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Amplifying Lewis acidity by oxidation: leveraging the redox-activity of bis(3,6-di-*tert*-butyl-catecholato)silane†

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Bis(catecholato)silanes were showcased as strong Lewis acids, while their inherent redox activity remained unexplored in this context. In the present work, we study the oxidation of monomeric bis(3,6-di-*tert*-butyl-catecholato)silane (**1**), leading to the Lewis superacidic radicalic silylium ionradical $1^{+\cdot}$ (FIA 784 kJ mol⁻¹). Oxidation of **1** with [N(*p*-C₆H₄Br)₃][B(C₆F₅)₄] yielded [1][B(C₆F₅)₄], displaying strong catalytic activity in the Friedel–Crafts-dimerization, hydrodeoxygenation and carbonyl-olefin-metathesis. It demonstrates how Lewis acidity can be amplified through oxidation without needing an add-on redox-active substituent. Instead, it synergizes the constraining effect of catecholates with their inherent redox non-innocence to unlock enhanced catalytic performance.

Lewis acids are extensively used in all kinds of chemistry, ranging from materials science over organic chemistry and drug discovery to biological research.^{1–7} This broad applicability fostered a continuous development that led to numerous new p-block Lewis acids – an interest further propelled by the field of frustrated Lewis pairs.⁸ Frequently, the effect of a Lewis acid is related to its strength;⁹ a precept fueling the search for continuously stronger Lewis (super)acids.¹⁰ Typical strategies for increasing Lewis acidity include, among others, the installation of electron-withdrawing substituents, the introduction of cationic charge, or structural constraints. Other approaches aim to exploit a Lewis acidity enhancement on demand to overcome obstacles associated with the limited stability of the most potent Lewis acids. For instance, aryl- or alkyl-silylium ions are usually synthesized *in situ* by hydride abstraction through carbocations to mitigate side reactions, *e.g.*, with the solvent or the counteranion.^{11–14} Another strategy relies on photochemical concepts to release Lewis acids upon irradiation.^{15–18} Moreover, redox approaches were shown to

stimulate Lewis acidity. A change in the main group element oxidation states for increased reactivity was exemplified for pnictogen- and tin-compounds.^{19–22} As an alternative, the oxidation of redox-non-innocent ligands instead of the central elements was considered more recently (Fig. 1a). Paradies and coworkers investigated a row of ferrocenyl-substituted boranes and unlocked Lewis superacidity by oxidation (Fig. 1b).²³ Caputo and coworkers presented a phenothiazine-substituted borane as transition metal free representative for this concept (Fig. 1c).²⁴

In recent years, we pursued the search for novel main-group Lewis superacids based on the catecholato ligand.^{25–33} The bidentate ligand has been shown to have a multifold impact on the increase of Lewis acidity. First, it exhibits a bite angle

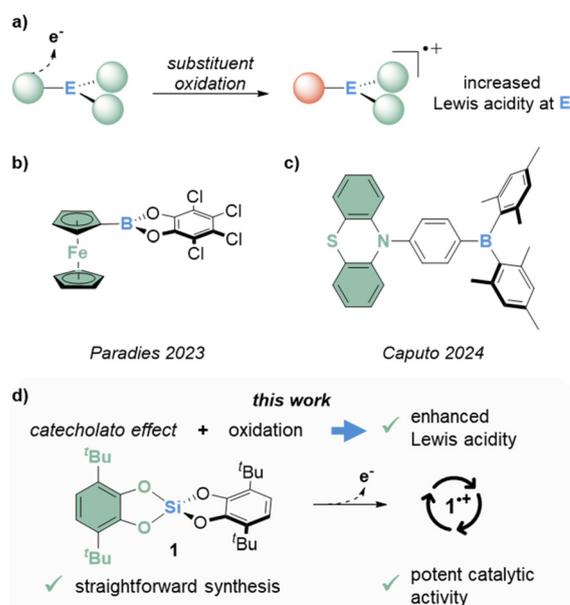


Fig. 1 (a) Schematic representation of the strategy of Lewis acidity amplification by oxidation, (b/c) examples of previously reported boranes with redox-active substituents and (d) the redox-active silicon Lewis acid **1** presented in this work.

