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Bimetallic iron–tin catalyst for N₂ to NH₃ and a silyldiazenido model intermediate†

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A tin-supported iron catalyst produces 5.9 turnovers of NH₃ from N₂, using [Ph₂NH₂]OTf as the acid and CoCp₂* as the reductant. Two redox states of the Fe(N₂) adduct and an Fe silyldiazenido complex were characterized using X-ray crystallography along with NMR and Mössbauer spectroscopies. Density functional theory calculations reveal that the charge on the Sn center correlates strongly with both the polarization of the N₂ moiety and the charge on the distal N atom.

The conversion of dinitrogen into reduced feedstocks using well-defined transition-metal catalysts has steadily advanced since Schrock and Yandulov reported the Mo triamidoamine catalyst in 2003.¹ The development of other metal-based catalysts for N₂ fixation has led to a greater understanding of the diverse mechanisms and increasingly high catalytic turnovers.² Notably, Nishibayashi and coworkers reported a Mo pincer catalyst capable of producing 4350 equiv. of NH₃ using HOCH₂·CH₂OH/SmI₂ as a coupled proton and electron source.³ However, these developments are weighted primarily toward early transition metals. Comparatively, the number of late-transition metal catalysts is limited, including the Fe-based catalysts (Fig. 1).⁴

Here, we report an Fe catalyst that is largely inspired by Peters' nitrogen fixation catalyst, P₃^BFe⁺, (P₃^B = tris(*o*-diisopropylphosphinophenyl)borane).^{4b,5} In comparison to other anchoring atoms such as C and Si, Peters and coworkers have concluded that borane uniquely enhances the catalytic performance by conferring stability to the hydrazido intermediate, FeNNH₂.⁶ Using a previously reported bimetallic Fe–Sn system,⁷ we generated the N₂

adduct, LSnFeN₂ (**1**), where L is the double-decker ligand, [N(*o*-(NCH₂PⁱPr₂)(C₆H₄)₃)]^{3–}. Complex **1** mediates the catalytic reduction of N₂ to NH₃ with 5.9 turnovers. The properties of **1**, its reduced analogue, K(THF)₃·LSnFe(N₂) (**2**), and the N₂-functionalized diazenido complex, LSnFeN₂SiMe₃ (**3**), were characterized structurally, spectroscopically, and theoretically. To the best of our knowledge, this work provides the first example of catalytic N₂ reduction that leverages a direct Fe–Sn interaction. Also, this study adds to the limited examples of Sn-supported first-row transition metal complexes.⁸

The addition of FeBr₂ to the metalloligand Li(THF)₃·LSn in THF led to the previously reported bimetallic complex, LSnFeBr.⁷ Crystallization of LSnFeBr by Et₂O diffusion into a concentrated benzene solution provided deep-red crystals in 68% yield. Next, the one- and two-electron reductions of LSnFeBr in THF under a N₂ atmosphere were affected by adding 1.1 equiv. and 2.2 equiv. KC₈, respectively, whereupon the solution changed color from red to yellow orange and then to deep orange.

