Valence Tautomerism of p-Block Element Compounds – An Eligible Phenomenon for Main Group Catalysis?

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Valence tautomerism has had a remarkable impact on several branches of transition metal chemistry. By switching between different valence tautomeric states, physicochemical properties and reactivities can be triggered reversibly. Is this phenomenon transferrable into the p-block – or is it already happening there? This *Perspective* collects observations of p-block element-ligand systems that might be assignable to valence tautomerism.

Further, it discusses occurrences in p-block element compounds that exhibit the related effect of redox-induced electron transfer. As disclosed, the concept of valence tautomerism with p-block elements is at a very early stage. However, given the substantial disparity in the properties of those elements in different redox states, it might offer a valid extension for future developments in main group catalysis.

Introduction

Metal-centered redox chemistry has been at the heart of transition metal chemistry ever since its early beginnings. The ability of the ligands to undergo redox state changes instead of the metal center caused a significant expansion of the chemistry of transition metal complexes.[1] This field of redox-active ligands originated from pure fundamental curiosity, influenced our understanding of bioinorganic transformations,[2] and developed potential in catalysis, controlled radical reactivity,[3] and materials science.[4] Strikingly, by the support of ligand-centered redox events (redox non-innocence), inactive metal centers were imparted with reaction pathways previously proprietary to precious metal complexes only.[5] An aspect that came along with redox-active ligands was the recognition of valence tautomerism (VT).[6] Valence tautomers have an identical constitution but may differ in the distribution of their electron density, i.e., in the formal oxidation states of separated parts of the complex (Figure 1a). A seminal example is the cobalt bis(dioxolene)(bpy) complex **1** that can either exist in its Co^{III}(cat)(sq)(bpy) state **1A** or its Co^{II}(sq)$_2$(bpy) state **1B** (cat = catecholate, sq = semiquinone, Figure 1b).[6a] Several d-block metal-ligand combinations and factors such as temperature, pressure, ligands, counterions, or matrix polarity, were identified to populate one over the other valence tautomer since then.[6b,c,7] Does VT play a role also in p-block element
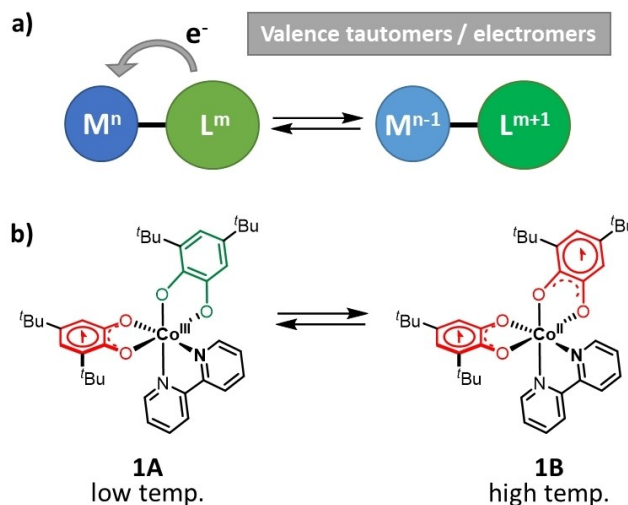
Figure 1. (a) Schematic representation of electromerism/valence tautomerism. (b) A seminal example of valence tautomerism in a cobalt bis(dioxolene) complex.

chemistry? The present *Perspective* deals with potential occasions of VT or related effects with p-block elements – a connection that has rarely been made. Given the huge impact of VT in transition metal chemistry and catalysis, this comparison shall encourage future efforts toward a more dedicated projection of this effect onto main-group elements – as a potential avenue for enhanced reactivity and catalysis.

First, a comment about the terminology seems required. In the field of transition metal complexes, the term "valence tautomers" was introduced at a very early stage and firmly adopted by the community. However, this name might create confusion since "tautomers" usually denote *constitutional* isomers that readily interconvert.[8] However, in valence tautomers, the constitution remains unchanged. Instead, the term "electromers" appears more appropriate, in agreement with previous suggestions. The first mention of electromers can be dated back to a very early theory of chemical bonding in 1911.[9] The name was used later by G. N. Lewis and G. T.