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that suits the geometry of hypervalent structures.^{34,35} Second, the pronounced electronegativity of the primary oxygen substituents stabilizes the non-bonding orbitals in the 3-center-4-electron (3c4e) bonds that supports hypercoordinate adduct formation. Lastly, the aromatic system allows for adjustment of the mesomeric π -acidity by introducing electron-withdrawing substituents in the ligand backbone. This synergistic impact on Lewis acidity was recently termed the *catecholato effect*.³⁶ Interestingly, catecholates are mainly known as prototypical redox-active ligands, which can be oxidized to semiquinone (sq) radicals or quinones. Even though this property was investigated holistically with transition metals,³⁷ and also found application in the context of main group chemistry,³⁸ it remained unconsidered in the design of catecholate Lewis acids. In contrast to previous approaches that require the aimed installation of a redox-active substituent (*e.g.*, Fig. 1b and c), bis(catecholato)silanes are easily prepared and already exhibit considerable Lewis acidity through the *catecholato effect*.²⁶ In this work, we identify bis(3,6-di-*tert*-butyl-catecholato)silane (**1**) as suitable model system that allows first insights on the oxidation chemistry of bis(catecholato)silanes (Fig. 1d). We then continue to investigate the chemical oxidation to 1^{+} and subsequently assess its increased Lewis acidity through computations and catalytic activity.

Common bis(catecholato)silanes readily undergo oligomerization *via* low-barrier dynamic covalent processes.²⁸ Thus, to simplify the investigation for redox chemistry, we first screened for a bis(catecholato)silane representative that does not undergo oligomerization. Previous work suggested that the self-aggregation of bis(catecholato)silanes can be steered by suitable substitution of the catechol ligand.²⁸ Whereas the parent compound bis(catecholato)silane ($\text{Si}(\text{cat}^{\text{H}})_2$) forms cyclic decamers as the favored configuration in the solid state (Fig. 2a), 3,5-substituted (*tert*-butyl or cumyl) catecholates are present as dimer, and related *ortho*-amidophenolates exhibit monomeric forms.^{28,39} These examples suggested that an increased steric demand around the silicon center will cause a decreased nuclearity of silicon atoms in the thermodynamic minimum. Thus, we proposed that a monomeric bis(catecholato)silane can be realized from a 3,6-substituted catechol ligand. In analogy, the use of 3,6-di-*tert*-butyl-catechol ($\text{H}_2\text{cat}^{3,6-t\text{Bu}}$) was previously shown to prevent oligomerization of 3d metal complexes.^{40,41} Therefore, we synthesized $\text{H}_2\text{cat}^{3,6-t\text{Bu}}$ according to Ershov's procedure⁴² (Fig. 2b) and subsequently converted it with HSiCl_3 in acetonitrile to give $\text{Si}(\text{cat}^{3,6-t\text{Bu}})_2$ (**1**) in 82% yield (Fig. 2c). While **1** was known from previous studies,^{43–45} a thorough characterization and unambiguous structure assignment has been lacking, while recent work even stated problems regarding its purification.⁴⁵ We found that the present synthetic route yields analytically pure **1** as a colorless precipitate right from the reaction mixture.

