Inorganica Chimica Acta 516 (2021) 120118

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Research paper

Anion metathesis and chlorination of late transition metal pincer complexes: Comparing Co, Rh and Zn

Alyssa C. Cabelof, Alec M. Erny, Veronica Carta, Maren Pink, Kenneth G. Caulton *

Department of Chemistry, Indiana University, Bloomington, IN 47405, United States

ARTICLE INFO

Keywords:
Pincer
Nitrate
N-chlorosuccinimide

ABSTRACT

The ability of (PNNH)$CoCl_2$ (where PNNH is a phosphino and pyrazole substituted pyridine pincer) to serve as a precursor to coordinate the weak anion nitrate is investigated, giving a product with two coordinated nitrates, which demonstrate remarkable variability of nitrate binding in an overall six coordinate divalent cobalt complex. A synthetic variant with only one chloride per Co(II) is characterized, and retains coordination number 5. Comparison is made to rhodium, initially in oxidation state +1, including a carbonyl reporter ligand. The tridentate pincer displaces chloride and PPh_3 from $Rh(PPh_3)_2(CO)Cl$ to form the salt [(PNNH)Rh(CO)]Cl. That compound reacts with *N*-chloro succinimide with oxidation to trivalent rhodium, loss of carbon monoxide, but also with inadvertent chlorine substitution of pyrazole ring CH bond. As a comparison standard for PNNH ligand with a redox inert metal, (PNNH)$ZnCl_2$ is characterized; bond lengths within the ligand allow the conclusion that the iron and cobalt analogs show no major back donation into the pincer ligand.

1. Introduction.

A pincer ligand [1,2] bearing pyridine, pyrazole and phosphine arm (Scheme 1) has been shown to support iron [3] and cobalt [4,5] chemistry in several different oxidation states between 2+ and 0. It has also been deprotonated at the pyrazole β nitrogen without the pyrazolate adopting a bridging role and forming aggregated species that has been seen with similar ligand scaffolds [6,7]. We were interested here in coordination of weak ligands such as nitrate, as a preliminary to establishing redox reactivity within that ligand. The study of nitrate chemistry is particularly important due to the rise of aquatic dead zones as a result of excessive nitrate production derived from agricultural fertilizer, demanding routes to sequester and transform this anion into value-added products [8–11]. These transformations have been accomplished by a variety of methods, including photochemical, electrochemical, and with the use of chemical reductants [12–18]. Comparison to monovalent rhodium, a more spectroscopically informative metal, allowed us to focus on metal oxidation state change, and was designed to learn about redox chemistry combined with increased Brønsted acidity of pyrazole as metal is oxidized [19–21]. This work also installs PNNH onto a redox inert metal, Zn^{2+}, which has relevance to the emerging field of catalysts based on main group metals [22–25].

2. Results

2.1. Divalent cobalt

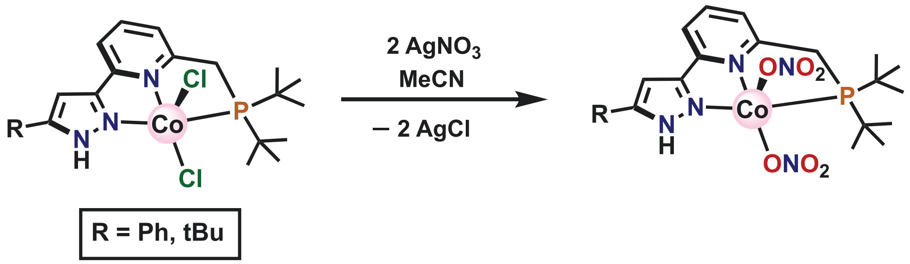
Nitrate was installed on (PNNH)$CoCl_2$ via salt metathesis with two equivalents of $AgNO_3$ in acetonitrile solvent according to Scheme 1. This proceeds rapidly, indicated by a color change from violet to lavender in fewer than 5 min and is accompanied by the precipitation of silver chloride. In this work, we employ both a tBu and Ph substituent on the C5 position of the pyrazole arm for their differences in solubility and crystallinity, but the reactivity of both is the same.