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Seaborg, to define *"two forms of a molecule with the atoms in similar positions and constitution, but with a different electronic distribution"*.[10] Several decades after, it was applied by S. Shaik in the context of transition metal-oxides and organic radical cations.[11] Finally, the term was brought in connection with valence tautomerism in transition metal complexes by T. Bally.[12] We will use the name electromerism in the remainder of this text.

Electromerism is categorized into three groups according to the Robin-Day classification.[13] Class I corresponds to electromeric states that are separated by substantial barriers and do not easily interconvert. In Class II, the states remain discrete, but the activation energy for a thermally induced electron transfer can be surpassed. Cases for which both states are not distinguishable (completely delocalized valency) are termed Class III. For class I/II electromerism to occur, spatially localized but energetically close-lying orbitals and a low bond covalency are favorable.[7a,c] Another feature that promotes the occurrence of discrete electromers is a structural difference, imposing barriers for electromer interconversion by considerable reorganization energies.[14]

How about p-block element compounds? On the one hand, the usually larger extend of covalency in bonds with p-block elements might favor Class III situations. On the other hand, p-block elements in different oxidation states exhibit substantial structural differences (e.g. tetrahedral Sn^{IV} vs. bent/pyramidal Sn^{II}), which might provoke considerable reorganization barriers. Besides, the spin-forbidden interconversion between singlet to triplet electromers might further increase barriers, particularly for lighter atoms that do not provide spin-orbit coupling.

The following text highlights the very few cases of p-block electromerism, discusses some less clear examples, and discloses similarities with transition metal complexes. Since examples of true electromerism are still relatively scarce in the p-block, it will also include cases in which redox-state changes are triggered by changes in the constitutional structure, e.g., by binding a Lewis base. These instances are termed pseudo-electromerism.

Class I/II-Electromerism and Pseudo-Electromerism with p-Block Elements

A seminal example of p-block pseudo-electromerism was reported by Vaid *et al.* for a germanium porphyrin complex **2** (Figure 2a).[15] The reaction of $GeCl_2$-dioxane with the lithium salt of deprotonated tetraphenylporphyrin (TPP) yielded **2A** as a green solid. NMR-, UV/Vis-spectroscopic and SCXRD studies revealed a Ge^{II} oxidation state and an aromatic 18e-porphyrin ligand. The compound slowly dissolved in pyridine with a concomitant color change to bright-red, yielding (**2B**)py$_2$. The chemical shift of the pyrrole-C$_\beta$ bound protons in (**2B**)py$_2$, upfield shifted by about 9 ppm compared to **2A**, strongly indicated an antiaromatic 20e-porphyrin character in (**2B**)py$_2$. This phenomenon was explained by the transfer of the lone pair electrons from Ge^{II} into the ligand's e_g-acceptor orbitals, forming a Ge^{IV} species as pyridine adduct. The electron shift was proposed to happen in an "all-or-none" manner (discrete, not continuous), as the involved orbitals are orthogonal. Determination of redox potentials of both forms disclosed that by pseudo-electromerism, the compound transforms into a pretty strong reductant. An oxidation wave at -1.24 V vs. Fc/Fc$^+$ (Fc = ferrocene) for the (**2B**)py$_2{}^{+/0}$ couple is anodically shifted compared to the aromatic **2A** in CH_3CN/benzene ($+0.2$ V). In (**2B**)py$_2$, the electrons are much easier released from the antiaromatic porphyrin ring system. Computations on the respective donor-free derivatives with Si, Sn and Pb revealed that the Si^{IV}-electromer **B** is favored for silicon. In contrast, for Sn and Pb, the M^{II} forms **A** with aromatic ring systems prevail. Another computational study supported the validity of the correct description of the electronic structure.[16] Interestingly, related conclusions were drawn from cyclic voltammetry studies