In contrast to previous representatives of bis(catecholato)silanes, **1** is exceptionally soluble in dichloromethane, which allowed us to undertake a more profound NMR spectroscopic investigation. Indeed, ^1H , ^{13}C , and ^{29}Si NMR spectroscopy revealed sharp signals, indicating a monomeric form in solu-

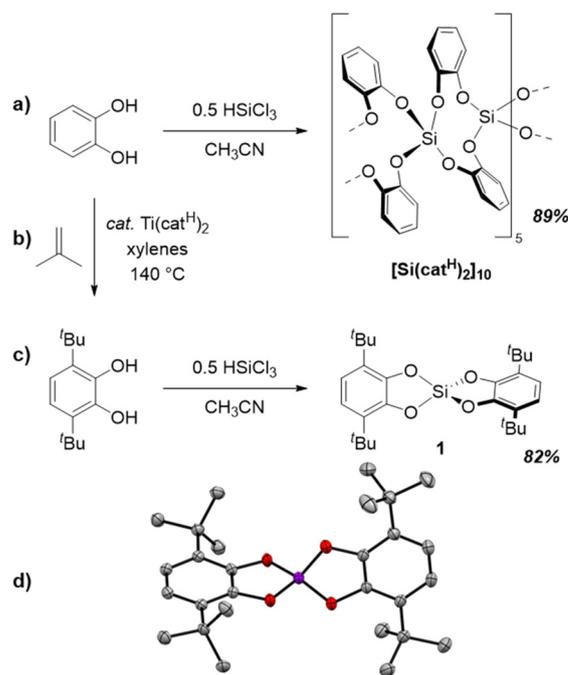


Fig. 2 Illustration of the syntheses of (a) the decamer of bis(catecholato)silane, (b) 3,6-di-*tert*-butyl-catechol according to Ershov's procedure, and (c) the monomeric bis(3,6-di-*tert*-butyl-catecholato)silane (**1**) investigated in this work. (d) SCXRD derived molecular structure of **1** (hydrogen atoms omitted for clarity; ellipsoids shown at 50% probability).

tion (details see ESI[†]). SCXRD analysis of single crystals, grown by liquid diffusion of acetonitrile into a CH_2Cl_2 solution of **1**, confirmed the monomeric, distorted tetrahedral entity in the solid state (Fig. 2d). Accompanying computations on the dimerization of **1** and related derivatives revealed a thermodynamic and not a kinetic inhibition of oligomerization (see ESI[†]). Of note, **1** showcases similar physicochemical properties to the previously reported bis(3,4,6-tri-*iso*-propyl-catecholato)silane ($\text{Si}(\text{cat}^{3,4,6-i\text{Pr}})_2$), for which the monomeric form could not be proven by scXRD.⁴⁶

With this monomeric bis(catecholato)silane in hand, we proceeded with the strategy of Lewis acidity amplification by oxidation. Oxidation of **1** would result in $\text{Si}(\text{cat}^{3,6-t\text{Bu}})_2$ ($\text{sq}^{3,6-t\text{Bu}}\text{cat}^{3,6-t\text{Bu}}$) (1^{+} , Fig. 3a). The computed fluoride ion affinity (FIA, (DLPNO-CCSD(T)/def2-QZVPP//PBE0-D3(BJ)/def2-TZVP)) of 784 kJ mol^{-1} confirms a significant increase compared to **1** (404 kJ mol^{-1}), surpassing the FIA of the prominent electrophilic phosphonium cation (EPC) $[\text{FP}(\text{C}_6\text{F}_5)_3]^+$ (ref. 47) and approaching even the strongest EPC known to date ($[\text{P}(\text{am}^{\text{F}}\text{ph}^{\text{F}})_2]^+$) (Fig. 3b).⁴⁸ The same holds for the solvation-corrected FIA_{soln} , which have been found mandatory for comparing Lewis acids of varying charge states.⁴⁹

Thus, the oxidation of **1** was explored. Cyclovoltammetry revealed an oxidation potential of 0.04 V (*vs.* Fc/Fc^+ , details see ESI[†]) for **1** in dichloromethane (Fig. 3c). In accordance with the determined potential, the ferrocenium salt $\text{Fc}[\text{B}(\text{C}_6\text{F}_5)_3]_4$