Characterization by ^{1}H NMR of the crude material shows a single paramagnetic product, distinct from $(PNN^{Ph}H)CoCl_2$. Interestingly, Ag^+ does not oxidize the divalent cobalt here. Despite the paramagnetism of Co(II), the ^{1}H NMR chemical shifts are sharp and integrate to the expected values for a single pincer, with one signal for the two tBu and one for two methylene protons, indicating retention of mirror plane symmetry (see SI Fig. S3). The infrared spectrum showed the presence of strong N—O stretches (1284 and 1471 cm^{-1}, Fig. S4) [26,27] which are absent in $(PNN^{Ph}H)CoCl_2$. Single crystal X-ray diffraction studies establish the composition $(PNN^{Ph}H)Co(NO_3)_2$ (Fig. 1). Despite the weak binding affinity of nitrate, even in the presence of coordinating solvent, we observe only the molecular species rather than any nitrate salt.

---

* Corresponding author.
E-mail address: caulton@indiana.edu (K.G. Caulton).

https://doi.org/10.1016/j.ica.2020.120118
Received 7 October 2020; Received in revised form 30 October 2020; Accepted 1 November 2020



Scheme 1. Synthesis of (PNNH)Co(NO_3)$_2$ from (PNNH)CoCl_2.

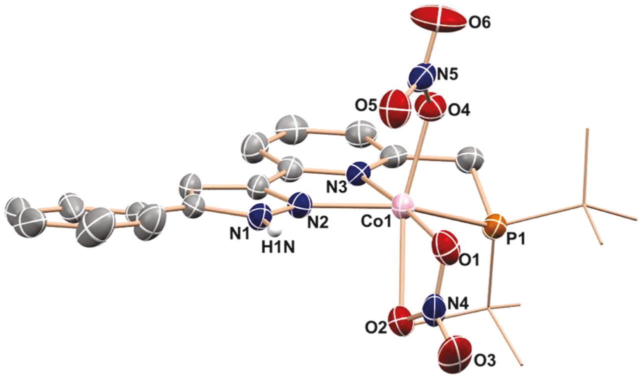


Fig. 1. Molecular structure (50% probability ellipsoids) of one molecule of (PNNH)Co(NO_3)$_2$, showing select atom labeling. Gray atoms are carbons and all hydrogens except the pyrazole proton are omitted. Co1–*P*1, 2.4838(11); Co1–O1, 2.122(3); Co1–O2, 2.317(3); Co1–O4, 2.047(3); Co1–N2, 2.076(3); Co1–N3, 2.180(3).

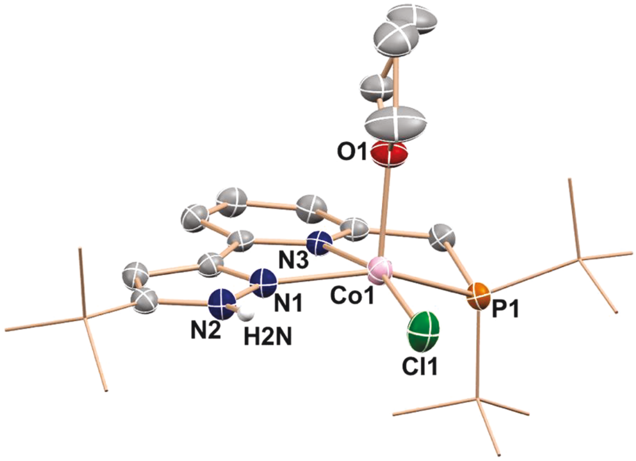


Fig. 2. Molecular structure (50% probability ellipsoids) of [(PNN^{tBu}H)Co(Cl)(THF)]$^+$ showing selected atom labeling. Gray atoms are carbon. The BPh_4^- counterion and all protons except the pyrazole proton have been removed for clarity. Selected structural parameters: Co1–*P*1, 2.4061(6); Co1–N1, 2.0541(15); Co1–N3, 2.1560(15); Co1–Cl1, 2.2808(6); Co1–O1, 2.0559(14).

