dange, C. Jones, D.M.P. Mingos, S. Aldridge**

***J. Am. Chem. Soc.*, 2014, 136, 15730-15741 (DOI: 10.1021/ja508979x)**



Labile charge neutral bora-acyl derivatives of the type $L_nM\{C(O)B(NDippCH)_2\}$ [$L_nM$ = $Mn(CO)_5$, $Re(CO)_5$, $CpFe(CO)_2$] can be synthesized which cleanly lose CO to generate M–B bonds. From a mechanistic standpoint, an archetypal organometallic mode of reactivity, carbonyl extrusion, has been shown to be applicable to the boryl ligand class, with $^{13}C$ isotopic labeling studies confirming a dissociation/migration pathway.

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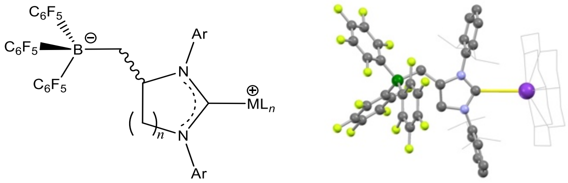
### 143. Anionic *N*-heterocyclic carbenes (NHCs): a versatile route to saturated NHCs bearing pendant weakly coordinating anions

**N. Phillips, R. Tirfoin, S. Aldridge**

***Dalton Trans.*, 2014, 43, 15279-15282 (DOI: 10.1039/C4DT02662D)**



A versatile methodology is reported for the synthesis of anionic NHCs featuring a 5-, 6-, or 7-membered saturated heterocyclic core. Lewis acid promoted exocyclic ring closure generates systems in which the pendant borate functionality is incorporated via a $CH_2$ linker, allowing for electronic and steric isolation of the anionic component. Hence, a library of NHCs can be accessed which incorporate metal binding environments essentially identical to the neutral parent donors, but with significantly altered solubility profiles.

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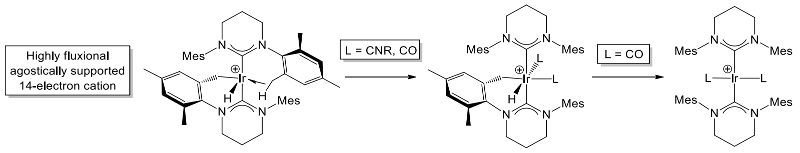
### 142. Rationalizing and disrupting fluxional processes in agostically stabilized 14-electon alkyliridium hydride complexes

**N. Phillips, L. Treasure, N.H. Rees, R. Tirfoin, J.E. McGrady, S. Aldridge**

***Eur. J. Inorg. Chem.*, 2014, 4877-4885 (DOI: 10.1002/ejic.201402516)**

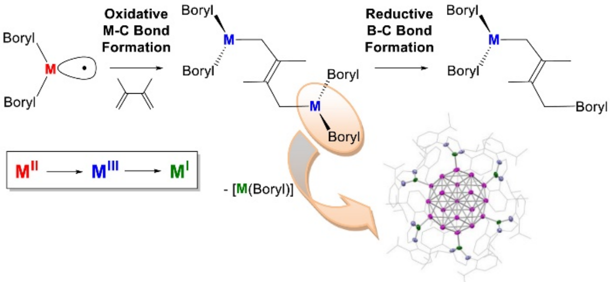


The mechanism of fluxional exchange in cationic *bis*(NHC) Ir(III) systems featuring an agostic C-H bond and *cis* alkyl /hydride ligands is shown by a combination of VT-NMR and DFT methods to feature an oxidative pathway. Related non-fluxional systems can be ‘trapped’ by the addition of two electron donors (L), and the stability of such systems to C-H reductive elimination tuned through the π-acceptor properties of L.

### 141. Five valence electron Main Group systems: oxidative bond formation and reductive bond cleavage

**A.V. Protchenko, D. Dange, A.D. Schwarz, M.P. Blake, C. Jones, P. Mountford, S. Aldridge**

***J. Am. Chem. Soc.,* 2014, 136, 10902-10905 (DOI: 10.1021/ja5062467)**



Monomeric five-valence-electron *bis*(boryl) complexes of gallium, indium and thallium undergo oxidative M-C bond formation with 2,3-dimethylbutadiene, in a manner consistent with both the redox properties expected for $M^{II}$ species and with metal-centered radical character. The weaker nature of the M-C bond for the heavier two elements leads to the observation of reversibility in M-C bond formation (for indium) and to the isolation of products resulting from subsequent B-C reductive elimination (for both indium and thallium).

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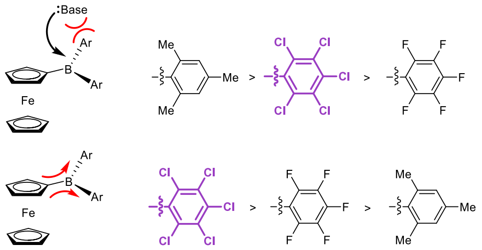
### 140. Synthetic, redox and coordination chemistry of *bis*(pentachlorophenyl)boryl ferrocene, $FcB(C_6Cl_5)_2$

**M.J. Kelly, R. Tirfoin, J. Gilbert, S. Aldridge**

***J. Organomet. Chem.*, 2014, 769, 11-16 (DOI: 10.1016/j.jorganchem.2014.07.003)**



Violet-blue bis(pentachlorophenyl)boryl ferrocene, $FcB(C_6Cl_5)_2$, can be synthesized from ferrocenyllithium and $ClB(C_6Cl_5)_2$, and features an extremely electron-deficient Fe(II) centre ($E_{1/2}$ = +550 mV vs. FcH/$FcH^+$). Studies of this and related ferrocenylboranes allow the relative steric and electronic properties of the $C_6Cl_5$ group to be ranked against other aryl substituents (shown below).