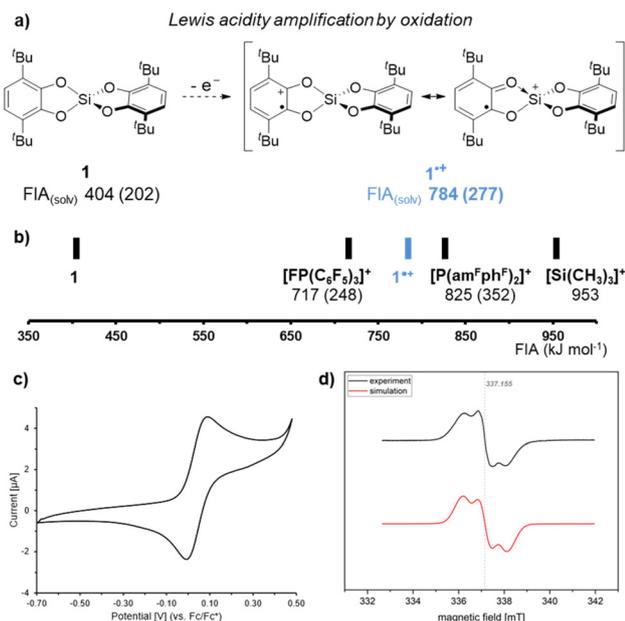


Fig. 3 (a) Illustration for the strategy of enhancing the Lewis acidity of **1** upon oxidation; (b) comparison of the FIAs of **1** and **1**⁺ with the electrophilic phosphonium cations $[FP(C_6F_5)_3]^+$ and $[P(am^Fph^F)_2]^+$ as well as with the trimethylsilylium cation; FIAs refer to *vacuum* values, FIAs in CH_2Cl_2 are shown in parentheses; details on the FIA data are given in the ESI†; (c) cyclic voltammogram of **1** (details see ESI†). (d) Stacked EPR spectra from experiment ($[1][B(C_6F_5)_4]$ in *o*- $C_6H_4F_2$) and simulation (**1**⁺).

did not indicate any reactivity with **1** in dichloromethane. When using $Ag[SbF_6]$ instead, the immediate coloration of the reaction mixture was accompanied by a paramagnetic species as judged by EPR spectroscopy. However, various signals in the ¹⁹F NMR spectrum suggested an undefined reactivity, likely involving ligand scrambling after initial fluoride abstraction from SbF_6^- by **1**⁺, supporting Lewis superacidic character. Thus, we tested silver salts with anions that were less prone to decomposition. When using $AgOTf$, $AgNTf_2$, or $Ag(o-C_6H_4F_2)[Al(O^tC_4F_9)_4]$ ⁵⁰ such reactivity was indeed absent. However, in those cases, the oxidation processes were found slow, with full conversion not reached even after several days. In sight of the light-sensitivity of $Ag(I)$ salts we aimed to reduce the reaction time by exploiting the increased oxidation capability of the Ag/I_2 system.⁵¹ Indeed, the addition of half an equivalent of molecular iodine tremendously accelerated the conversion of **1** with the silver salts. Again, a deep coloration of the reaction mixture in conjunction with an EPR active sample strongly supported the initial oxidation. However, EPR spectra did not match the expected pattern for **1**⁺ but indicated side reactivity under the harsh oxidation conditions.

Next, we considered $[N(p-C_6H_4Br)_3][B(C_6F_5)_4]$ as a suitable oxidant with a preference for outer-sphere electron-transfer⁵² and a low inner-sphere reorganization.⁵³ In an attempt to isolate the target radical cation, **1** was reacted with $[N(p-C_6H_4Br)_3][B(C_6F_5)_4]$ in *ortho*-difluorobenzene (*o*- $C_6H_4F_2$). While the oxidation process required several days, EPR monitoring