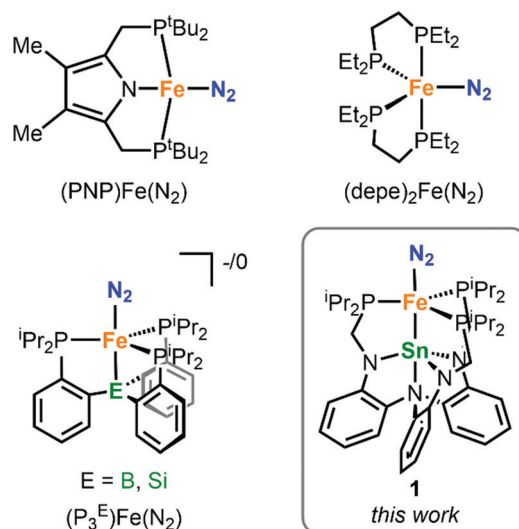


Fig. 1 Selected Fe-based catalysts for N₂ fixation.⁴

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The one-electron reduced species, $\text{LSnFe}(\text{N}_2)$ (**1**), is paramagnetic with an $S = 1/2$ ground state ($\mu_{\text{eff}} = 1.87 \mu_{\text{B}}$, Evans method). The N_2 ligand is bound in a terminal, end-on manner (*vide infra*). The N–N stretching frequency of 2011 cm^{-1} (IR, KBr pellet, ESI† Fig. S11) indicates the moderate activation of the N_2 unit that is comparable to other polyphosphine $\text{Fe}(\text{N}_2)$ complexes.⁹ The doubly reduced species, $\text{K}(\text{THF})_3\text{-LSnFe}(\text{N}_2)$ (**2**), is diamagnetic and displays a single $^{31}\text{P}\{^1\text{H}\}$ NMR peak at 88.2 ppm (THF- d_8). A ^{119}Sn NMR quartet peak was observed at 511.6 ppm, which arises from the ^{119}Sn nucleus coupling to three equivalent ^{31}P nuclei ($I = \frac{1}{2}$, 100%) through the Fe nucleus, with a $^2J_{\text{Sn-P}}$ value of 610 Hz (ESI† Fig. S4). The $^1\text{H}\{^{31}\text{P}\}$ NMR spectrum with seven unique resonances is consistent with a trigonal symmetry in solution (ESI† Fig. S2). The N–N stretching frequency for the [2.2.2]cryptand derivative, $\text{K}(\text{crypt-222})[\text{LSnFe}(\text{N}_2)]$, of 1944 cm^{-1} (IR, KBr pellet, ESI† Fig. S12), supports increased electron density at Fe, allowing for amplified backbonding into the $\text{N}_2 \pi^*$ orbitals.

Single-crystal X-ray diffraction studies were performed for **1** and **2** (see the ESI†). In both structures, the Fe center is trigonal bipyramidal with an end-on N_2 ligand in the axial position *trans* to the Sn center (Fig. 2). The N–N bond elongates by 0.03 Å from 1.112(2) Å in **1** to 1.143(6) Å in **2** (*cf.* free N_2 1.10 Å, Table S2, ESI†). The Fe– N_2 bond contracts by the same magnitude, consistent with increased Fe-to- $\text{N}_2 \pi$ -backbonding in **2**. Notably, all the other bonds around Fe contracted upon reduction. In comparing **2** to **1**, the Fe–Sn and avg Fe–P bonds are shorter by 0.03 and 0.07 Å, respectively. As an aside, the Fe–Sn bond lengths (2.4470(3) in **1** and 2.4215(8) Å in **2**) are both smaller

than the sum of their covalent radii (*cf.* 2.59 Å), suggesting the presence of a Fe–Sn bonding interaction. Complex **2** crystallized as a 1-D coordination polymer, where the bridging K^+ ion is chelated by the ligand backbone of one molecule while binding the N_2 ligand of another. Because of a singularly short K– N_{eq} interaction, one of the Sn– N_{eq} bonds is significantly elongated in **2**, precluding a direct comparison of the Sn first-coordination shell between **1** and **2**.

In heterobimetallic complexes, the presence of intermetal covalent bond(s) can complicate the assignment of formal oxidation states of the individual metal centers. Adapting the Feltham–Enemark notation¹⁰ to tally the total valence electrons of the bimetal unit,¹¹ the electronic configurations for LSnFeBr , **1**, and **2** are denoted as $\{\text{FeSn}\}^8$, $\{\text{FeSn}\}^9$, and $\{\text{FeSn}\}^{10}$. This redox triad was interrogated through the electrochemical study of **1** and **2**. The cyclic voltammograms (ESI† Fig. S14 and S15) revealed a reversible one-electron redox event at $E_{1/2} = -1.89 \text{ V}$ vs. $\text{FcPz}^{+/0}$, which is assigned to the $\{\text{FeSn}\}^{9/10}$ redox couple, and an irreversible oxidation at $E_{\text{pa}} \sim -0.76 \text{ V}$ (0.4 M $[\text{tBu}_4\text{N}][\text{PF}_6]$ in THF). For the latter oxidation, the irreversibility is likely due to N_2 dissociation from the cationic $\{\text{FeSn}\}^8$ species.

