PERSPECTIVE

Pincer-Supported Metal/Main-Group Bonds as Platforms for Cooperative Transformations

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Electron-rich late metals and electropositive main-group elements (metals and metalloids) can be combined to provide an ambiphilic façade for exploring metal–ligand cooperation, yet the instability of the metal/main-group bond frequently limits the study and application of such units. Incorporating main-group donors into pincer frameworks, where they are stabilized and held in proximity to the transition-metal partner, can allow discovery of new modes of reactivity and incorporation into catalytic processes. This Perspective summarizes common modes of cooperativity that have been demonstrated for pincer frameworks featuring metal/main-group bonds, highlighting similarities among boron, aluminium, and silicon donors and identifying directions for further development.

Introduction

Transition metals are indispensable members of the synthetic chemist's toolbox, enabling a wide variety of stoichiometric and catalytic transformations that can be tuned by judicious choice of metal and supporting ligands. Such reactivity is typically enabled by the presence of partially filled *d* orbitals that can engage in redox, ligand exchange, and a variety of "classic" organometallic transformations to break and form bonds.[1]

As chemists seek new mechanisms for metal-promoted reactions, significant effort has recently been invested in understanding and elaborating cooperative pathways, whereby multiple reactive units work together to effect otherwise unachievable transformations.[2, 3] This work represents a natural extension of our understanding that many processes occurring at single metal centres (e.g., oxidative addition of H_2) can be envisaged as resulting from synergistic activity of filled and empty metal-based orbitals (i.e., orbital cooperation),[4] and also builds strongly on the concept of Frustrated Lewis Pairs (FLPs) initially described using non-metals and metalloids.[5-7] The framework of cooperativity has been applied to a vast array of transition-metal systems, providing many opportunities for creative synthesis of scaffolds to promote new reactions.

The metalloid main-group elements, with their high Lewis acidity and low electronegativity, are appealing cooperative partners to pair with electron-rich late transition metals.[8, 9] However, examination of cooperative reactivity at transition metal/metalloid bonds is hindered somewhat by the instability of such linkages. Reactions at M–E bonds frequently result in M–E scission,[10, 11] making the processes difficult to interrogate and in some cases limiting applications. We and others have thus sought to stabilize and limit the configurational flexibility of such linkages by incorporating them into robust pincer-type frameworks, allowing us to unearth and study previously unobserved cooperative reactivity.

This short review highlights several classes of cooperative reactions occurring at pincer-supported transition-metal/main-group bonds, principally silicon, boron, and aluminium. An effort has been made to focus on commonalities among the systems, grouping similar reactions into four classes enabled by transition-metal/main-group cooperation: (1) substrate activation and directed reactions; (2) fluxional processes where substituents are reversibly shuttled between the metal and main-group donor; (3) 1,2-additions and cycloadditions; and (4) cooperative redox processes. In the spirit of focusing on unusual mechanisms (with the goal of inspiring continued development), this review will primarily examine stoichiometric reactivity. For more information on catalytic applications, including some of the processes discussed herein, the interested reader is directed to Takaya's recent review of catalysis promoted by transition-metal systems featuring bonds to main-group metals and metalloids.[12]

Substrate Activation and Directed Reactions

The three main-group elements considered here (boron, aluminium, and silicon), are quite electropositive. In many pincer-type complexes these elements serve as Lewis acids, opening the possibility of coordinating a Lewis base to initiate reactivity. Coordination of a Lewis base would be expected to increase electron density on the metal as well as potentially control the regioselectivity of subsequent reactions. Ozerov and co-workers provided an intriguing example of this sort of reactivity, where pyridine coordination to a (PBP)Ir(CO)$_2$ complex was followed by stereospecific C–H activation (Scheme 1).[13] Similar directed reactions have been observed for Al/Rh[14] and Al/Ni[15] systems, enabling catalytic hydropyridylation of alkenes with the Al/Rh system.

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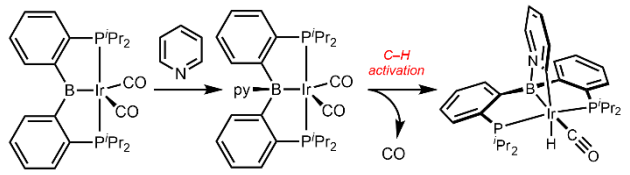
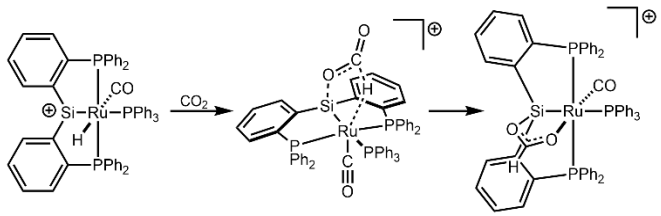


Scheme 1. Substrate coordination to boron directs C–H activation at (PBP)Ir

In most directed C–H activation reactions, the metal plays dual roles as Lewis acid and platform for C–H activation. The powerful approach outlined in Scheme 1 decouples the two roles, enabling a distinct selectivity from what is observed, e.g., with the Sanford-type Pd systems for functionalization of *N*-heterocycles.[16] In principle, creative ligand design can allow Lewis acid/base interactions to steer selectivity toward a variety of positions, in much the same way as substrate/protein interactions can lead to high stereospecificity in biological systems by controlling the orientation of substrate relative to the active site.