Lutz Greb studied chemistry in Freiburg and at the University Pierre et Marie Curie, Paris. In 2013, he received a Ph.D. for his work on the reactivity of Frustrated Lewis pairs in the groups of Prof. Jan Paradies (KIT Karlsruhe) and Prof. Douglas Stephan (University of Toronto). He joined the group of Prof. Jean-Marie Lehn (ISIS Strasbourg) as Feodor-Lynen fellow (A.v.H.), where he investigated the photoisomerization of imines for the generation of molecular switches, molecular motors, and photo-responsive materials. In 2016, Lutz Greb started his independent research as Liebig- (FCI), Emmy-Noether and ERC StG Fellow at Heidelberg. Recently, he accepted a position at the Freie Universität Berlin, Inorganic Chemistry Department. His group is currently interested in structural constraint, element-ligand cooperativity, Lewis acidity, and dynamic covalent chemistry.
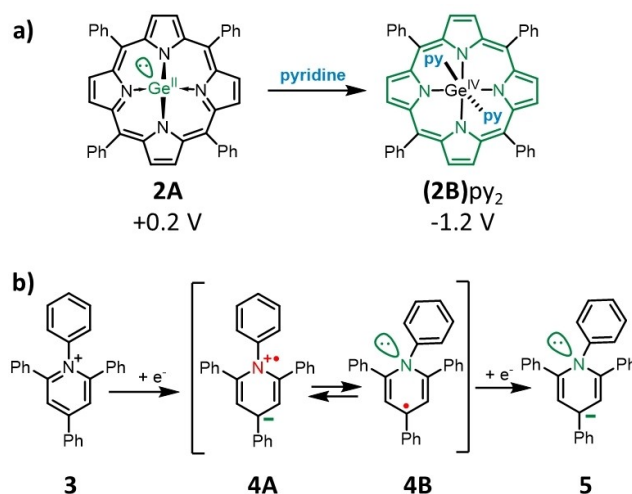
Figure 2. (a) Lewis Base binding triggered pseudo-electromerism in a germanium porphyrin complex **2** and the experimental redox potentials *vs.* Fc/Fc$^+$. (b) Electromerism in a reduced pyridinium **3**.

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of a Sn^{II} porphyrin complex already in 1991.[17] Overall, the process fulfills the criteria of pseudo-electromerism, triggered by the binding of a Lewis base.

Electromerism was also identified during the two-fold reduction of pyridinium cation **3** by computations and spectroscopy (Figure 2b).[18] The possibility of interconverting a planar, nitrogen centered radical electromer **4A** into the substituent based radical state **4B** (pyramidal at nitrogen) rationalized the unusual finding that the second one-electron reduction step (**4** to **5**) occurs at apparently the same electrochemical potential as the first reduction ("potential compression", see also Ref. [19]).

The Piskunov group studied M^{IV}-M^{II} electromerism for Si, Ge and Sn with 2,6-di-^{t}Bu−N-(R)-o-amidophenolate ligands (R=Ph, ^{t}Bu) by density functional theory (B3LYP/6-311++D(d,p)/SDD, Figure 3a).[20] Electromers ^{R}**6^{M}A** are characterized by a M^{IV} center with a pseudo tetrahedral coordination sphere, whereas electromers ^{R}**6^{M}B** exhibit oxidation state II for the central elements with a tetragonal-pyramidal arrangement and two ligands in their open shell imino-semiquinone state (ImSQ).

Energies of the triplet and the open-shell singlet diradical states of ^{R}**6^{M}B** (broken symmetry approach) did not differ by >0.1 kcal mol^{-1} from each other due to limited spin-spin coupling. With R=Ph and silicon as the central element, electromer ^{Ph}**6^{Si}A** is favored by 60 kcal mol^{-1} over electromer ^{Ph}**6^{Si}B**. For germanium, the Ge^{IV} species is favored, but with a substantially smaller preference (20 kcal mol^{-1}). In the case of tin, the situation is inverted, and the Sn^{II} form ^{Ph}**6^{Sn}B** is favored

by 16 kcal mol^{-1}. The Sn-compound was further studied with the ^{t}Bu substituted amidophenolate, ^{tBu}**7** (Figure 3b). Here, the calculated energy difference between both electromers (7.0 kcal mol^{-1}) is in a range of known interconvertible electromeric d-block metal complexes. Moreover, the minimal energy crossing path between the triplet state form ^{tBu}**7A** and the singlet state form ^{tBu}**7B** possesses a barrier of only 11.7 kcal mol^{-1} against the ground state electromer.