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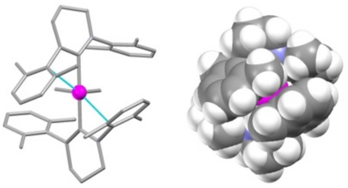
### 139. Modulating reactivity in iridium *bis*(N-heterocyclic carbene) complexes: influence of ring size on E-H bond activation chemistry

**N. Phillips, J.I. Bates, C.Y. Tang, R. Tirfoin, M.J. Kelly, A.L. Thompson, M.J. Gutman, S. Aldridge**

***Dalton Trans.*, 2014, 43, 12288-12298 (DOI: 10.1039/C4DT01398K)**

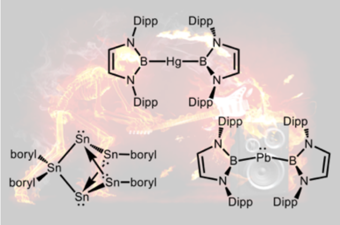


The changes in the steric and electronic properties of N-heterocyclic carbenes (NHCs) as a function of ring size have a profound effect on the reactivity of their late transition metal complexes. Comparison of closely related complexes featuring saturated 5- or 6-membered NHCs reveals that the larger ring is associated with an increased tendency for *intramolecular* C-H activation, but lower reactivity towards external substrates. Among systems of the type $[IrL_2(H)_2]^+$, highly labile $[Ir(5\text{-}Mes)_2(H)_2]^+$ can only be studied by trapping experiments, while $[Ir(6\text{-}Mes)_2(H)_2]^+$ is air and moisture stable, and unreactive towards amineboranes.

### 138. Heavy metal boryl chemistry: complexes of cadmium, mercury and lead

**A.V. Protchenko, D. Dange, A.D. Schwarz, C.Y. Tang, N. Phillips, P. Mountford, C. Jones, S. Aldridge**

***Chem. Commun.,* 2014, 50, 3841-3844 (DOI: 10.1039/C4CC00697F)**



Heavy metal boryl complexes: the first boryl complexes of cadmium and mercury are reported via transmetallation from boryllithium; the syntheses of related tin and lead systems highlight the additional factors associated with extension to more redox-active post-transition elements.

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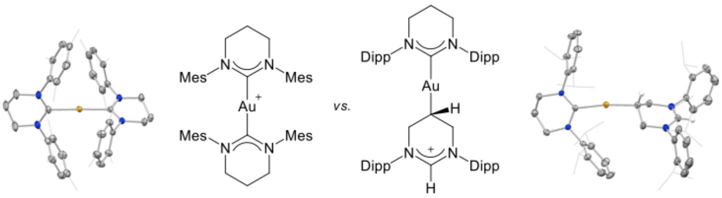
### 137. Probing the limits of ligand steric bulk: C-H and C-N bond activation in highly encumbered expanded ring N-heterocyclic carbenes

**N. Phillips, R. Tirfoin, S. Aldridge**

***Chem.-Eur. J.*, 2014, 20, 3825-3830 (DOI: 10.1002/chem.201304243)**



The consequences of extremely high steric loading have been probed for late transition metal complexes featuring the expanded ring NHC 6-Dipp. In the presence of [(6-Dipp)Au]$^+$, the first example of backbone C-H activation of a saturated N-heterocyclic carbene is revealed, proceeding *via* a mechanism which involves free carbene in addition to the Au(I) centre.

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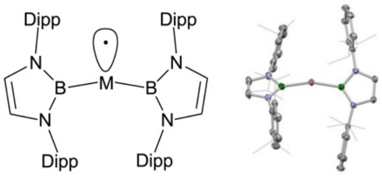
### 136. Stable $GaX_2$, $InX_2$ and $TlX_2$ radicals

**A.V. Protchenko, D. Dange, J. Harmer, C.Y. Tang, A.D. Schwarz, M.J. Kelly, N. Phillips, K.H. Birjkumar, C. Jones, N. Kaltsoyannis, P. Mountford, S. Aldridge**

***Nature Chem.,* 2014, 6, 315-319 (DOI:10.1038/nchem.1870)**



In this study, we report the synthesis and structural characterization of the first thermally robust monomeric $MX_2$ species of gallium, indium and thallium. By making use of the high steric loading of the $B(NDippCH)_2$ substituent (Dipp = 2,6-$^iPr_2C_6H_3$), synthetic routes to mono-metallic compounds of the type $M^{II}\{B(NDippCH)_2\}_2$ (M = Ga, In, Tl) – each of which decomposes only above 130 °C – can be devised from either $M^I$ or $M^{III}$ precursors.

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M.J. Kelly, J. Gilbert, R. Tirfoin, S. Aldridge
*Angew. Chem., Int. Ed.*, 2013, 52, 14094-14097 (DOI: 10.1002/anie.201308475)

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J. Turner, J.A.B. Abdalla, J.I. Bates, R. Tirfoin, M.J. Kelly, N. Phillips, S. Aldridge
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A.V. Protchenko, A.D. Schwarz, M.P. Blake, C. Jones, N. Kaltsoyannis, P. Mountford, S. Aldridge
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