A highly electrophilic metalloid attached to the transition-metal centre can also activate a substrate toward nucleophilic attack. We showed that a pincer-supported cationic ruthenium silylene complex can promote hydride transfer to CO_2.[17] The process occurs via [3+2]-cycloaddition to a ruthenium hydride, with the electrophilic silylene serving to polarize the C=O bond and stabilize the intermediate and ultimate product by forming a strong Si–O bond (Scheme 2). This reaction bears close similarity to Hazari's report that CO_2 can be activated toward hydride transfer from iridium through interaction with an N–H hydrogen bond donor that is the central element in a PNP pincer ligand.[18]



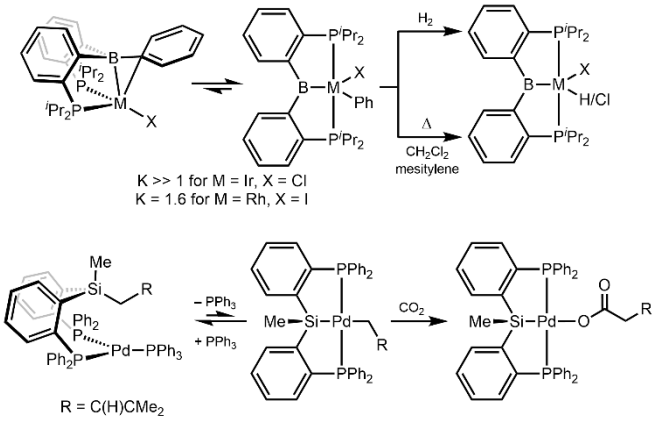
Scheme 2. An electrophilic silylene activates CO_2 toward hydride transfer

Reversible Bond Formation and Fluxionality

The kinetic lability of organoboron and organosilicon compounds allows for their use as nucleophilic partners in cross-coupling reactions,[19, 20] and facile exchange of neutral (L-type) ligands is a key step in directed catalytic C–H functionalization of the sort discussed in the previous section.[14] Thus, it should come as no surprise that pincer complexes featuring metalloid donors are prone to rearrangements and redistribution of substituents between the transition metal and metalloid.

The simplest case of such a process is exemplified by the reversible oxidative addition of boron–carbon bonds at rhodium and iridium centres reported by Ozerov (Scheme 3, top).[21] As expected based on periodic trends, the more reducing iridium centre favours complete insertion into the B–Ph bond, whereas a rhodium analogue forms an equilibrium mixture of boryl and borane complexes, related to each other through reversible 1,2-migration of the phenyl group. The equilibrium is highly sensitive not only to the metal, but also to the co-ligands.[22] For instance, exchange of phenyl for hydride (reaction with H_2) or chloride (thermolysis in the presence of CH_2Cl_2) leads to exclusive conversion to the inserted product.[21] Related bond activations and redistributions (e.g., B–Ph → B–I)[23] have been reported for group 10 metals by Tauchert and co-workers, highlighting the generality of these processes for (PBP)M systems.

Pincer-complexes featuring central silicon donors exhibit much of the same fundamental reactivity as the (PBP)M complexes. For instance, Takaya and Iwasawa have demonstrated reversible Si–H and Si–C oxidative addition at group 10 metal centres,[24] including the carboxylation of a prenyl group via silicon-to-palladium migration followed by CO_2 insertion (Scheme 3, bottom).[25] As with (PBP)M systems, the position of the oxidative addition equilibrium is dependent on the metal (e.g., platinum favours Si–H oxidative addition to a much greater extent than palladium or nickel), and one might expect that it can be tuned through judicious choice of co-ligands.

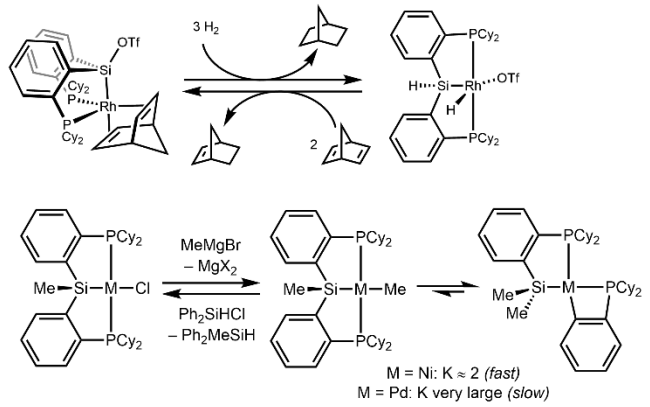


Scheme 3. Reversible metal insertions into B–C and Si–C bonds

In a similar vein, our research has shown that (PSiP)Rh complexes undergo a variety of bond redistributions, enabling the interconversion of Si–H with Si–Cl and Si–OTf (Scheme 4, top),[26, 27] processes that are largely off-cycle during hydrogenation catalysis but may be useful in other catalytic reactions under investigation. Lee has reported similar fluxionality for (PSiP)Ni, where exchange of aryl and amide ligands between silicon and nickel is proposed to play a key role in facilitating carbamate formation by amide transfer to CO_2.[28]