An experimental realization was provided two years later by the same group (Figure 3b).[21] Tin complex ^{tBu}**7** was isolated as diamagnetic form ^{tBu}**7A** as a yellow-orange crystalline solid from a concentrated hexane solution. SCXRD analysis confirmed pseudo-tetrahedral coordination around a tin(IV), with the "metric oxidation state" indicative of a dianionic nature of the ligands. Upon dissolution in non-polar solvents such as toluene, an intense yellow-green coloration developed, with UV/Vis-absorption bands (600–900 nm) and EPR-characteristics of the ImSQ state, showcasing electromerism into ^{tBu}**7B**. Remarkably, the addition of pyridine triggered the disappearance of the radical form ^{tBu}**7B**, and the formation of the complex ^{tBu}**7A-py$_2$** was confirmed by SCXRD analysis. The equilibrium between the free form ^{tBu}**7A** and ^{tBu}**7B** was studied further experimentally. Evans NMR method and Mössbauer spectroscopy identified only 11–13% of form ^{tBu}**7B** present at room temperature (Figure 3a). Increasing the temperature from 293 K to 363 K resulted in lowering the equilibrium concentration of ^{tBu}**7B**. Notably, those observations were in contrast to the computed lower energy of ^{tBu}**7B**. The authors accused entropy of this conflict. However, in transition metal systems, the formation of high-spin electromers is entropically favored since compounds in high spin states possess longer bonds (higher vibrational state density) and higher spin state degeneracy (cf. Figure 1b).[7c,22] Yet, for ^{tBu}**7** the high-spin state seems to be favored at lower temperatures. The authors further proposed intermolecular interactions between the diradicals ^{tBu}**7B** as an alternative cause for the favored high spin state at lower temperatures. Another explanation might be the applied computational method, which is density functional theory without dispersion correction, leading to imprecise computed thermodynamics.
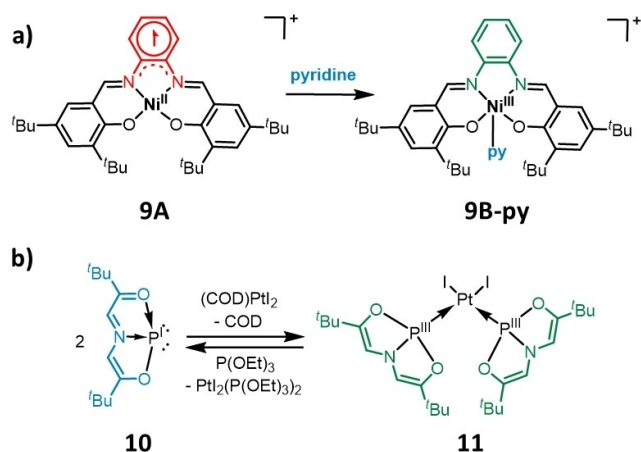
A related electromerism was proposed by Tuck to explain EPR- and UV/Vis-observations for a putative free bis(3,5-di-^{t}Bu-catecholato)germane **8** (Figure 3c).[23] However, this interpretation contradicts the computationally predicted clear preference for the Ge^{IV} and other experimental findings.[20,24]

The two given cases of pseudo-electromerism (Figure 2a and Figure 3b) are triggered by the coordination of Lewis bases to the central element. Indeed, similar examples are known for transition metal systems. In the one-electron oxidized Ni(II)-bis(salicylidene)diamine complex **9A**, the ligand-centered radical transforms to a Ni(III) species **9B-py** with a reduced ligand upon coordination of pyridine (Figure 4a).[25] The reverse electron flow was observed for a Ni(III)-catecholato complex, wherein the coordination of DMF or nitrate to Nickel triggers a transformation into the Ni(II)-semiquinonate state.[26]