Starting from the $\{\text{FeSn}\}^{10}$ species **2**, N_2 functionalization was affected by using an electrophilic reagent in accordance with the previous literature.^{9c} Reaction of **2** with a slight excess of Me_3SiCl yielded the diazenido complex, $\text{LSnFeN}_2\text{SiMe}_3$ (**3**), as a lavender powder that is highly soluble in organic solvents ranging from pentane to THF. Structurally characterized Fe diazenido complexes that are derived from N_2 are still limited in the literature.^{6c,9c,12} The N–N vibration at 1756 cm^{-1} (IR, KBr pellet, ESI† Fig. S13) for **3** compares well with the reported values for Fe diazenido complexes (ESI† Table S3).^{9c,12a} Complex **3** was characterized using a suite of heteronuclear NMR spectroscopies (Fig. 2). A downfield $^{31}\text{P}\{^1\text{H}\}$ NMR resonance at 101.3 ppm was observed with satellites arising from $^2J_{\text{P-Sn}}$ coupling to the ^{119}Sn (natural abundance: 7.7%) and ^{117}Sn (8.6%) nuclei of 561 and 538 Hz, respectively. In the ^{119}Sn NMR spectrum, a quartet was observed at 441.5 ppm, with a matching $^2J_{\text{Sn-P}}$ value of 559 Hz. Compared to **2**, **3** has a slightly lower $^2J_{\text{Sn-P}}$ value, which is consistent with the longer Fe–Sn bond in **3**. The ^{29}Si NMR resonance at -11.0 ppm falls well within the range of previously reported resonances for Fe silyldiazenido complexes.^{9c,12a}

Single crystals of **3** were grown from a concentrated Et_2O solution stored at -30°C for 48 h (Fig. 2). The structure shows that the N–N bond lengthened to 1.182(3) Å, which is intermediate between a double (1.25 Å) and triple (1.10 Å) N–N bond. The Fe–N bond contracted to 1.686(2) Å, indicative of multiple bond character.¹³ The remaining bonds in the Fe first-coordination shell are expanded in **3** relative to **2**, where the avg Fe–P and Fe–Sn bonds increase by 0.04 and 0.05 Å, respectively. The N–N–Si vector has a corresponding bond angle of $162.7(3)^\circ$, a value that is between linear and bent ($\sim 130^\circ$).¹⁴ This bond angle is similar to that in $(\text{P}_3^{\text{Si}})\text{Fe}(\text{N}_2\text{SiMe}_3)$ (165.6°), but in sharp contrast to bent angles in $[\text{Fe}(\text{diphosphine})_2(\text{N}_2\text{SiMe}_3)][\text{BAR}_4\text{F}]$ complexes (127° , 134°).^{9c,12a} Diazenido ligands, which are isoelectronic to nitrosyl ligands, are redox non-innocent, and hence,

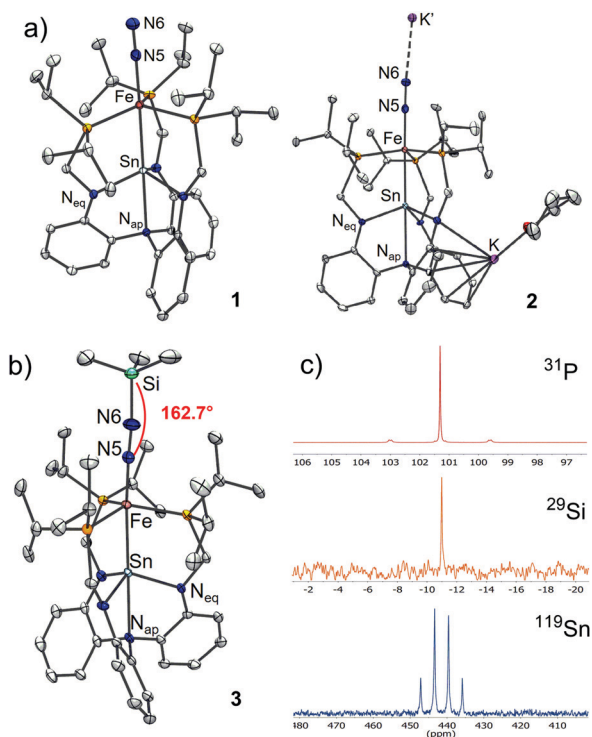


Fig. 2 (a and b) Solid-state structures of **1**, **2**, and **3**. Thermal ellipsoids set at 50% probability with hydrogen atoms omitted. (c) $^{31}\text{P}\{^1\text{H}\}$, ^{29}Si , and ^{119}Sn NMR spectra of **3** in THF- d_8 . (See the ESI† for the full spectra.)