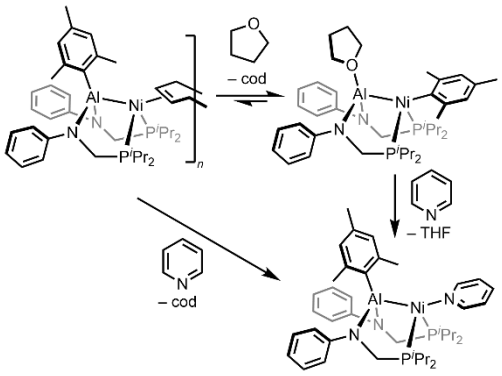
The fluxionality of (PSiP)M complexes can also lead to disruption of the pincer motif. For instance, Turculet and co-workers demonstrated reversible silicon-to-metal migration of the phenylene linker of the pincer ligand in group 10 (PSiP)M–CH_3 complexes (Scheme 4, bottom).[29] The rate of this process and the degree to which the rearranged product is favoured depend strongly on the metal, with nickel complexes quickly achieving an equilibrium mixture of isomers at ambient temperature and palladium complexes exclusively forming the

rearranged, non-pincer complex but requiring elevated temperatures to do so. Investigation of allene carboxylation by Hazari and co-workers revealed similar processes, and as with the hydrogenation reactions demonstrated by our lab, rearrangement was implicated in off-cycle equilibria but not the primary catalytic cycle.[30]



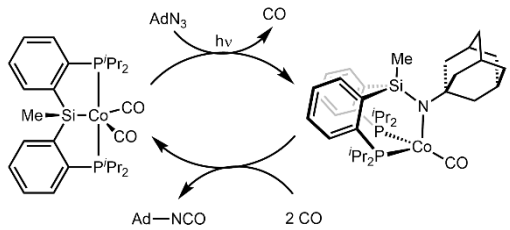
Scheme 4. Reversible substituent exchange at (PSiP)M complexes

Lu and co-workers have recently reported similar reactions for a (PAlP)Ni complex, where addition of a Lewis base promotes aluminium-to-nickel migration of a mesityl group (Scheme 5).[15] The reaction appears to proceed via (1) attack of the Lewis base at aluminium, leading to decoordination from nickel, then (2) oxidative addition of the Al–C bond at the resulting Ni(0) complex. This mechanistic proposal is supported by observation of the relevant intermediate both in solution and the solid state. Of particular interest is the fact that aryl migration is promoted by oxygen-containing Lewis bases but not other donors. Phosphine oxides and tetrahydrofuran coordinate preferentially to the highly oxophilic aluminium, whereas pyridine, phosphines, and alkenes coordinate to nickel and do not initiate aryl migration. As might be expected based on the metallic nature of aluminium, (PAlP)M complexes are highly kinetically labile at Al, leading in one extreme case to (PAlP)Rh→(PBP)Al "transelementation" in the presence of boron trifluoride.[31]



Scheme 5. Reversible Al-to-Ni aryl-group migration at (PAlP)Ni

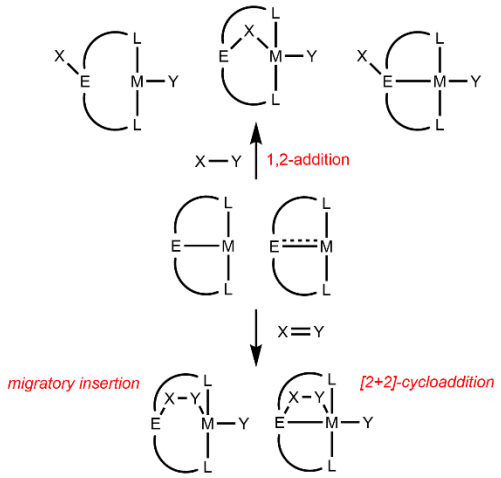
An intriguing and scarcely explored area where reversible bond formation may prove useful involves the ability of electropositive central donors such as silicon to mask the reactivity of multiply bonded or similar units. A first demonstration of this sort was reported by Sola, who showed that a (PSiP)Ru alkylidene complex underwent reversible insertion of the alkylidene into Ru–Si upon addition of neutral donors such as trimethyl phosphite, acetonitrile, or carbon monoxide. The inserted alkylidene retained some reactivity, enabling a coupling with carbon monoxide to generate the corresponding ketene or C–H insertion into an acetylacetonate co-ligand.[32] Very recently, Lee and co-workers have reported a similar conversion of carbon monoxide to adamantyl isocyanate upon Si-enabled nitrene-group transfer from adamantyl azide at (PSiP)Co (Scheme 6).[33] The observed silylamido intermediate behaves as a silyl-protected imido complex, and its formation prevents the irreversible phosphine oxidation by nitrene insertion that would degrade the catalyst and consume azide.[34-36] Analogy to reversible insertion reactions into M–N at (PNP)Ir reported by Grubbs[37] and Tilley[38] suggests that this sort of transformation may be quite general, and the kinetic lability of metalloids mentioned above is likely to play a key role in enabling catalytic applications.