The reverse case, that is, Lewis acid-binding triggered pseudo-electromerism, is also known for p-block elements.
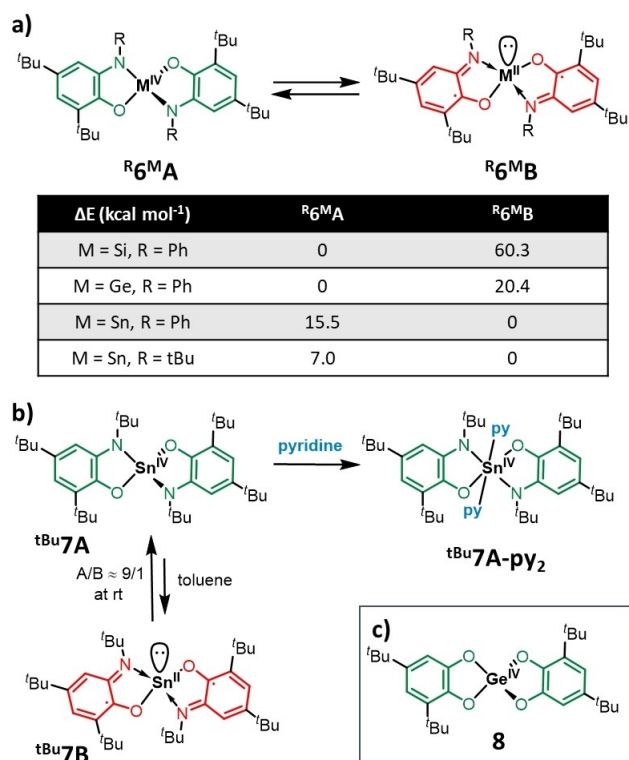
Figure 3. (a) Theoretical evaluation of electromerism in group 14 amidophenolate complexes of the general form ^{R}**6**. (b) The experimental realization of p-block electromerism with ^{tBu}**7**. (c) A related germanium bis(catecholate) complex **8** that does not show electromerism.

ΔE (kcal mol^{-1})	^{R}**6^{M}A**	^{R}**6^{M}B**
M = Si, R = Ph	0	60.3
M = Ge, R = Ph	0	20.4
M = Sn, R = Ph	15.5	0
M = Sn, R = tBu	7.0	0

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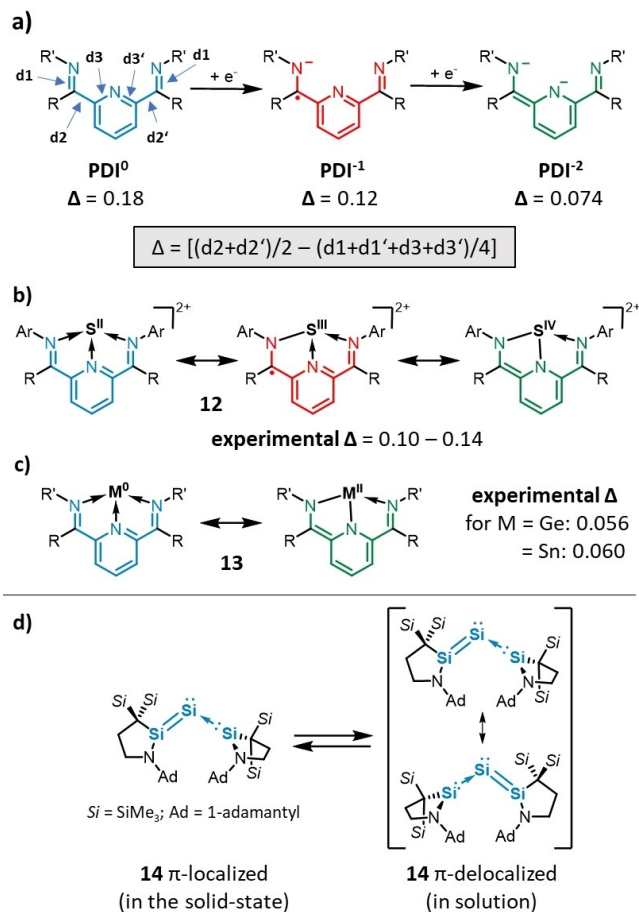**Europe**
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Figure 4. (a) Transition metal analog of Lewis base-binding triggered electromerism in a nickel complex **9**. (b) Lewis acid-binding triggered electromerism for the phosphorous complex **10**.

Figure 5. (a) Deviation of **Δ**-value for the PDI ligand by metric parameters and the ideal values for the three different charge states. (b) Electronic structure representation and experimental **Δ**-value for **12**, here shown for the sulfur derivative. (c) Electronic structure representation and experimental **Δ**-value for **13**. (d) Phase-dependent switching of electromerism in the silicon(0) complex **14**.

Arduengo's peculiar T-shaped 10-P-3 compound **10** is best considered a P^I species in a threefold coordination environment and two lone pairs at phosphorous (Figure 4b).[27] Upon reaction with (cod)PtI$_2$, the formation of complex **11** was observed.[28] Remarkably, the process can be reversed upon the addition of triethyl phosphite. Based on solid-state structural characteristics of **11**, the ligands transform into the 8-P-3 electromers, that is, P^{III} with a reduced ligand.