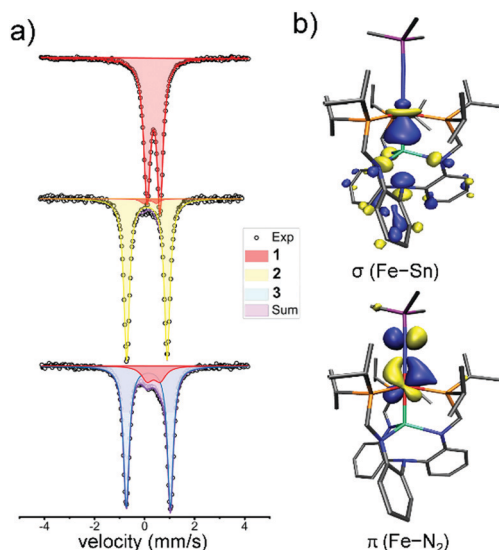


Fig. 3 (a) Zero-field ^{57}Fe Mössbauer spectra recorded at 80 K. Experimental data are indicated by the dotted points. In samples of **2** and **3**, LSnFeN_2 (**1**) is present as an impurity at 3% and 14%, respectively. Tabulated parameters can be found in Table S4 (ESI †). (b) DFT-calculated MOs of **3** showing the Fe–Sn σ -bond and the enhanced Fe–N $_2$ π -backbonding upon silylation.

metal diazenido species can be described using two limiting resonance structures: $\text{M}=\text{N}=\text{N}-\text{R}$ and $\text{M}-\text{N}\equiv\text{N}-\text{R}$.¹⁴ The former features a bent diazenido ligand (*i.e.* bent N–N–R angle) that is formally classified as a 3-electron, LX-donor; the latter is best described as a diazenium ligand, which akin to NO^+ is a cationic 2-electron L-donor. Collectively, the structural parameters in **3** support bonding that is in between these two resonance forms.

Solid samples of **1**, **2**, and **3** were subjected to zero-field ^{57}Fe Mössbauer spectroscopy at 80 K. Each spectrum showed a relatively clean quadrupole doublet (Fig. 3a, Fig. S17 and Table S4, ESI †). The isomer shift (δ) steadily decreases from **1** to **2** to **3**: 0.47, 0.35, and 0.26 mm s^{-1} , respectively. The observed decrease in δ upon reduction is typical for low-valent Fe systems.¹⁵ The lowering of δ has been attributed to the increase in the Fe 4s population that arises from greater Fe-to-L π -backbonding, or shorter, more covalent Fe–L bonds.^{15a,16} In this series, the only bond that consistently contracts is the Fe–N bond (whether the ligand is N_2 or N_2SiMe_3), which decreases from 1.793(1) Å in **1** to 1.762(5) Å in **2**, and then to 1.686(2) Å in **3**. The quadrupole splitting ($|\Delta E_Q|$) increases from 0.52 mm s^{-1} in **1** to 1.62 mm s^{-1} in **2**, but only slightly increases to 1.76 mm s^{-1} in **3**. The trends in both δ and $|\Delta E_Q|$ match well to those reported for $[(\text{P}_3^{\text{Si}})\text{Fe}(\text{N}_2)]^{0/-}$ and $(\text{P}_3^{\text{Si}})\text{Fe}(\text{N}_2\text{SiMe}_3)$ (Table S4, ESI †).^{9c,17} The δ values for **2** and **3** are different ($\Delta\delta = 0.11 \text{ mm s}^{-1}$), whereas the $|\Delta E_Q|$ values are similar. Hence, it remains unclear whether the configuration of $\{\text{SnFe}(\text{N}_2\text{R})\}^{10}$ in **3** would be best described as an $\{\text{FeSn}\}^{10}$ unit that π -backbonds into a silyldiazenium(1+) moiety or an $\{\text{FeSn}\}^8$ unit with a π -donating diazenido(2-) ligand.

Density functional theory (DFT) calculations (M06-L, see the ESI † for computational details) were also performed to probe the electronic structures of **1–3**. Overall, there is good agreement between the computed and experimental geometries (ESI † , Table S5). The resulting MO diagrams for **1–3** all show a

covalent Fe–Sn σ -bond, where the Sn (5p $_z$, 5s) and Fe (3d $_z^2$) contributions are almost equal (Fig. 3b and ESI † , Fig. S18–S20). The ground-state configurations of **1** and **2** are consistent with $(\sigma_{\text{Fe-Sn}})^2(\text{Fe } d_{xz}, d_{yz})^4(\text{Fe } d_{xy}, d_{x^2-y^2})^n(\sigma_{\text{Fe-N}_2}^*)^0$, where n is 3 and 4, respectively. The MO diagram for **3** also shows highly covalent π -bonds between Fe and N_2SiR_3 , and is consistent with the ground-state configuration: $(\sigma_{\text{Fe-Sn}})^2(\pi_{\text{Fe-N}_2})^4(\text{Fe-}d_{xy}, d_{x^2-y^2})^4(\pi_{\text{Fe-N}_2}^*)^0(\sigma_{\text{Fe-Sn}}^*)^0$.