Scheme 6. A cobalt silylamide serves as a masked nitrene for catalytic CO oxidation

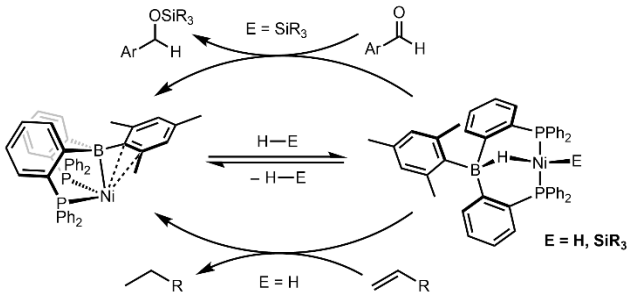
Cooperative Bond Scissions: 1,2-Additions and Cycloadditions

The complementary electronic characteristics of electropositive main-group donors and electron-rich late transition metals offer a powerful platform for cooperative bond scissions. In many cases, the concept of frustrated Lewis pairs (FLPs)[5-7] provides a useful organizational framework for such transformations, and the reactions can be understood as resulting from synergistic Lewis acid/base activation of substrate. The products formed via cleavage of σ or π bonds at a metal/main-group unit are quite varied, as shown in Scheme 7. However, all of these processes are conceptually related and will be discussed together.



Scheme 7. Substrate activation across metal/main-group single or multiple bonds

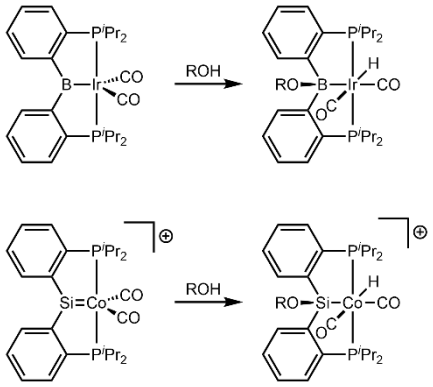
Harman and Peters reported the heterolytic cleavage of hydrogen at (PBP)Ni, an early demonstration of FLP reactivity at a pincer-supported metal/main-group bond. This finding enabled a distinct approach to efficient catalytic alkene hydrogenation (Scheme 8, bottom).[39] Further work with these systems led to development of catalytic carbonyl hydrosilylation following a similar mechanism (Scheme 8, top).[40] 1,2-Additions of H_2, such as the one depicted in Scheme 8, have been shown for pincer complexes featuring metal–aluminium[15] and –silicon bonds,[41] including an (SiOSi)Ni complex that splits H_2 by transferring one hydrogen to each silicon donor.[42] Conceptually similar 1,2-addition of H_2 has been reported at a (PPP)Co complexes with *N*-heterocyclic phosphide central donor, but the presence of a more electronegative, Lewis-basic donor renders this system more similar to the heterolytic H_2 splitting utilized by Noyori-type hydrogenation catalysts.[43] Likewise, the impressive array of 1,2-additions reported by Piers[44] and Iluc[45] for (PCP)M complexes featuring a carbene central donor are omitted here because the reversed polarization of the $M^{\delta+}=C^{\delta-}$ bond leads to distinct outcomes from those observed for more electropositive Si, B, and Al.



Scheme 8. FLP-type hydrogenation and hydrosilylation at a (PBP)Ni complex

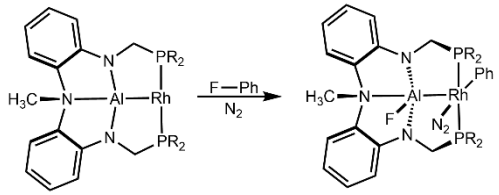
As with the original σ-frustrated phosphine/borane Lewis pairs, 1,2-addition results in partial or total cleavage of the metal/main-group bond; however, the pincer configuration of these transition-metal complexes holds the pieces together, allowing them to react as a single unit. The general process described in Scheme 8 can be realized for a range of substrates, and Tauchert has shown that allyl acetate can be cooperatively (and reversibly) split at (PBP)Pd, attaching acetate to the boron and allyl to the nickel center.[46]

Pincer complexes that contain an unsaturated metal/main-group bond (i.e., boryl, aluminyl, and silylene) may undergo net 1,2-addition without cleavage of the M–E bond. Ozerov reported the 1,2-additions of alcohols and *n*-butylamine to $(PBP)Ir(CO)_2$ (Scheme 9, top),[47] reactions that apparently occur not by concerted 1,2-addition but either by (1) initial protonation of the iridium centre, followed by binding of the alkoxide base to boron (for alcohols), or (2) binding of the substrate to boron, followed by stepwise (possibly bimetallic) proton transfer (for amines). In collaborative studies with the Ozerov lab, we investigated related 1,2-additions of alcohols and water at a cationic cobalt silylene complex (Scheme 9, bottom).[48] Although a thorough mechanistic study has not been conducted, the cationic nature of the complex and the high oxophilicity of silicon suggest that oxygen binding to silicon precedes proton transfer. As with $(PBP)Ir(CO)_2$ reactions with amines, we cannot rule out a bimetallic pathway where silylene-bound ROH is deprotonated by a second cobalt complex.