Given the particular difference of p-block electromers, e.g., with Sn(II) and Sn(IV) center, in reactivity or Lewis acidity, one might perceive concepts like "on-site" or "on-demand" substrate activation, triggered upon binding of a donor functionality. Thus, Class I/II-electromerism is arguably the most promising approach for integration into p-block element-based catalysis, yet examples are missing.

Potential forms of Class III-Electromerism with p-Block Elements

Class III-electromerism with vanishing barriers between the electromers is, to some extent, a matter of perspective and not always unambiguous. Examples will be sketched based on a recently introduced "metric oxidation state"[29] for the PDI ligand by Wieghardt *et al.*[30] By considering the characteristic bond lengths d1-d3 in the PDI ligand, the authors formulated a Δ-value that provides a straightforward linear relation between structural parameters and observed oxidation state, as validated for metal complexes with clear-cut redox states (Figure 5a). Based on the Δ-value, a range of "non-innocent" p-block PDI complexes was revisited. For instance, the PDI ligand-based chalcogen dications **12** were evaluated (Figure 5b). Those sulfur, selenium, and tellurium species were obtained as yellow/amber powders and analyzed by SCXRD.[31] The complexes are T-shaped, with both imine nitrogen atoms occupying the axial positions of a trigonal bipyramid and the pyridine nitrogen and the two proposed lone pairs in the equatorial positions.

In the original publication, the authors chose to present the electronic structure as $[M^{II}(pdi)^0]^{2+}$. Analysis of the Δ-value performed by Wieghardt *et al.* supported the electromeric formulation $[M^{III}(pdi^\bullet)^-]^{2+}$ with a strong intramolecular antiferromagnetic coupling between the s^2p^1 configured M^{III} ion and the a_2 ligand orbital. Yet, neither of the spectroscopic results supported an open-shell singlet, but it might also be represented as a resonance hybrid of $[M^{IV}(pdi^{2-})]^{2+} \leftrightarrow [M^{II}(pdi)^0]^{2+}$. For monocationic group 15 PDI complexes, Pn^I species (Pn = P, As) with PDI^0 ligands were chosen as representation,[32] although the Δ-value is supporting the $[Pn^{III}(pdi^{2-})]^+$ formulation.

Two diamagnetic neutral complexes of the form [M(pdi)] **13** were described by Flock (M = Sn)[33] and Nikonov (M = Ge)[34] (Figure 5c). Both groups chose the electronic structure formulation $[M^0(pdi)^0]$, although the Δ-value indicated the $[M^{II}(pdi)^{2-}]$ state. Quantum theoretical analyses revealed the HOMO of the compounds as fully delocalized across the π-system of the PDI ligand. NBO analyses disclosed that the second lone pair at M has an occupancy of 0.27 electrons only as a consequence of π-delocalization, thus also supporting the $[M^{II}(pdi)^{2-}]$ description.

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Although the resonance between both closed-shell electromers clearly has a stabilizing effect, the representation as $[M^{II}(pdi)^{2-}]$ seems more appropriate.

More recently, Iwamoto identified a phase-dependent switching between Class I to Class III-electromerism for a low-valent group 14 compound.[35] The bis-cyclic (alkyl)(amino)silylene substituted silicon(0) complex **14** adopts a green π-localized ylidene structure in the solid-state but reversibly switches into a purple π-delocalized ylidene structure upon transfer into solution phase (Figure 5d).

The integration of Class III-electromeric effects into p-block element-based catalysis appears less straightforward. Rather, it is a clear-cut understanding of the electronic structure and how to establish a dedicated control is that needs to be developed first. Extremely electron-deficient/electron-rich *loci* might come into reach by light-induced charge transfer strategies.