Table 1
Bond distances (Å) within the Co(NO_3)$_2$ subunit of four crystallographically independent molecules. For labels, see Fig. 1.

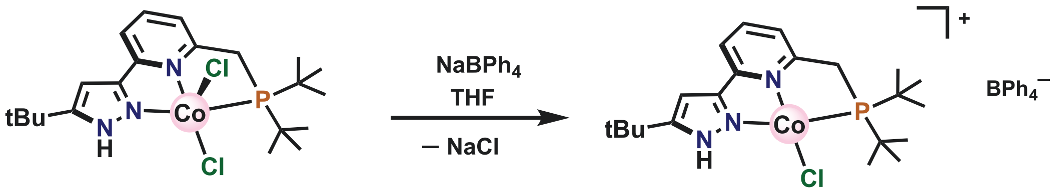
Molecule	Co1–O1	Co1–O2	Co1–O4	Co1–O5
A	2.122(3)	2.317(3)	2.047(3)	2.940(3)
B	2.084(3)	2.388(3)	2.047(3)	2.787(3)
C	2.083(3)	2.376(3)	2.073(3)	2.607(3)
D	2.208(3)	2.254(3)	2.250(4)	2.313(4)

The compound crystallizes with four molecules in the asymmetric unit (Z′ = 4) and in every case, the rotational conformation of monodentate nitrate shows no evidence for intramolecular hydrogen bonding. Instead, every –NH functionality hydrogen bonds to a different THF guest molecule in the lattice. The presence of protons on the pyrazole β nitrogen is further supported by large N—N—C angles of 111.30–112.19° [28]. The Co(NO_3)$_2$ subunit (Table 1) shows remarkable variation among the four crystallographically unique molecules, which are labelled with letters from A to D.

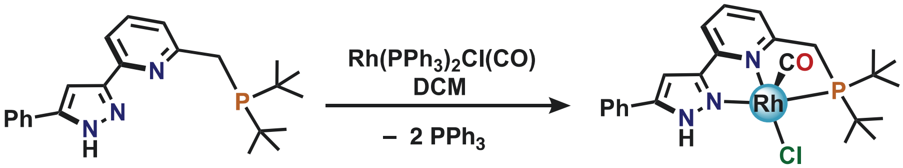
The Co-O distance variability within the four individual molecules speaks to the flexibility of the nitrate anion; this ligand can bind mono- or bidentate, and since there is no preference for coordination of one oxygen over another, we expect that these are rapidly exchanging in solution. This dynamic process suggests that molecules A–D are best described as conformers, and explains why we observe only one tert-butyl signal in the ^{1}H NMR. Molecule D is distinct from A–C in having four similar (±0.1 A) Co-O distances. The κ^1 and κ^2 nitrate linkage implies inequivalent tert-butyl protons on the phosphorus atom, but due to the rapid conversion between mono- and bidentate binding modes, only one signal is observed on the NMR timescale. Overall, this suggests the potential energy surface of this moiety is very soft, with numerous local minima. This claim is supported by single point energy calculations (B3LYP/6-311G(d) level of theory, see SI for details) of the four crystallographically independent molecules. We found that the energetic difference between all four molecules was less than 3 kcal/mol.

We were also interested in studying complexes with only one coordinated anion, for simplicity in subsequent deoxygenation reactivity [17,18]. We sought a cobalt mono-chloride (Scheme 2) as a precursor to a mono-nitrate species.

The 1:1 chloride abstraction reaction in THF occurs rapidly, indicated by a color change from violet to brown in <5 min upon addition of



Scheme 2. Proposed route to a mono-chloro cobalt complex.



Scheme 3. Synthetic scheme anticipated for installing PNNH onto Rh(I).