Scheme 9. Analogous 1,2-additions of alcohols at boryl and silylene complexes

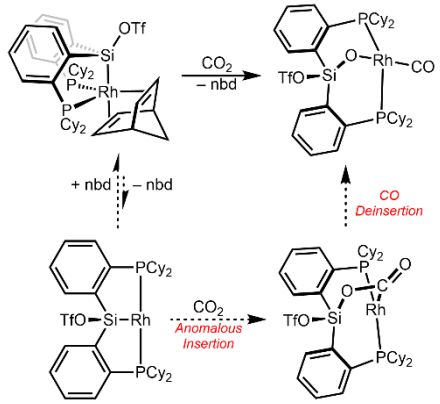
Reactions of the sort shown in Scheme 9 are driven at least in part by the strong B–O and Si–O bonds that are formed. The fact that boron, aluminium, and silicon form even stronger bonds to fluorine,[49] combined with strong literature precedent,[50, 51] suggests that C–F bonds could also be broken cooperatively at these complexes. Indeed, Sakaki, Nakao, and co-workers recently showed that a (PAlP)Rh system can effect the cleavage of Ph–F via addition of C–F to the rhodium/aluminyl unit (Scheme 10).[52] When performed in the presence of magnesium, this process was shown to enable the catalytic magnesiation of aryl fluorides. A related study extended this process to cooperative C–O activation in the reduction of aryl ethers.[53]



Scheme 10. Carbon–fluorine scission via 1,2-addition to (PAlP)Rh

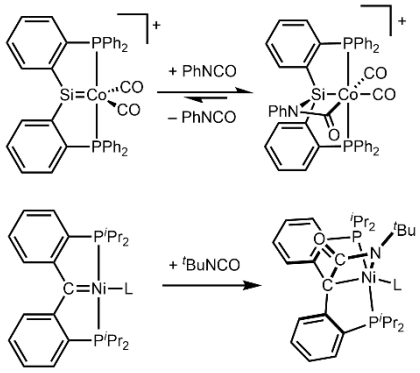
Transformations of the sort discussed in this section are not limited to singly bonded substrates. The reaction of an unsaturated substrate (X=Y in Scheme 7) with a metal/main-group bond will typically leave the substrate linkage intact, and the process will fall into the 'migratory insertion' or 'cycloaddition' categories of organometallic transformation. Nevertheless, these processes are conceptually similar to 1,2-addition of single bonds.

In one instance, we showed that reaction of a (PSiP)Rh complex featuring an electrophilic silyl donor reacted with CO_2 to afford a siloxide carbonyl complex of rhodium.[54] The process occurs by 'anomalous insertion' of CO_2 into the Rh–Si bond, followed by deinsertion of the CO unit (Scheme 11). The reaction is notable because it occurs with a different regioselectivity from metal alkyl (and many metal silyl) complexes, which our computations attribute to the reversed polarization of Rh–Si versus Rh–C bonds, in addition to the high oxophilicity of silicon. These considerations suggest that the process should be controllable in general for metal/main-group bonds, and it also highlights the ways in which bonds between electron-rich metals and electropositive metalloids can achieve considerably different outcomes from analogous metal–carbon bonds.



Scheme 11. CO_2 cleavage at (PSiP)Rh by anomalous insertion

When an unsaturated metal–element bond interacts with an unsaturated substrate, it is possible for form a stable or transient [2+2]-cycloadduct. This process had previously been demonstrated for metal silylene,[55] borylene,[56] and germylene[57] complexes but was only recently extended to (PSiP)Co silylenes. We showed that phenyl isocyanate undergoes a well-defined and reversible [2+2]-cycloaddition with cationic (PSiP)Co silylenes (Scheme 12, top).[58] The considerable blue-shift in CO stretching frequencies upon formation of the cycloadduct supports a Co(I)→Co(III) oxidation. Computational investigations indicate that the interaction is weak ($\Delta G°$ = –1.8 kcal mol^{-1}), a finding that is consistent with the observation that PhNCO can be displaced by diethyl ether. To this point, no further reactivity of the bound isocyanate has been uncovered.

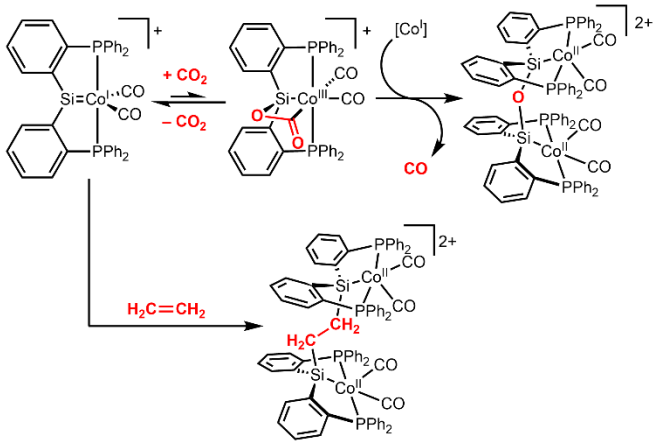


Scheme 12. [2+2]-cycloaddition of isocyanates occurs with different regiochemistry for silylene versus carbene complexes

It is instructive to compare the [2+2]-cycloaddition reactions at (PSiP)Co silylenes with related cycloadditions of isocyanates and carbon dioxide reported by Piers for a (PCP)Ni carbene complex, where the products are consistent with a $Ni^{\delta+}=C^{\delta-}$ formulation (Scheme 12, bottom).[59] This reversal in regioselectivity is analogous to what was seen in the anomalous insertion of CO_2 into Rh–Si bonds described above, and the finding emphasizes how pincer complexes with electropositive metalloids can enable distinct cooperative reactivity from those featuring other main-group donors.