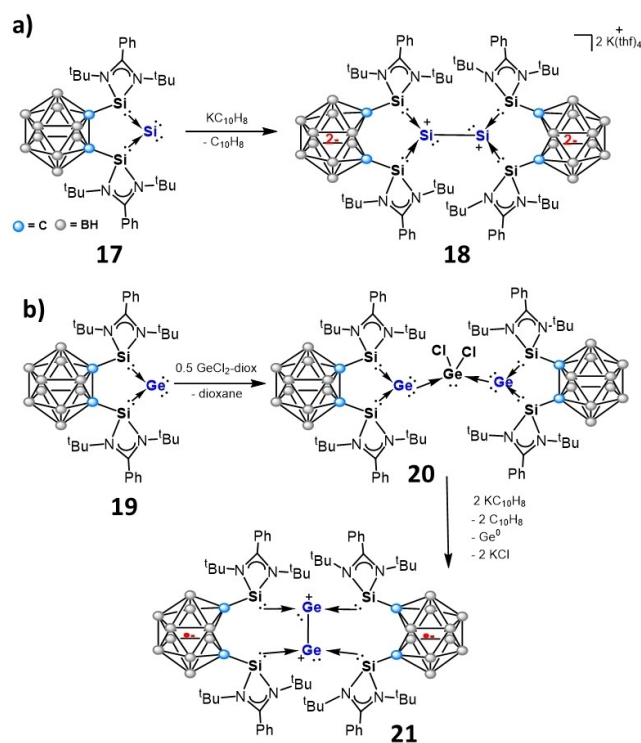## Redox-Induced Electron Transfer (RIET) in p-Block Element Compounds

Another exciting feature of electromeric transition metal complexes are situations in which the oxidation of the compound causes a formal reduction of a specific part of the molecule by intramolecular electron transfer. This effect, which can also occur in the inverse direction, has been termed redox-induced electron transfer (RIET).[36] For example, the one-electron oxidation of a dinuclear tetraoxolene cobalt(II) complex **15** (Figure 6a) leads to the concomitant electron transfer of the second cobalt(II) center to the ligand.[37] Although RIET finds analogs in p-block element chemistry, they have never been considered as such before.
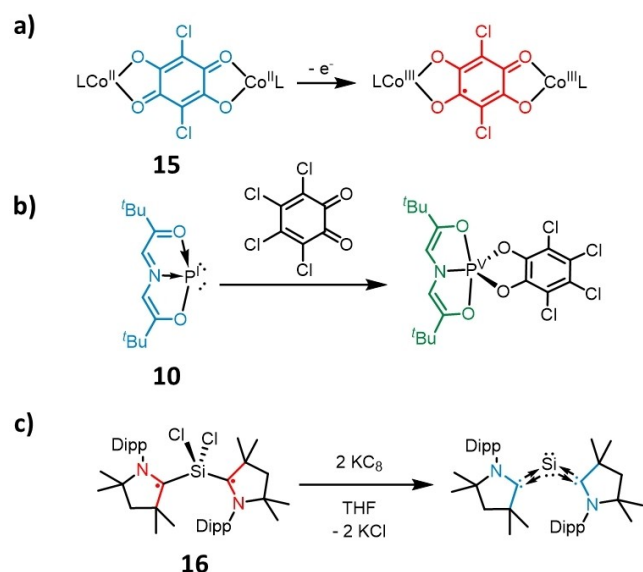
By the reaction of Arduengo's phosphorous ONO-P^I complex **10** with the two-electron oxidant *ortho*-chloranil (Q^{Cl}), the P^I center gets oxidized to P^V. At the same time, *both* ligands are reduced (Figure 6b). Thus, the ONO ligand undergoes a formal reduction in the overall oxidation event, reminiscent of a RIET. The same line of arguments holds for the oxidative addition reactions recently disclosed by Radosevich.[38] An inverse kind of RIET-type process was observed during the reduction of a two-fold cyclic alkyl amino carbene substituted $SiCl_2$ **16** by Roesky et al. (Figure 6c).[39] In **16**, the spin density is localized at the carbene carbon atoms, and the complex is best described as Si^{IV} species with the open-shell carbon atoms, formally as C^I. The reduction of the compound by two electrons leads to the formation of a formal Si^0 species with carbene ligands, thus C^{II}. Hence, by reduction of **16**, the ligand carbon atoms get formally oxidized from C^I to C^{II}. Indeed, this last example is debatable, as electron back donation of Si^0 into the carbene π-acceptor orbitals makes oxidation state assignment less meaningful.