To elucidate the bonding in **1–3**, the Fe–N and N–N bond orders were analyzed using the density derived electrostatic and chemical (DDEC6) method.¹⁸ This analysis revealed a gradual increase in the Fe–N bond order from **1** to **2** to **3**: 1.13, 1.20, and 1.50, respectively (ESI † , Fig. S21). Simultaneously, the N–N bond order decreases from **1** to **2** to **3**: 2.58, 2.56, and 2.18, respectively. Indeed, coordination of the SiMe_3^+ group results in a more polarized and weakened N–N bond, as reflected by the increased negative charge on the distal N-atom in **3** (–0.37) compared to **1** (–0.15) and **2** (–0.24) (ESI † , Table S9). Similar trends were observed upon the coordination of Lewis acidic boranes to the distal N of $\text{Fe}(\text{depe})_2(\text{N}_2)$, culminating in the selective protonation at the distal N site due to its enhanced negative charge.^{12b} In **1–3**, the charge of the distal N and the charge difference between the N atoms were found to correlate best with the charge of Sn ($R_{\text{adj}}^2 = 0.997$ and 0.988, respectively, Fig. S23 and S24, ESI †). These strong correlations suggest that the identity of the atom *trans* to the N_2 unit may have a substantial effect on the distal N's nucleophilicity, which would likely govern how readily the N_2 unit can undergo further functionalization.

Next, we investigated the catalytic performance of **1–3** in reducing N_2 to NH_3 . Using similar conditions to those developed by Peters and coworkers,^{4b} the catalyst (2.3 μmol), $[\text{Ph}_2\text{NH}_2]\text{OTf}$ (108 equiv.), CoCp_2^* (54 equiv.), and Et_2O were sealed in a vessel while under 1 atm N_2 at -196°C , and then stirred at -78°C for 3 h. The Ph_2NH_2^+ acid and the CoCp_2^* reductant are proposed to initially form the protonated metallocene, $\text{Co}(\eta^4\text{-Cp}^*\text{H})(\text{Cp}^*)$, which mediates the proton-coupled electron transfer during N_2 reduction.⁵ Table 1 summarizes the results of the catalytic runs, which were performed in triplicate (ESI † , Table S10). Catalyst **1** generated 5.9(5) turnovers of NH_3 (33% yield, entry 1). Moreover, catalytic activity was retained in the presence of $\text{Hg}_{(s)}$ (entry 2), supporting an active species that is homogeneous. In comparison, the $\text{P}_3^{\text{B}}\text{Fe}^+$ catalyst produced 12.8 turnovers of NH_3 in a single catalytic run and reached 84 NH_3 turnovers after 3 consecutive runs (entries 5 and 6).⁵ For NH_3 production under these specific conditions, **1** is half as active as $\text{P}_3^{\text{B}}\text{Fe}^+$ in a single catalytic run, and outperforms both $\text{P}_3^{\text{Si}}\text{Fe}(\text{N}_2)$ ⁵ and $\text{Fe}(\text{depe})_2(\text{N}_2)$ ^{12a} five-fold (entries 7 and 8). We note that other Fe catalysts require harsher reagents such as $\text{H}(\text{Et}_2\text{O})_2\text{B}(\text{Ar}^{\text{F}})_4$ and KC_8 to mediate N_2 to NH_3 .^{4c-e,19a,b}

The N_2 reduction reaction, however, was rendered substoichiometric when **2** was used as the catalyst (entry 3), presumably due to the low solubility of **2** in Et_2O . On the other hand, catalyst **3** gave comparable turnovers (entry 4) as **1**, supporting the ability of a metal silyldiazenido species to enter the N_2 reduction cycle. Because metal silyldiazenido species are proposed as intermediates in catalytic N_2 silylation, we also tested **3** for N_2