Metalloid-Mediated Redox

The [2+2]-cycloaddition of isocyanates with cobalt silylenes described in the previous section suggests that similar reactivity might be achieved for other heteroallenes or even alkenes. However, reaction of a cationic (PSiP)Co silylene with carbon dioxide leads to a starkly different, paramagnetic product featuring two Co(II) centers (Scheme 13).[58] Experimental and computational investigations suggest that the reaction occurs first by endergonic [2+2]-cycloaddition of CO_2, followed by a bimolecular, electron-transfer step to form a new Si–O bond and release CO. Reaction with N_2O affords the same product with release of N_2, most likely via [3+2]-cycloaddition.[60] A related reaction occurs with ethylene to afford an ethylene-bridged Co(II)/Co(II) product. Although the mechanism for the ethylene transformation is not clear, it seems likely also to proceed via initial [2+2]-cycloaddition of C_2H_4 followed by a bimolecular, electron-transfer step to afford the bridged product. In some respects, these processes resemble the halogen abstraction by an Os(II) silylene that occurred with Os(II)→Os(III) oxidation.[61]



Scheme 13. Silylene-mediated multielectron redox transformations at (PSiP)Co

The transformations depicted in Scheme 13 demonstrate a potentially powerful use of main-group donors in pincer complexes. In each case, the silicon donor acts as a template for a multielectron redox transformation, where the reducing equivalents come from two different cobalt centres. The new bonds are primarily formed to silicon, whereas the reducing equivalents to form those bonds come from the cobalt centres. The enthalpic stabilization provided by the Si–O/Si–C bonds offsets the entropic penalty associated with bringing three reactants together, and the strength of the Si–O/Si–C bonds in the products offset the need for a strongly reducing metal centre that would otherwise be necessary to promote CO_2 reduction. These reactions also highlight a new strategy for enabling multielectron transformations at 3*d* metals: utilize main-group donors as templates to bring multiple metal centres and a reactive substrate together.

Conclusions and Outlook

This paper has highlighted several classes of cooperative reactions that have been elucidated in detail for pincer complexes featuring metal/main-group bonds. One commonality across many of the reactions explored is that they resemble processes that can be envisioned for bimetallic species. Indeed, in many cases a metalloid donor can be understood as a supporting metal partner for cooperative reactions, and analogies can certainly be made to early/late-metal heterobimetallics.[62] The stability and predictability that are enabled by incorporating main-group donors into robust pincer frameworks allow us to delineate the rules governing reactivity in ways that may enable a wide array of catalytic applications of polarized metal/main-group bonds. Of course, considerable room exists for further development, including but not limited to the following areas:

Tuning Reactivity of the Metal/Main-Group Unit. Viewing the main-group donor like a second metal centre highlights the fact that reactivity may be tuned in important ways through adjusting the coordination environment of the main-group partner. Most examples utilize aryl or anilide donors for the main-group element, but pyrrolides[31] have been introduced more recently and a number of other frameworks may prove fruitful. Incorporation of a hemi-labile donor into the main-group framework can be envisioned to shift equilibria for donor binding/release in directed reactions or fluxional processes such as those highlighted above. Creating frameworks that are robust and engender weak enough main-group/element bonds to allow facile release under catalytic conditions (and without strong reductants) is a key challenge. An additional important observation is that most of the systems explored in this Perspective involve pairing a hard main-group Lewis acid with a softer late-transition metal, offering possibilities for tuning reactivity based on different bonding preferences (e.g., the preference for binding oxygen ligands at aluminium and nitrogen/carbon ligands at nickel in Lu's (PAlP)Ni system).[15]

Exploiting Redox. There are a number of examples where a main-group donor participates in or enables two-electron redox at a single metal centre (e.g., changing from an X-type aluminyl to Z-type alane upon 1,2-addition across a M–Al bond). However, templating one-electron processes is much less common, and this approach is potentially valuable for 3*d* metals that favour one-electron redox. It remains to be demonstrated whether the metalloid-mediated one-electron process described in the previous section can be generalized and exploited. Another key area for development focuses on redox involving the main-group element and its surrounding ligand framework. For instance, germanium and tin frequently exist in both divalent and tetravalent states. Can silicon be tuned to access the Si(II)/Si(IV) redox couple in a catalytically productive way? Similar B(I)/B(III) and Al(I)/Al(III) couples can be envisioned, though they are often quite difficult to access. Along these lines, one can imagine incorporating boron, aluminium, or silicon donors into redox-active frameworks[63] to enable new cooperative transformations at the metal/main-group unit.