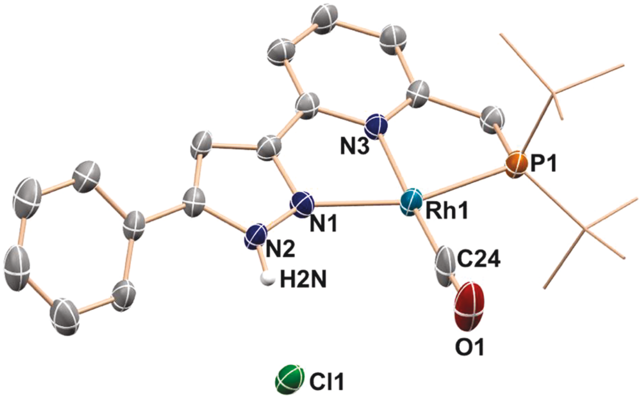


Fig. 3. Molecular structure (50% probability ellipsoids) of [(PNN^{Ph}H)Rh(CO)]$^+$Cl$^-$, with selected atom labeling and showing the hydrogen bond. Selected structural parameters: Rh1-C24, 1.811(6); Rh1-N3, 2.064(4); Rh1-N1, 2.107(3); Rh1-*P*1, 2.2429(12); O1-C24, 1.159(6); C24-Rh1-N3, 177.68(17).

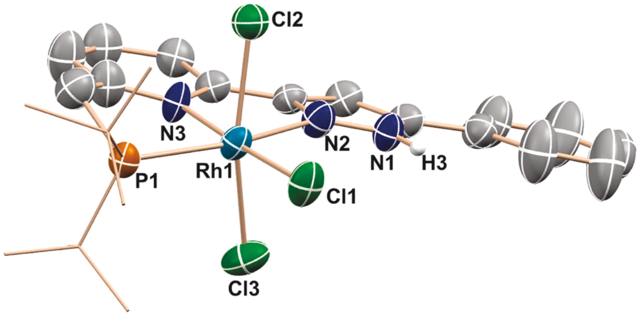


Fig. 4. Molecular structure (50% probability ellipsoids) of (PNN^{Ph}H)RhCl$_3$, with selected atom labeling. Selected structural parameters (Å): Rh1-N2, 2.137 (7); Rh1-N3, 2.035(6); Rh1-*P*1, 2.308(2); Rh1-Cl1, 2.355(2); Rh1-Cl3, 2.349(2); Rh1-Cl3, 2.341(2).

NaBPh$_4$. Removal of volatile material after 12 h yields a green powder. Characterization by ^{1}H NMR shows the presence of a single paramagnetic product, distinct from (PNN^{tBu}H)CoCl$_2$. Crystals suitable for X-ray diffraction were grown by slow vapor diffusion of pentane vapors into a concentrated THF solution, establishing the composition of [(PNNH)Co(Cl)(THF)]$^+$BPh$_4^-$ (Fig. 2), where a THF molecule coordinates to satisfy the Lewis acidity of cobalt; four coordinate Co^{II} is not formed. The presence of a proton on the pyrazole arm is confirmed by a large N—N—C angle of 111.3°, and the BPh$_4^-$ anion is completely non-interacting.

The Co1-O1 distance (2.0559(14) Å) is similar to the Co1-N1 distance for pyrazole nitrogen, indicating that THF is not loosely bound. Despite coordination of a THF molecule, the chloride abstraction was successful, and therefore [(PNNH)Co(Cl)(THF)]$^+$BPh$_4^-$ is a promising precursor for mononitrate species in future studies.

2.2. Comparison to rhodium

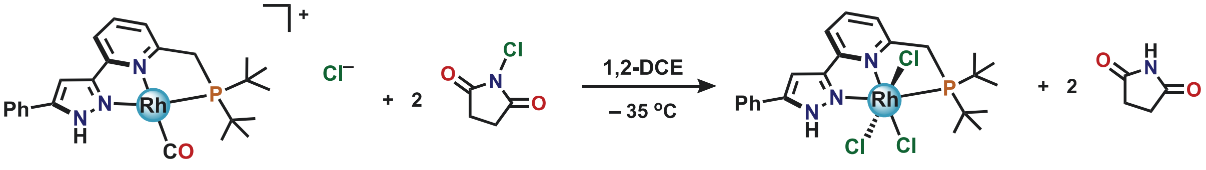
The above cobalt chemistry has not utilized the weak Brønsted acid character of the pyrazole proton. In addition, the metal oxidation state has remained unchanged. We now move to consider doing redox chemistry at the metal, and with a potentially more Brønsted basic reagent. To broaden the scope of this PNNH chemistry, we also moved to a 4d transition metal, and one whose nuclear spin can be informative of metal oxidation state, via NMR coupling constant [29,30]. Finally, we wanted to include a carbonyl ligand as a reporter of donor power. These are the motivations behind attempting to install the PNN^{Ph}H pincer ligand on a monovalent rhodium carbonyl complex. Reaction of equimolar PNN^{Ph}H with RhCl(CO)(PPh$_3$)$_2$ at 25 °C in dichloromethane (Scheme 3) shows complete conversion to a new product in less than 12 h, and ^{31}P NMR shows the formation of free PPh$_3$ and a product doublet ($^2J_{\text{Rh-P}} = 157$ Hz) for the coordinated pincer.