suggested cleaner oxidation. After a complete reaction, an intensely colored oil was isolated, which solidified after trituration with *n*-hexane. Simulation of the room temperature recorded EPR spectrum revealed a resonance at $g^{iso} = 2.00269$ with a triplet hyperfine coupling constant of $A_H^{iso} = 716 \mu T$ from two equivalent hydrogens ($S = 1/2$) (Fig. 3d). Comparison of the IR spectra of **1** and $[1][B(C_6F_5)_4]$ indicated altered C–O stretching modes (Fig. S13†), in line with typical catecholato and semiquinonato ligands.⁵⁴ The compound was additionally characterized by mass spectrometry and elemental analysis, further supporting the proposed structural motif, but also indicating partial decomposition. This observation aligns with previously reported decomposition pathways for $cat^{3,6-tBu}$ and related *tert*-butyl-phenol derivatives under Lewis acidic^{55–58} or oxidative^{59,60} conditions. Unfortunately, the viscous nature of the compound prevented crystallization and analysis of a solid-state structure by scXRD. We also attempted oxidation in the presence of donors. However, scXRD analysis of proposed adducts with donors could not be achieved, as the resulting species suffered from the same obstacle. However, the isolated species allowed us to probe the initial hypothesis of whether **1**⁺ displays an amplified Lewis acidity over **1**. A Gutmann-Beckett classification was judged as unsuitable given the paramagnetic nature of the target species.⁶¹ Thus, we attempted to gauge the Lewis acidic potential by testing the catalytic activity of $[1][B(C_6F_5)_4]$. Indeed, using 5 mol% $[1][B(C_6F_5)_4]$ enabled efficient and fast Friedel–Crafts dimerization of 1,1-diphenylethylene (Fig. 4a). Notably, $[1][B(C_6F_5)_4]$ was also found to be catalytically applicable in the reductive hydrodeoxygenation of benzophenone (Fig. 4b). To utilize the full potential of **1**⁺ we next attempted the more challenging carbonyl-olefin-metathesis (COM) as its outcome is known to be critically dependent on the strength of the applied Lewis acid.^{62–68}

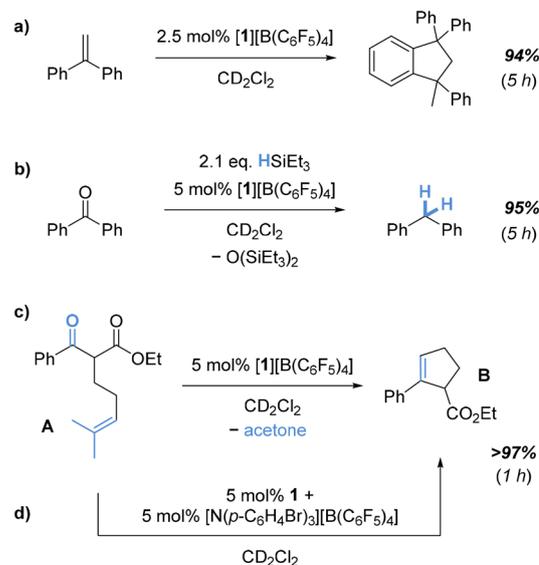


Fig. 4 Representative (a) Friedel–Crafts dimerization, (b) hydrodeoxygenation, and (c) carbonyl-olefin-metathesis (COM) catalyzed by $[1][B(C_6F_5)_4]$; (d) *in situ* generation of the catalytic species for the COM.



Indeed, 5 mol% of $[1][B(C_6F_5)_4]$ enabled complete formation of the cyclization product **B** from the substrate **A** within one hour, thus ranging above the activity of the neutral bis(pertrifluoromethylcatecholato)silane³⁰ but similar to the hitherto most active bis(catecholato)phosphonium ions²⁹ (Fig. 4c). Strikingly, the catalytic activity of 1^{+} can be unlocked by *in situ* generation before substrate addition (Fig. 4d). Of note, the formation of **B** was not observed in the presence of **1** or the $[N(p-C_6H_4Br)_3]^{+}$ cation alone, supporting 1^{+} as catalytically active species.