Photochemical Reactivity. Photochemical reactivity of the main-group or metal/main-group unit is closely related to the redox concepts explored above. The photochemical and photoelectrochemical reactions of metal/main-group single and multiple bonds have not been well investigated, and pincer systems provide appealing platforms for uncovering new reactivity. Furthermore, incorporating the main-group donor into a conjugated framework may lead to interesting interactions with the transition-metal centre. Integrating well-defined photochemical reactivity into the arsenal of techniques available to metal/main-group pincer systems affords the possibility of accessing reactivity not available through purely thermal means.

Pincer systems featuring metal/main-group bonds, particularly the M–Si, M–B, and M–Al units explored here, have led to the discovery of several new modes of reactivity, in some cases contributing to novel catalytic processes. Further investigation of these complexes promises to offer new avenues for small-molecule transformations with applications as diverse as organic synthesis and sustainable fuels.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

1 J. F. Hartwig, *Organotransition Metal Chemistry: From Bonding to Catalysis*, University Science Books, Sausalito, CA, 2010.
2 J. R. Khusnutdinova and D. Milstein, *Angew. Chem., Int. Ed.*, 2015, **54**, 12236-12273.
3 V. Lyaskovskyy and B. de Bruin, *ACS Catal.*, 2012, **2**, 270-279.
4 G. J. Kubas, *J. Organomet. Chem.*, 2001, **635**, 37-68.
5 D. W. Stephan, *J. Am. Chem. Soc.*, 2015, **137**, 10018-10032.
6 D. W. Stephan and G. Erker, *Angew. Chem., Int. Ed.*, 2015, **54**, 6400-6441.
7 D. W. Stephan, *Science*, 2016, **354**, aaf7229.
8 M. T. Whited, *Beilstein J. Org. Chem.*, 2012, **8**, 1554-1563.
9 M. T. Whited and B. L. H. Taylor, *Comments Inorg. Chem.*, 2020, **40**, 217-276.
10 C. Kleeberg, M. S. Cheung, Z. Y. Lin and T. B. Marder, *J. Am. Chem. Soc.*, 2011, **133**, 19060-19063.
11 A. L. Wierschen, N. Romano, S. J. Lee and M. R. Gagné, *J. Am. Chem. Soc.*, 2019, **141**, 16024-16032.
12 J. Takaya, *Chem. Sci.*, 2021, **12**, 1964-1981.
13 W. C. Shih and O. V. Ozerov, *J. Am. Chem. Soc.*, 2017, **139**, 17297-17300.
14 N. Hara, T. Saito, K. Semba, N. Kuriakose, H. Zheng, S. Sakaki and Y. Nakao, *J. Am. Chem. Soc.*, 2018, **140**, 7070-7073.
15 B. J. Graziano, M. V. Vollmer and C. C. Lu, *Angew. Chem., Int. Ed.*, 2021, **60**, 15087-15094.
16 T. W. Lyons and M. S. Sanford, *Chem. Rev.*, 2010, **110**, 1147-1169.
17 M. T. Whited, J. Zhang, S. Ma, B. D. Nguyen and D. E. Janzen, *Dalton Trans.*, 2017, **46**, 14757-14761.
18 T. J. Schmeier, G. E. Dobereiner, R. H. Crabtree and N. Hazari, *J. Am. Chem. Soc.*, 2011, **133**, 9274-9277.
19 A. Suzuki, *Angew. Chem., Int. Ed.*, 2011, **50**, 6722-6737.
20 Y. Nakao and T. Hiyama, *Chem. Soc. Rev.*, 2011, **40**, 4893-4901.
21 W. C. Shih, W. X. Gu, M. C. MacInnis, S. D. Timpa, N. Bhuvanesh, J. Zhou and O. V. Ozerov, *J. Am. Chem. Soc.*, 2016, **138**, 2086-2089.
22 W. C. Shih, W. X. Gu, M. C. MacInnis, D. E. Herber and O. V. Ozerov, *Organometallics*, 2017, **36**, 1718-1726.
23 D. Schuhknecht, F. Ritter and M. E. Tauchert, *Chem. Commun.*, 2016, **52**, 11823-11826.
24 J. Takaya and N. Iwasawa, *Dalton Trans.*, 2011, **40**, 8814-8821.
25 J. Takaya and N. Iwasawa, *Organometallics*, 2009, **28**, 6636-6638.
26 M. T. Whited, A. M. Deetz, J. W. Boerma, D. E. DeRosha and D. E. Janzen, *Organometallics*, 2014, **33**, 5070-5073.
27 M. T. Whited, A. M. Deetz, T. M. Donnell and D. E. Janzen, *Dalton Trans.*, 2016, **45**, 9758-9761.