Byproduct PPh$_3$ was removed with copious ether washings. The molecule shows by ^{1}H NMR spectroscopy mirror symmetry (two equivalent CH$_2$ protons and 18 equivalent tBu protons), consistent with a planar four coordinate structure as opposed to the anticipated 5 coordinate species. The compound was determined to retain the carbonyl ligand by IR spectroscopy ($\nu_{\text{CO}} = 1983$ cm^{-1}) and single crystal X-ray diffraction study (Fig. 3) establishes a chemical formula [(PNNH)Rh(CO)]$^+$Cl$^-$. The hydrogen on the pyrazole moiety hydrogen bonds to the chloride anion, with N2-Cl1 distance of 3.025(4) Å.

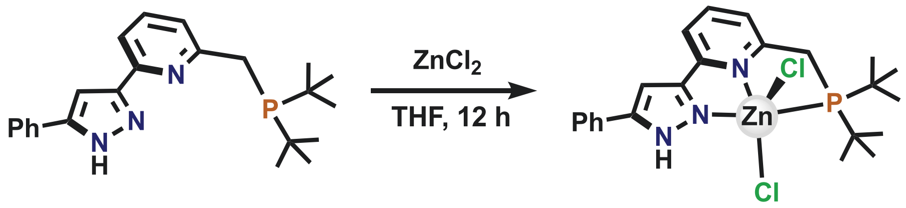
Oxidation of [(PNN^{Ph}H)Rh(CO)]$^+$Cl$^-$ was accomplished with reagent *N*-chloro succinimide [31–33] to form (PNN^{Ph}H)RhCl$_3$ (Scheme 4) in 1,2-dichloroethane solvent at −35 °C. While we did not establish the source of the NH hydrogens, solvent is a likely source.

The 1:2 reaction proceeds with a color change from yellow to red in 10 min. Characterization of the diamagnetic product by ^{1}H NMR shows equivalent tBu and methylene signals, consistent with retention of a mirror plane. The ^{31}P NMR shows a single new doublet, distinct from the starting material ($^2J_{\text{Rh-P}} = 86$ Hz) confirming that only one new phosphorus-containing product was formed. This smaller *J* value is consistent with Rh(III). The infrared spectrum (no CO stretch present) indicates loss of the carbonyl ligand. Single crystal X-ray diffraction of crystals grown by vapor diffusion of pentane vapors into a concentrated 1,2-DCE solution confirms the anticipated product formula, (PNN^{Ph}H) RhCl$_3$ (Fig. 4).

The geometry about the Rh is octahedral, and the large N—N—C



Scheme 4. Synthetic scheme for oxidation of [(PNN^{Ph}H)Rh(CO)]$^+$Cl$^-$ with *N*-chlorosuccinimide.



Scheme 5. Synthesis of (PNNH)$ZnCl_2$.

