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Nitrogen Oxyanion Reduction by Co(II) Augmented by a Proton Responsive Ligand: Recruiting Multiple Metals

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Deoxygenation of nitrite oxygen with divalent cobalt was achieved using (PNNH)CoCl₂, carrying a pyridyl pincer ligand with one P(*t*-Bu)₂ arm and one pyrazole arm. Reaction of (PNNH)CoCl₂ with NaNO₂ at a 2:5 mole ratio promptly forms equimolar (PNNH)Co(NO₂)₃ and (PNN)Co(NO₂)(NO), {CoNO}⁸ with lost ligand proton combined with removed oxo as hydroxide. These two Co^{III} products are characterized, showing a bent CoNO unit as the fate of the reduced nitrogen. DFT calculations are consistent with two one-electron Co^{III} reductants binding to one NO₂⁻ bridge, then proton transfer being needed for facile N/O bond scission. A species detected by low temperature execution of this reaction contains cobalt in two oxidations states with an N,O briding nitro group and pincer ligands that have been deprotonated, showing the active participation of the proton responsive ligand.

Introduction

Aquatic dead zones are expanding in lakes and coastal regions across the planet originating from excessive influx of nitrate derived from agricultural fertilizer.¹ One way to address this problem is to invent and better understand reactions which systematically and even catalytically modify the oxidation state of nitrogen oxyanions, beginning with NO₃^{-,2} Given the large number of nitrogen oxidation states, redox conversion at every N oxidation state deserves attention, including how to accomplish selectivity in the reduced form of nitrogen. The ultimate goal of such work is to recycle nitrogen lost to aquifers, and even recycle it into value-added chemicals.

The energetic cost of heterolytic bond cleavage (N deoxygenation) is frequently paid by electron transfer in contrast to simply nucleophilic substitution of e.g. $S_N 1$ or $S_N 2$ chemistry. For the task at hand here, N/O cleavage is perhaps part of a two electron process, but one electron conversion of nitrate has been implicated via Ce^{III} \rightarrow Ce^{IV}O[•].³ Since liberation of a naked oxide ion will be energetically costly, the dianion is most often captured by an arriving electrophile. This can be H⁺, which opens up the entire subject of proton coupled electron transfer, or this can also be any metal cation or Lewis acid. The field of inner sphere electronic transfer, pioneered in the works of Taube,⁴ combines both reducing agent and electrophile in a single species, initially divalent chromium. While these were all one-electron transfers (monovalent atom transfers), in the work of Taube, eq. 1a,^{4d} the whole field has been generalized to

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participating metals.⁵

$$[CoCl]^{2+} + [CrCl]^{2+} \rightarrow [CoCl]^{2+} + [CrCl]^{2+} \qquad (1a)$$

include oxygen atom transfer and nitride transfer between two

$$M(NO_2) + M' \rightarrow M(NO) + OM'$$
(1b)

We envision here nitrogen oxyanion reduction (deoxygenation), eq. 1b, as a generalization of these previous discoveries, but with intervention of an additional atom which remains bonded to one metal while the oxo is carried off by a second metal. Depending on the oxidation state preferences of each of the two metal centers involved, this offers the potential for delivery of a variable number of electrons. While Taube precedent usually involved different metals, we explore here an example with identical metals and with the additional functionality of an intramolecular proton, thereby introducing the topic of proton responsive pincer ligands.⁶ We have recently introduced the mixed donor pincer ligand, PNNH, and shown its chemistry on divalent cobalt⁷ (Scheme 1) including both



Scheme 1. Established reactivity of PNNHCo compounds (HMDS = (Me₃Si)₂N⁻)

deprotonation of the pyrazole NH, as well as the ability to reach metal oxidation state Co(I). We herein report here one example of a fast, clean N^{III}/O cleavage reaction where two one-electron reducing agents deoxygenate one nitrogen, with involvement of a pincer ligand proton.

Results and Discussion

Nitrite reduction

In this work, we employ the PNNH ligand with a pendant phenyl group (Scheme 1, R = Ph), for improved crystallization properties. The t-Bu analog has also been synthesized. The $P(t-Bu)_2$ and methylene components communicate whether the pincer plane is a mirror symmetry element in new products. Evans method for magnetic susceptibility determination on (PNNH)CoCl₂ at 25° C in CD₂Cl₂ yielded a value of μ_{eff} of 4.3 μ_B indicating it exists an S = 3/2 spin state. Sodium nitrite was reacted with (PNNH)CoCl₂ initially in a 2:1 mole ratio in CH_2Cl_2 solvent, with the expectation that simple anion exchange would form (PNNH)Co(NO₂)_{2.} The reaction proceeds within 1 hour, indicated by a color change from violet to brown. A white precipitate was removed, and a crude brown material was isolated. As opposed to the expected single paramagnetic species, characterization by ¹H NMR showed the presence of two major diamagnetic products with minor impurities. Of the major products, one has equivalent t-Bu and methylene resonances, indicating that a mirror plane contains the pyridyl plane. The second major product shows different chemical shifts for the two *t*-Bu groups, suggesting that there is no reflection symmetry in the molecule. The ¹³C NMR spectrum of one compound has two chemical shifts proving chemically inequivalent t-Bu quaternary carbons and methyl carbons, whereas the $^{\rm 13}{\rm C}$ NMR spectrum of the other compound shows only one signal for quaternary and methyl carbons. The IR spectrum of the crude material showed candidates for nitrite stretches (1299 and 1415 cm⁻¹) and a strong nitrosyl stretch (1670 cm⁻¹). The ³¹P NMR spectra were broad to unobservable in CD_2Cl_2 at 25 °C, which we attribute to intermediate relaxation rates by the quadrupolar cobalt neighbor yielding broad lines. To test this hypothesis, we used a technique termed "thermal decoupling:"8 low temperature, and higher solvent

viscosity causes more rapid relaxation of the cobalt nuclear spin states and effectively decouples cobalt from what would otherwise be an 8-line ³¹P NMR multiplet. In this case the product mixture, which shows a nearly undetectable broad line at room temperature in dichloromethane, shows a two line spectrum at -60 °C (see SI) allowing us to again utilize phosphorus chemical shift to identify a particular compound, and also to identify the occurrence of a mixture.