Overall, the disclosed approach of combining two stable pre-catalysts for the generation of a Lewis superacid that takes profit from a combination of the *catecholato effect* and its redox activity states a valuable alternative to existing methods. The *in situ* oxidation approach allows the mitigation of long-term instability and represents a valuable extension of previous strategies for generating silylium ions.

Author contributions

T. T. and L. G. devised the project and designed the experiments. T. T. carried out the calculations, conducted experimental work and characterization, and analyzed the data. T. T. and L. G. wrote the manuscript. M. S. refined and finalized the scXRD structure.

Data availability

The data supporting this article have been included as part of the ESI.†

Crystallographic data has been deposited under CCDC 2402241.†

Conflicts of interest

There are no conflicts to declare.

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References

- H. Yamamoto, *Lewis acids in organic synthesis*, Wiley-VCH, Weinheim, 2002.
- A. Corma and H. García, *Chem. Rev.*, 2003, **103**, 4307–4366.
- H. Yamamoto, *Lewis acid reagents: a practical approach*, Knovel, Norwich, NY, 2007.
- H. Yamamoto and K. Ishihara, *Acid catalysis in modern organic synthesis*, Wiley-VCH, Weinheim, 2008.
- S. Kobayashi and K. Manabe, *Pure Appl. Chem.*, 2000, **72**, 1373–1380.
- S. J. Lippard and J. M. Berg, *Principles of bioinorganic chemistry*, University Science Books, Mill Valley, CA, 1994.
- J. J. Badillo, N. V. Hanhan and A. K. Franz, *Curr. Opin. Drug Discovery Dev.*, 2010, **13**, 758–776.
- G. C. Welch, R. R. S. Juan, J. D. Masuda and D. W. Stephan, *Science*, 2006, **314**, 1124–1126.
- G. A. Olah and D. A. Klumpp, *Superelectrophiles and their chemistry*, Wiley-Interscience, Hoboken, 2008.
- L. Greb, *Chem. – Eur. J.*, 2018, **24**, 17881–17896.
- H. F. T. Klare and M. Oestreich, *Dalton Trans.*, 2010, **39**, 9176–9184.
- R. N. Perutz, *Science*, 2008, **321**, 1168–1169.
- C. Douvris and O. V. Ozerov, *Science*, 2008, **321**, 1188–1190.
- V. J. Scott, R. Çelenligil-Çetin and O. V. Ozerov, *J. Am. Chem. Soc.*, 2005, **127**, 2852–2853.
- V. Lemieux, M. D. Spantulescu, K. K. Baldrige and N. R. Branda, *Angew. Chem., Int. Ed.*, 2008, **47**, 5034–5037.
- A. Y. Khalimon, W. E. Piers, J. M. Blackwell, D. J. Michalak and M. Parvez, *J. Am. Chem. Soc.*, 2012, **134**, 9601–9604.
- A. Y. Khalimon, B. K. Shaw, A. J. V. Marwitz, W. E. Piers, J. M. Blackwell and M. Parvez, *Dalton Trans.*, 2015, **44**, 18196–18206.
- R. Mizutsu, R. Asato, C. J. Martin, M. Yamada, Y. Nishikawa, S. Katao, M. Yamada, T. Nakashima and T. Kawai, *J. Am. Chem. Soc.*, 2019, **141**, 20043–20047.
- M. Schorpp, R. Yadav, D. Roth and L. Greb, *Angew. Chem., Int. Ed.*, 2022, **61**, e2022079.
- R. Prakash, J. Joseph, A. P. Andrews, B. Varghese and A. Venugopal, *Inorg. Chem.*, 2023, **62**, 14828–14832.
- M. Yang, D. Tofan, C. H. Chen, K. M. Jack and F. P. Gabbaï, *Angew. Chem.*, 2018, **130**, 14064–14068.
- O. Planas, F. Wang, M. Leutzsch and J. Cornella, *Science*, 2020, **367**, 313–317.
- L. Köring, A. Stepen, B. Birenheide, S. Barth, M. Leskov, R. Schoch, F. Krämer, F. Breher and J. Paradies, *Angew. Chem., Int. Ed.*, 2023, **62**, e202216959.
- T. P. L. Cosby, A. Bhattacharjee, S. K. Henneberry, J. LeBlanc and C. B. Caputo, *Chem. Commun.*, 2024, **60**, 5391–5394.
- R. Maskey, M. Schädler, C. Legler and L. Greb, *Angew. Chem., Int. Ed.*, 2018, **57**, 1717–1720.
- D. Hartmann, M. Schädler and L. Greb, *Chem. Sci.*, 2019, **10**, 7379–7388.
- D. Roth, H. Wadepohl and L. Greb, *Angew. Chem., Int. Ed.*, 2020, **59**, 20930–20934.
- D. Hartmann, T. Thorwart, R. Müller, J. Thusek, J. Schwabedissen, A. Mix, J. H. Lamm, B. Neumann, N. W. Mitzel and L. Greb, *J. Am. Chem. Soc.*, 2021, **143**, 18784–18793.