More recently, Driess reported a remarkable series of results based on the redox-active nature of *ortho*-carborane substituents, comprising several RIET events. Upon reduction of the bis(silylene) coordinated silylone **17** with potassium naphthalide, the Si–Si coupled product **18** was isolated in high yields (Figure 7a).[40] Here, the closo-carborane ligand gets reduced by one external electron and a second intramolecular electron transfer oxidizes silicon(0) to silicon(I). The process was supported by density functional theory. A similar observation was made during the reduction of the corresponding

Figure 6. (a) Example for redox-induced electron transfer (RIET) in dinuclear cobalt complex **15** (L = tris(2-pyridylmethyl)amine). (b) A formal RIET during the reaction of **10** with *ortho*-chloranil. (c) A formal RIET during the reduction of **16**.

Figure 7. (a) A RIET from Si(0) to Si(I) during the reduction of *o*-carborane bis(silylene) stabilized silylone **16**. (b) Complexation of $GeCl_2$ by *o*-carborane bis(silylene) stabilized germylone **18**, and its reduction, to yield **20**, a formal dimeric electromer of **18**.

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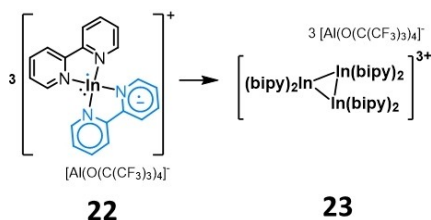
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bis(silylene) stabilized germylene **19** (Figure 7b).[41] Additionally, the reaction of **19** with GeCl₂-dioxane provided Lewis adduct **20**, which was subsequently reduced, yielding the diradicaloid species **21** in minor amounts. Remarkably, **21** can be considered as a formal electromeric dimer of **19**. The germanium(0) is oxidized, and the ligand is reduced by one electron. Due to the different coordination nature of **19** and **21**, no direct equilibrium has been observed. A related electronic communication between the *o*-carborane, silicon and a nitrogen(I) center was found in later studies on bis(silylene) stabilized monovalent nitrogen complexes.[42]

Generally, 2,2'-bipyridine (*bipy*)[43] or the related diazabutadiene[44] have a long and diverse history in the context of p-block element-ligand redox non-innocence (not to be covered here).[45] In a recent example, Krossing and coworkers reported the potential role of electromerism during the formation of unique cationic indium cluster compounds.[46] Upon addition of *bipy* to the indium(I) source [In(C₆F₅F)₂]⁺ [Al(O(C(CF₃)₃)₄]⁻, the formation of tri- and tetranuclear clusters such as [In₃(bipy)₆]³⁺ (**23**) was observed (Figure 8). Based on DFT computations, the formation of putative [In(bipy)₂]⁺ (**22**) in its triplet state was proposed, which readily trimerizes. Hence, the coordination of In(I) by *bipy* and a concomitant electromerism into the In(II)/bipy⁻• state is operative.

The given examples of p-block element-based RIET and related processes in this last section illustrate how unexpected reaction channels transpire upon the involvement of ligand redox non-innocence and electromerism. A similar extension of operation modes in catalytic cycles seems likely.

Summary and Outlook

Manipulating electrons at the molecular level is a challenging task, but at the same time, it is at the heart of chemistry.[47] It touches diverse fields from molecular electronics over artificial photosynthesis to molecular catalysis. Valence tautomerism, better called electromerism, offered a unique strategy for electronic-structure tuning in transition metal complexes. Why not projecting this potential into the p-block? Although far away from maturity, several examples discussed in this *Perspective* indicate that electromerism is also happening in p-block element compounds. The distinct coordination structure of p-block elements in different oxidation states should allow creating barriers between both electromers, offering the chance to stabilize discrete states. Most remarkable is, hence the herewith demarcated foray concerning a potential impact of electromerism in main group catalysis, that electromers of p-block elements dramatically change their chemical behavior! A distinct control over electromers of p-block elements might offer unique ways to reach unusual oxidation states,[48] to shuffle oxidative-addition and reductive-elimination propensity,[49] to enable reactivity *via* radical(oid) states,[50] or to tune donor-acceptor capabilities if used as Lewis acids or bases. All these features appear highly relevant for the future development of main-group catalysis.[51] Thus, like for transition metal chemistry, electromerism, has a distinct chance of being not only "l'art pour l'art", but of a yet to be developed potential.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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Figure 8. Trimerization of triplet-state **22**, that is formed by potential electromerism from In(I) and *bipy*, to form tricationic cluster **23**.

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