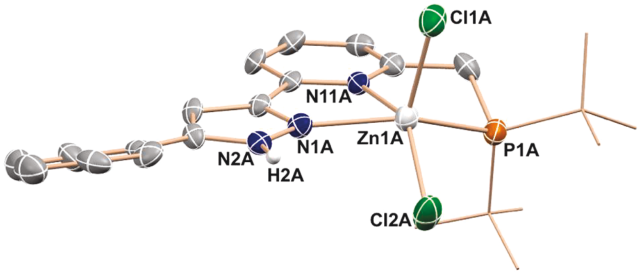


Fig. 5. Molecular structure (50% probability ellipsoids) of ($PNN^{Ph}H$)$ZnCl_2$ showing selected atom labelling. Gray atoms are carbon. Hydrogen atoms have been omitted for clarity, except for the pyrazole proton. Selected structural parameters: Zn1A–P1A, 2.503(5); Zn1A–Cl1A, 2.272(5); Zn1A–Cl2A, 2.338(5); Zn1A–N1A, 2.153(8); Zn1A–N11A, 2.284(8).

angle (109.5°) confirms the presence of a proton on N1. The presence of this proton is further confirmed by a hydrogen bonding interaction with a water molecule that co-crystalizes. If the reaction is repeated at room temperature and in the more oxidizing dichloromethane solvent, over-oxidation occurs on the ligand pyrazole arm. Crystal structure determination of this reaction product shows the unit cell to contain a 53:47 mixture of ($PNN^{Ph}H$)$RhCl_3$ and its analog where one pyrazole ring carbon has been chlorinated [31–34] to form ($ClPNN^{Ph}H$)$RhCl_3$ (see SI for more details).

2.3. *($PNN^{Ph}H$)$ZnCl_2$*

Finally, we were interested in synthesizing a complex with $PNN^{Ph}H$ on a redox inert metal to serve as a comparison standard to those containing redox active metals. We have previously reported the synthesis of the analogous (PNNH)$FeCl_2$ and (PNNH)$CoCl_2$ [3–5], and therefore this (PNNH)Zn species will allow comparing intra-ligand bond lengths to gauge whether there is population of the ligand π* of $PNN^{Ph}H$ in the case of divalent metals. To this end, $PNN^{Ph}H$ was reacted with equimolar $ZnCl_2$ in THF (Scheme 5).

Upon addition of ligand to metal, no observable color change was noted. The reaction was stirred at room temperature for 12 h with a persistent yellow color. Subsequent NMR monitoring indicates reaction completion (based on depletion of ligand ^{31}P NMR signals) within 2 h. The resulting ($PNN^{Ph}H$)$ZnCl_2$ was isolated as the only product, and was characterized by ^{1}H, ^{31}P, and ^{13}C NMR (Figs. S13 and S14), and all these data are consistent with a single, diamagnetic product distinct from free ligand. Finally, this compound was characterized by X-ray diffraction. Single crystals were grown via vapor diffusion of pentane vapors into a concentrated THF solution, and the structure unambiguously identifies the compound as ($PNN^{Ph}H$)$ZnCl_2$ (Fig. 5).

This compound now exists as a reference compound to the previously synthesized (PNNH)$FeCl_2$ and (PNNH)$CoCl_2$, both of which contain potentially redox active metals. We compared intra-ligand bond lengths between these two species and this Zn compound, and we found minimal differences between the three (see SI Fig. S17 and Table S7) and therefore we can conclude that there is no evidence for population of ligand π* orbitals, and thus no evidence of redox noninnocence in the case of divalent iron and cobalt.

3. Conclusions

These results show that the PNNH ligand can be a constant factor on divalent cobalt, leaving up to three coordination sites available for variable ligand manipulation. The d^7 configuration leaves the metal indifferent between coordination number five or six because nitrate ligands are shown to be either monodentate or bidentate. The ligand protons are readily observable, and structurally diagnostic, by ^{1}H NMR even in the paramagnetic divalent cobalt setting. PNNH can also be installed on a later metal, Rh, and can support this metal in two different oxidation states. Finally, a redox-inert example was synthesized and used to show that with M^{2+} examples (M = Co, Fe), PNNH is a redox-innocent ligand.

CRediT authorship contribution statement

Alyssa C. Cabelof: Conceptualization, Methodology, Investigation. **Alec M. Erny:** Investigation. **Veronica Carta:** Investigation. **Maren Pink:** Investigation. **Kenneth G. Caulton:** Supervision, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgment

This work was supported by the Indiana University Office of Vice President for Research and the National Science Foundation by grant CHE-1362127.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ica.2020.120118.