Table 1 Results of catalytic reduction of dinitrogen to ammonia using Fe–Sn complexes (**1–3**) and comparisons to known Fe catalysts

$\text{N}_2 + \text{CoCp}^*_2 + [\text{Ph}_2\text{NH}_2]\text{OTf} \xrightarrow[\text{Et}_2\text{O}, -78^\circ\text{C}, 3\text{ h}]{\text{Fe catalyst}} \text{NH}_3$					
x equiv		y equiv			
Entry	Catalyst	x (equiv.)	y (equiv.)	NH ₃ turnovers	Yield ^a (%) Ref.
1	1	54	108	5.9(5)	33 —
2	1 + Hg(s) ^b	54	108	5.2(8)	29 —
3	2	54	108	0.8(5)	5 —
4	3	54	108	4.6(2)	26 —
5	P ₃ ^B Fe ⁺	54	108	12.8(5)	72 4b
6	P ₃ ^B Fe ⁺	162 × 3 ^c	322 × 3 ^c	84(8)	52 4b
7	P ₃ ^{Si} Fe(N ₂)	54	108	1.2(1)	7 4b
8	(depe) ₂ Fe(N ₂)	54	108	1.1(2) ^d	6 4g

^a Yield is based on the reductant. ^b 200 equiv. Hg was added to the reaction vessel before the start of catalysis. ^c In each of the 3 cycles, the reaction was cooled to -196°C to replenish the reagents and solvents. ^d (depe)₂Fe(N₂) is selective for hydrazine with 8.9(1) equiv. N₂H₄ in addition to 1.1(2) equiv. NH₃.

silylation using Me₃SiCl and KC₈ as the added reagents. Disappointingly, **3** only generated 1.2 equiv. of N(SiMe₃)₃, which is relatively poor compared to other reported systems.^{2b}

In summary, a family of Fe–Sn bimetallic complexes has enabled the characterization and comparison of a series of nitrogen fixation catalysts, capable of generating ammonia in up to 5.9 equivalents. Experimental and computational results together show a clear and comparable trend of increased N₂ activation evidenced by decreased N₂ bond order, stretching frequency, and increased negative charge on the distal nitrogen upon reduction from **1** to **2**, and even more so in the silylation of **2** to **3**. For all of these complexes, a direct Fe–Sn covalent interaction was present, and a linear trend was found between the charge on Sn and the charge on the distal nitrogen in the N₂ moiety. This points to another potential impact of the supporting atom *trans* to the N₂ moiety on N₂ functionalization. Under the same catalytic conditions, the Fe–Sn bimetallic catalyst compares well with Peters' Fe–E systems, outperforming E = Si and C, but is less active than E = B. This type of comparison lends additional understanding into the factors that generate active Fe–E catalysts. Additional studies with different supporting atoms and further functionalization of the presented complexes are currently underway.

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Conflicts of interest

There are no conflicts to declare.