- 29 D. Roth, J. Stirn, D. W. Stephan and L. Greb, *J. Am. Chem. Soc.*, 2021, **143**, 15845–15851.
- 30 T. Thorwart, D. Roth and L. Greb, *Chem. – Eur. J.*, 2021, **27**, 10422–10427.
- 31 N. Ansmann, D. Hartmann, S. Sailer, P. Erdmann, R. Maskey, M. Schorpp and L. Greb, *Angew. Chem., Int. Ed.*, 2022, **61**, e202203947.
- 32 N. Ansmann, T. Thorwart and L. Greb, *Angew. Chem., Int. Ed.*, 2022, **61**, e202210132.
- 33 Q. Luo and L. Greb, *Eur. J. Inorg. Chem.*, 2023, **26**, e202300186.
- 34 C. L. Frye, *J. Am. Chem. Soc.*, 1964, **86**, 3170–3171.
- 35 J. J. Harland, R. O. Day, J. F. Vollano, A. C. Sau and R. R. Holmes, *J. Am. Chem. Soc.*, 1981, **103**, 5269–5270.
- 36 L. Greb, *Synlett*, 2023, A–Q.
- 37 D. L. J. Broere, R. Plessius and J. I. van der Vlugt, *Chem. Soc. Rev.*, 2015, **44**, 6886–6915.
- 38 R. Maskey and L. Greb, Catecholate Complexes of p-Block Elements: Redox Activity, *Encycl. Inorg. Bioinorg. Chem.*, 2022, 1–15.
- 39 T. Thorwart, D. Hartmann and L. Greb, *Chem. – Eur. J.*, 2022, **28**, e202202273.
- 40 C.-M. Liu, E. Nordlander, D. Schmech, R. Shoemaker and C. G. Pierpont, *Inorg. Chem.*, 2004, **43**, 2114–2124.
- 41 C. W. Lange, B. J. Conklin and C. G. Pierpont, *Inorg. Chem.*, 1994, **33**, 1276–1283.
- 42 I. Belostotskaya, N. Komissarova, E. Dzhuryan and V. Ershov, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1972, **21**, 1535–1536.
- 43 A. Prokof'ev, T. Prokofe'va, N. Bubnov, S. Solodovnikov, I. Belostotskaya, V. Ershov and M. Kabachnik, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1978, **27**, 1726–1733.
- 44 A. I. Prokof'ev, T. I. Prokof'eva, I. S. Belostotskaya, N. N. Bubnov, S. P. Solodovnikov, V. V. Ershov and M. I. Kabachnik, *Tetrahedron*, 1979, **35**, 2471–2482.
- 45 K. V. Arsenyeva, A. V. Klimashevskaya, M. V. Arsenyev, I. A. Yakushev, A. V. Cherkasov, P. V. Dorovatovskii, A. V. Maleeva, O. Y. Trofimova and A. V. Piskunov, *Russ. Chem. Bull.*, 2024, **73**, 117–130.
- 46 R. Maskey, T. Thorwart, S. F. Ebel, A. Jovic, D. Hartmann and L. Greb, *Chem. – Eur. J.*, 2023, **29**, e202300269.
- 47 C. B. Caputo, L. J. Hounjet, R. Dobrovetsky and D. W. Stephan, *Science*, 2013, **341**, 1374–1377.
- 48 D. Roth, T. Thorwart, C. Douglas and L. Greb, *Chem. – Eur. J.*, 2022, **29**, e202203024.