References

[1] E. Peris, R.H. Crabtree, Key factors in pincer ligand design, Chem. Soc. Rev. 47 (2018) 1959–1968.

[2] K.-A. Green, P.N. Nelson, S.C. Lorraine, M.A.W. Lawrence, Pincer ligands-tunable, versatile and applicable, Polyhedron 143 (2018) 11–27.

[3] A.V. Polazhaev, C.J. Liss, J. Telser, C.-H. Chen, K.G. Caulton, A PNNH pincer ligand allows access to monovalent iron, Chem. Eur. J. 24 (2018) 1330–1341.

[4] A.V. Polazhaev, C.-H. Chen, Y. Losovyj, K.G. Caulton, A multifunctional pincer ligand supports unsaturated cobalt: five functionalities in one pincer, Chem. Eur. J. 23 (2017) 8039–8050.

[5] A.C. Cabelof, V. Carta, C.-H. Chen, K.G. Caulton, Nitrogen oxyanion reduction by Co(II) augmented by a proton responsive ligand: recruiting multiple metals, Dalton Trans. 49 (2020) 7891–7896.

[6] B.J. Cook, A.V. Polazhaev, C.-H. Chen, M. Pink, K.G. Caulton, Deprotonation, chloride abstraction, and dehydrohalogenation as synthetic routes to bis-pyrazolate pyridyl iron (II) complexes, Eur. J. Inorg. Chem. 2017 (2017) 3999–4012.

[7] B.J. Cook, C.-H. Chen, M. Pink, K.G. Caulton, Dehydrohalogenation of proton responsive complexes: versatile aggregation via pyrazolate pincer ligand arms, Dalton Trans. 47 (2018) 2052–2060.

[8] R.J. Diaz, R. Rosenberg, Spreading dead zones and consequences for marine ecosystems, Science 321 (2008) 926–929.

[9] W.W. Bouska, J.L. Eitzmann, T.J. Pilger, K.L. Pitts, A.J. Riley, J.T. Schloesser, D. J. Thornbrugh, W.K. Dodds, Eutorphication of U.S. freshwaters: analysis of potential economic damages, Environ. Sci. Technol. 43 (2009) 12–19.

[10] M.A. Sutton, J. Galloway, Z. Klimont, W. Winiwarter, J.W. Erisman, How a century of ammonia synthesis changed the world, Nat. Geosci. 1 (2008) 636–639.

[11] J.N. Galloway, J.D. Aber, J.W. Erisman, S.P. Seitzinger, R.W. Howarth, E. B. Cowling, B.J. Cosby, The nitrogen cascade, Bioscience 53 (2003) 341–356.

[12] J.A. Craig, R.H. Holm, Reduction of nitrate to nitrite by molybdenum-mediated atom transfer: a nitrate reductase analogue system, J. Am. Chem. Soc. 111 (1989) 2111–2115.

[13] M. Delgado, J.D. Gilbertson, Ligand-based reduction of nitrate to nitric oxide utilizing a proton-responsive secondary coordination sphere, Chem. Commun. 53 (2017) 11249–11252.

[14] C.L. Ford, Y.J. Park, E.M. Matson, Z. Gordon, A.R. Fout, A bioinspired iron catalyst for nitrate and perchlorate reduction, Science 354 (2016) 741–743.

[15] S. Xu, D.C. Ashley, H.-Y. Kwon, G.R. Ware, C.-H. Chen, Y. Losovyj, X. Gao, E. Jakubikova, J.M. Smith, A. Flexible, Redox-active macrocycle enables the electrocatalytic reudction of nitrate to ammonia by a cobalt complex, Chem. Sci. 9 (2018) 4950–4958.

[16] J. Gwak, S. Ahn, M.-H. Baik, Y. Lee, One metal is enough: a nickel complex reduces nitrate anions to nitrogen gas, Chem. Sci. 10 (2019) 4767–4774.

[17] D.M. Beagan, V. Carta, K.G. Caulton, A reagent for heteroatom borylation, including iron mediated reductive deoxygenation of nitrate yielding a dinitrosyl complex, Dalton Trans. 49 (2020) 1681–1687.