28 J. Kim, Y. E. Kim, K. Park and Y. Lee, *Inorg. Chem.*, 2019, **58**, 11534-11545.
29 S. J. Mitton, R. McDonald and L. Turculet, *Angew. Chem., Int. Ed.*, 2009, **48**, 8568-8571.
30 H. W. Suh, L. M. Guard and N. Hazari, *Chem. Sci.*, 2014, **5**, 3859-3872.
31 Q. H. Lai, N. Bhuvanesh and O. V. Ozerov, *J. Am. Chem. Soc.*, 2020, **142**, 20920-20923.
32 M. J. Bernal, O. Torres, M. Martin and E. Sola, *J. Am. Chem. Soc.*, 2013, **135**, 19008-19015.
33 J. So, S. Kim, K. B. Cho and Y. Lee, *Chem. Commun.*, 2021, **57**, 3219-3222.
34 M. J. Ingleson, M. Pink, H. Fan and K. G. Caulton, *J. Am. Chem. Soc.*, 2008, **130**, 4262-4276.
35 W. A. Chomitz and J. Arnold, *Chem. Commun.*, 2008, 3648-3650.
36 Y. Park, S. P. Semproni, H. Y. Zhong and P. J. Chirik, *Angew. Chem., Int. Ed.*, 2021, **60**, 14376-14380.
37 M. T. Whited and R. H. Grubbs, *Organometallics*, 2008, **27**, 5737-5740.
38 E. Calimano and T. D. Tilley, *J. Am. Chem. Soc.*, 2009, **131**, 11161-11173.
39 W. H. Harman and J. C. Peters, *J. Am. Chem. Soc.*, 2012, **134**, 5080-5082.
40 S. N. MacMillan, W. H. Harman and J. C. Peters, *Chem. Sci.*, 2014, **5**, 590-597.
41 T. Komuro, T. Arai, K. Kikuchi and H. Tobita, *Organometallics*, 2015, **34**, 1211-1217.
42 Y. W. Wang, A. Kostenko, S. L. Yao and M. Driess, *J. Am. Chem. Soc.*, 2017, **139**, 13499-13506.
43 K. Abdur-Rashid, S. E. Clapham, A. Hadzovic, J. N. Harvey, A. J. Lough and R. H. Morris, *J. Am. Chem. Soc.*, 2002, **124**, 15104-15118.
44 D. V. Gutsulyak, W. E. Piers, J. Borau-Garcia and M. Parvez, *J. Am. Chem. Soc.*, 2013, **135**, 11776-11779.
45 C. C. Comanescu and V. M. Iluc, *Chem. Commun.*, 2016, **52**, 9048-9051.
46 T. Schindler, M. Lux, M. Peters, L. T. Scharf, H. Osseili, L. Maron and M. E. Tauchert, *Organometallics*, 2015, **34**, 1978-1984.
47 Y. H. Cao, W. C. Shih and O. V. Ozerov, *Organometallics*, 2019, **38**, 4076-4081.
48 J. Zhang, B. J. Foley, N. Bhuvanesh, J. Zhou, D. E. Janzen, M. T. Whited and O. V. Ozerov, *Organometallics*, 2018, **37**, 3956-3962.
49 Y.-R. Luo, *Handbook of Bond Dissociation Energies in Organic Compounds*, CRC Press, 2003.
50 M. Aizenberg and D. Milstein, *Science*, 1994, **265**, 359-361.
51 A. L. Raza, J. A. Panetier, M. Teltewskoi, S. A. Macgregor and T. Braun, *Organometallics*, 2013, **32**, 3795-3807.
52 I. Fujii, K. Semba, Q. Z. Li, S. Sakaki and Y. Nakao, *J. Am. Chem. Soc.*, 2020, **142**, 11647-11652.
53 R. Seki, N. Hara, T. Saito and Y. Nakao, *J. Am. Chem. Soc.*, 2021, **143**, 6388-6394.
54 M. T. Whited, J. Zhang, T. M. Donnell, V. H. Eng, P. O. Peterson, M. J. Trenerry, D. E. Janzen and B. L. H. Taylor, *Organometallics*, 2019, **38**, 4420-4432.
55 G. P. Mitchell and T. D. Tilley, *J. Am. Chem. Soc.*, 1997, **119**, 11236-11243.
56 S. De, G. A. Pierce, D. Vidovic, D. L. Kays, N. D. Coombs, E. D. Jemmis and S. Aldridge, *Organometallics*, 2009, **28**, 2961-2975.
57 K. E. Litz, K. Henderson, R. W. Gourley and M. M. B. Holl, *Organometallics*, 1995, **14**, 5008-5010.
58 M. T. Whited, J. Zhang, A. M. Conley, S. J. Ma, D. E. Janzen and D. Kohen, *Angew. Chem., Int. Ed.*, 2021, **60**, 1615-1619.

59 E. A. Lapierre, W. E. Piers and C. Gendy, *Organometallics*, 2018, **37**, 3394-3398.
60 N. D. Harrold, R. Waterman, G. L. Hillhouse and T. R. Cundari, *J. Am. Chem. Soc.*, 2009, **131**, 12872-12873.
61 P. W. Wanandi, P. B. Glaser and T. D. Tilley, *J. Am. Chem. Soc.*, 2000, **122**, 972-973.
62 B. G. Cooper, J. W. Napoline and C. M. Thomas, *Catal. Rev.: Sci. Eng.*, 2012, **54**, 1-40.
63 L. A. Berben, *Chem. Eur. J.*, 2015, **21**, 2734-2742.