- 49 P. Erdmann, M. Schmitt, L. M. Sigmund, F. Krämer, F. Breher and L. Greb, *Angew. Chem., Int. Ed.*, 2024, **63**, e202403356.
- 50 I. Krossing, *Chem. – Eur. J.*, 2001, **7**, 490–502.
- 51 P. J. Malinowski, D. Himmel and I. Krossing, *Angew. Chem., Int. Ed.*, 2016, **55**, 9262–9266.
- 52 N. G. Connelly and W. E. Geiger, *Chem. Rev.*, 1996, **96**, 877–910.
- 53 M. Quiroz-Guzman and S. N. Brown, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 2010, **66**, m171–m173.
- 54 A. Vlček Jr., *Comments Inorg. Chem.*, 1994, **16**, 207–228.
- 55 V. B. Vol'eva, T. I. Prokof'eva, I. S. Belostotskaya, N. L. Komissarova, D. B. Gorbunov and L. N. Kurkovskaya, *Russ. J. Org. Chem.*, 2011, **47**, 1310.
- 56 E. V. Ilyakina, O. G. Mishchenko, A. V. Piskunov, S. V. Maslennikov, I. V. Spirina, Y. A. Kurskii and A. V. Lado, *Russ. J. Gen. Chem.*, 2009, **79**, 724–727.
- 57 S. M. Kulikov, I. V. Kozhevnikov, M. N. Fomina and A. P. Krysin, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1987, **36**, 681–684.
- 58 I. A. Novikova, V. B. Vol'eva, N. L. Komissarova, I. S. Belostotskaya and V. V. Ershov, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1981, **30**, 1732–1735.
- 59 K. U. Ingold, *Can. J. Chem.*, 1963, **41**, 2807–2815.
- 60 J. J. Conradi and G. A. McLaren, *J. Am. Chem. Soc.*, 1960, **82**, 4745–4745.
- 61 P. Erdmann and L. Greb, *Angew. Chem., Int. Ed.*, 2022, **61**, e202114550.
- 62 J. R. Ludwig, P. M. Zimmerman, J. B. Gianino and C. S. Schindler, *Nature*, 2016, **533**, 374–379.
- 63 A. Djurovic, M. Vayer, Z. Li, R. Guillot, J.-P. Baltaze, V. Gandon and C. Bour, *Org. Lett.*, 2019, **21**, 8132–8137.
- 64 H. Albright, H. L. Vonesh and C. S. Schindler, *Org. Lett.*, 2020, **22**, 3155–3160.
- 65 A. J. Davis, R. B. Watson, D. J. Nasrallah, J. L. Gomez-Lopez and C. S. Schindler, *Nat. Catal.*, 2020, **3**, 787–796.
- 66 R. Wang, Y. Chen, M. Shu, W. Zhao, M. Tao, C. Du, X. Fu, A. Li and Z. Lin, *Chem. – Eur. J.*, 2020, **26**, 1941–1946.
- 67 H. Albright, A. J. Davis, J. L. Gomez-Lopez, H. L. Vonesh, P. K. Quach, T. H. Lambert and C. S. Schindler, *Chem. Rev.*, 2021, **121**, 9359–9406.
- 68 S. R. Todtz, C. W. Schneider, T. Malakar, C. Anderson, H. Koska, P. M. Zimmerman and J. J. Devery III, *J. Am. Chem. Soc.*, 2023, **145**, 13069–13080.