[18] J. Seo, A.C. Cabelof, C.-H. Chen, K.G. Caulton, Selective deoxygenation of nitrate to nitrosyl using trivalent chromium and the mashima reagent: reductive silylation, Chem. Sci. 10 (2019) 475–479.

[19] J. Zhang, E. Balaraman, G. Leitus, D. Milstein, Electron-rich PNP- and PNN-type ruthenium(II) hydrido borohydride pincer complexes. Synthesis, structure, and catalytic dehydrogenation of alcohols and hydrogenation of esters, Organometallics 30 (2011) 5716–5724.

[20] J. Bootsma, B. Guo, J.G. de Vries, E. Otten, Ruthenium complexes with PNN pincer ligands based on (chiral) pyrrolidines: synthesis, structure, and dynamic stereochemistry, Organometallics 39 (2020) 544–555.

[21] Z. Tang, E. Otten, J.N.H. Reek, J.I. van der Vlugt, B. de Bruin, Dynamic ligand reactivity in a rhodium pincer complex, Chem. Eur. J. 21 (2015) 12683–12693.

[22] S. Enthaler, Rise of the zinc age in homogeneous catalysis? ACS Catal. 3 (2013) 150–158.

[23] P.P. Power, Main-group elements as transition metals, Nature 463 (2010) 171–177.

[24] D.J. Liptrot, C. Weetman, M.S. Hill, Alkaline earths as main group reagents in molecular catalysis, Chem. Soc. Rev. 45 (2016) 972–988.

[25] M. Rauch, S. Kar, A. Kumar, L. Avram, L.J.W. Shimon, D. Milstein, Metal-ligand cooperation facilitates bond activation and catalytic hydrogenation with zinc pincer complexes, J. Am. Chem. Soc 142 (2020) 14513–14521.

[26] E.J. Duff, M.N. Hughes, K.J. Rutt, Structure and Infrared Spectra of Some Nitrato-complexes of Cobalt(II), Nickel(II), and Zinc(II) with Heterocyclic Ligands, J. Chem. Soc. A. 2126–2128 (1969).

[27] M. Choca, J.R. Ferraro, K. Nakamoto, Vibrational spectra of anhydrous metal pyridine nitrates, J. Chem. Soc. Dalton Trans (1972) 2297–2301.

[28] S. Kuwata, T. Ikariya, β-protic pyrazole and n-heterocyclic carbene complexes: synthesis, properties, and metal-ligand cooperative bifunctional catalysis, Chem. Eur. J. 17 (2011) 3542–3556.

[29] S.O. Grim, R.A. Ference, Tertiary phosphine complexes of rhodium(III) and rhodium(I), Inorg. Chim. Acta 4 (1970) 277–282.

[30] S. Al-Jibori, C. Crocker, B.L. Shaw, Direct oxidative addition-reductive elimination reactions between *trans*-$[MCl(CO)L_2]$ and $[MCl_3(CO)L_2]$ or *trans*-$[PtCl_4(PEt_3)_2]$ (M = Rh or Ir, L = tertiary phosphine), J. Chem. Soc. Dalton Trans (1981) 319–321.

[31] S.R. Whitfield, M.S. Sanford, Reactivity of Pd(II) complexes with electrophilic chlorinating reagents: isolation of Pd(IV) products and observation of C-Cl bond-forming reductive elimination, J. Am. Chem. Soc. 129 (2007) 15142–15143.

[32] S.R. Whitfield, M.S. Sanford, Reactions of platinum (II) complexes with chloride-based oxidants: routes to Pt(III) and Pt(IV) products, Organometallics 27 (2008) 1683–1689.

[33] M. Gucma, W.M. Gołębiewski, Applications of *N*-chlorosuccinimide in organic synthesis, Synthesis 23 (2007) 3599–3619.

[34] Z.-G. Zhao, Z.-X. Wang, Halogenation of pyrazoles using *N*-halosuccinimides in CCl_4 and in water, Synth. Commun. 37 (2007) 137–147.