Notes and references

- D. V. Yandulov and R. R. Schrock, *Science*, 2003, **301**, 76–78.
- (a) D. Singh, W. R. Buratto, J. F. Torres and L. J. Murray, *Chem. Rev.*, 2020, **120**, 5517–5581; (b) S. Kim, F. Loose and P. J. Chirik, *Chem. Rev.*, 2020, **120**, 5637–5681; (c) M. J. Chalkley, M. W. Drover and J. C. Peters, *Chem. Rev.*, 2020, **120**, 5582–5636.
- Y. Ashida, K. Arashiba, K. Nakajima and Y. Nishibayashi, *Nature*, 2019, **568**, 536–540.
- (a) J. Higuchi, S. Kuriyama, A. Eizawa, K. Arashiba, K. Nakajima and Y. Nishibayashi, *Dalton Trans.*, 2018, **47**, 1117–1121; (b) M. J. Chalkley, T. J. Del Castillo, B. D. Matson and J. C. Peters, *J. Am. Chem. Soc.*, 2018, **140**, 6122–6129; (c) R. Imayoshi, K. Nakajima, J. Takaya, N. Iwasawa and Y. Nishibayashi, *Eur. J. Inorg. Chem.*, 2017, 3769–3778; (d) S. Kuriyama, K. Arashiba, K. Nakajima, Y. Matsuo, H. Tanaka, K. Ishii, K. Yoshizawa and Y. Nishibayashi, *Nat. Commun.*, 2016, **7**, 12181; (e) S. E. Creutz and J. C. Peters, *J. Am. Chem. Soc.*, 2014, **136**, 1105–1115; (f) Y. Sekiguchi, S. Kuriyama, A. Eizawa, K. Arashiba, K. Nakajima and Y. Nishibayashi, *Chem. Commun.*, 2017, **53**, 12040–12043; (g) P. J. Hill, L. R. Doyle, A. D. Crawford, W. K. Myers and A. E. Ashley, *J. Am. Chem. Soc.*, 2016, **138**, 13521–13524; (h) J. S. Anderson, J. Rittle and J. C. Peters, *Nature*, 2013, **501**, 84–87.
- M. J. Chalkley, T. J. Del Castillo, B. D. Matson, J. P. Roddy and J. C. Peters, *ACS Cent. Sci.*, 2017, **3**, 217–223.
- (a) B. D. Matson and J. C. Peters, *ACS Catal.*, 2018, **8**, 1448–1455; (b) M. M. Deegan and J. C. Peters, *Chem. Sci.*, 2018, **9**, 6264–6270; (c) J. Rittle and J. C. Peters, *J. Am. Chem. Soc.*, 2016, **138**, 4243–4248.
- S. C. Coste, B. Vlaisavljevich and D. E. Freedman, *Inorg. Chem.*, 2017, **56**, 8195–8202.
- D. Das, S. S. Mohapatra and S. Roy, *Chem. Soc. Rev.*, 2015, **44**, 3666–3690.
- (a) J. S. Anderson, M. E. Moret and J. C. Peters, *J. Am. Chem. Soc.*, 2013, **135**, 534–537; (b) L. R. Doyle, P. J. Hill, G. G. Wildgoose and A. E. Ashley, *Dalton Trans.*, 2016, **45**, 7550–7554; (c) Y. Lee, N. P. Mankad and J. C. Peters, *Nat. Chem.*, 2010, **2**, 558–565; (d) M. E. Moret and J. C. Peters, *J. Am. Chem. Soc.*, 2011, **133**, 18118–18121.
- J. H. Enemark and R. D. Feltham, *Coord. Chem. Rev.*, 1974, **13**, 339–406.
- (a) B. Wu, M. J. Wilding, S. Kuppaswamy, M. W. Bezpalko, B. M. Foxman and C. M. Thomas, *Inorg. Chem.*, 2016, **55**, 12137–12148; (b) R. J. Eisenhart, P. A. Rudd, N. Planas, D. W. Boyce, R. K. Carlson, W. B. Tolman, E. Bill, L. Gagliardi and C. C. Lu, *Inorg. Chem.*, 2015, **54**, 7579–7592.
- (a) A. D. Piascik, P. J. Hill, A. D. Crawford, L. R. Doyle, J. C. Green and A. E. Ashley, *Chem. Commun.*, 2017, **53**, 7657–7660; (b) J. B. Geri, J. P. Shanahan and N. K. Szymczak, *J. Am. Chem. Soc.*, 2017, **139**, 5952–5956.
- P. L. Holland, *Dalton Trans.*, 2010, **39**, 5415–5425.
- J. R. Dilworth, *Coord. Chem. Rev.*, 2017, **330**, 53–94.
- (a) F. Neese, *Inorg. Chim. Acta*, 2002, **337**, 181–192; (b) P. Gutlich, E. Bill and A. X. Trautwein, *Mössbauer Spectroscopy and Transition Metal Chemistry*, Springer, 2011.
- J. T. Moore, S. Chatterjee, M. Tarrago, L. J. Clouston, S. Sproules, E. Bill, V. Bernales, L. Gagliardi, S. Ye, K. M. Lancaster and C. C. Lu, *Inorg. Chem.*, 2019, **58**, 6199–6214.
- P. A. Rudd, N. Planas, E. Bill, L. Gagliardi and C. C. Lu, *Eur. J. Inorg. Chem.*, 2013, 3898–3906.
- (a) N. G. Limas and T. A. Manz, *RSC Adv.*, 2018, **8**, 2678–2707; (b) T. A. Manz, *RSC Adv.*, 2017, **7**, 45552–45581.
- (a) Y. Nishibayashi, *Dalton Trans.*, 2018, **47**, 11290–11297; (b) T. J. Del Castillo, N. B. Thompson and J. C. Peters, *J. Am. Chem. Soc.*, 2016, **138**, 5341–5350.