This allows us to establish that the two major products form in a 1:1 ratio. The two major products were both characterized by single crystal X-ray diffraction (Figure 1a and 1b). From the mixture, both crystals grow independently by slow diffusion of cyclohexane vapors into a CH₂Cl₂ solution, but can be manually separated; one is orange and one is red. Figure 1a shows the orange product, which contains three nitrite ligands and based on the ring N-N-C angle of 111.4°, the pyrazole βN is protonated. The neutral pincer and three anionic nitrites indicate that this product, (PNNH)Co(NO₂)₃, contains trivalent cobalt. The red product, depicted in Figure 1b contains one nitrite and one nitrosyl ligand. The N-N-C angle in this product is more contracted, 105.4°, suggesting a deprotonated pincer.⁹ In this product, the nitrite is oriented away from the pyrazolate βN , further supporting deprotonation at this position. The nitrosyl is bent, and therefore anionic, with a Co-N-O angle of 123.5°. With these data, we conclude that the formula of the complex is (PNN)Co(NO₂)(NO), so this second product also contains trivalent cobalt. We hypothesize that the proton lost from one of the PNNH pincers leaves with the oxygen from the deoxygenated nitrite as OH⁻, which departs with an available Na⁺ cation, yielding the crystallographically established (PNN)Co(NO₂)(NO). This is supported by a basic pH (8.35 in water, see SI for details) measured at the end of the reaction.

We discovered that by using an excess of NaNO₂, (PNNH)Co(NO₂)₃ and (PNN)Co(NO₂)(NO) are the only cobaltcontaining products. We therefore attribute the formation of minor impurities in the 2:1 mole ratio case to an insufficient amount of NO₂⁻ present to fully displace all Cl⁻ and OH⁻, and thus giving rise to a small amount of products containing varied X type ligands. We eventually found empirically that the best ratio is 5 NaNO₂:2 (PNNH)CoCl₂, as this is the only ratio that gives the two Co products with no impurities and leaves no excess NaNO₂ behind. All together, we attribute the formation of these two species to equation (2).

2 (PNNH)Co(NO₂ + 5 NaNO₂
$$\rightarrow$$
 (PNN)Co(NO₂)(NO) +
(PNNH)Co(NO₂)₃ + 4 NaCl + NaOH (2)



Figure 1. a) Molecular structure of (PNNH)Co(NO₂)₃ showing selected atom labelling. Gray atoms are carbon. Hydrogen atoms have been omitted for clarity, except for the pyrazole proton.. Selected structural parameters: Co1–P1, 2.313(3); Co1–N1, 1.964(8); Co1–N2, 1.947(8); Co1–N4, 1.884(9); Co1–N5, 1.947(9); Co1–N6, 1.963(9). **b)** Molecular structure of (PNN)Co(NO₂)(NO) showing selected atom labelling Hydrogen atoms and solvent molecules have been omitted for clarity. Selected structural parameters: Co1–P1, 2.257(4); Co1–N1, 1.940(5); Co1–N3, 1.914(8); Co1–N4, 1.886(10); Co1–N5, 1.780(11). Ellipsoids are plotted at the 50% probability level

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Transformation of nitrite to anionic nitrosyl is a two-electron reduction of nitrogen, and these two electrons come from the two cobalt centers, which are each oxidized by 1 electron. This also shows the role the pincer proton plays in N/O bond cleavage. The structures obtained here show four N-bound NO_2^- examples, suggesting that the nitro isomer is more favorable here than the nitrito.

Mechanism

With the stoichiometry and redox balance established, it is possible to begin discussion of mechanism with focus on the N/O bond scission event. Nitrogen oxyanion reduction can be described as N/O bond scission, but that conceals the aspect of electron transfer. Upon N/O bond cleavage, the nitrogen oxidation state can stay unchanged (eq 3a), or the nitrogen can be reduced by 1 electron (eq. 3b), or by 2 electrons (eq. 3c). O^{2-} is not a viable product (too Bronsted basic) in our environment, so it must be stablized by either

$$NO_2^- \rightarrow NO^+ + O^{2-}$$
 (3a)
 $NO_2^- + 1 e^- \rightarrow NO + O^{2-}$ (3b)
 $NO_2^- + 2 e^- \rightarrow NO^- + O^{2-}$ (3c)

protons of PNNH or by a Lewis acid, likely Co^{III}. The 2 e⁻ reduction product requires consumption of two d⁷ divalent cobalt per NO_2^- , and this brings us to the possible inner sphere electron transfer via an intermediate or transition state shown in eq. 4. For simplicity, this discussion will focus only on the metal ions and one nitrite.

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The N/O bond scission within this species delivers two electrons to N as both cobalt centers reach an oxidation state of +3. This immediately delivers the observed product unit $[Co(NO)]^{2+}$, but also delivers a high-energy $[Co^{III}O]^+$ unit,¹⁰ which undergoes protonation to give $[Co^{III}(OH)]^{2+}$. Since this is not the observed product, it would undergo substitution on the observed timescale, given the abundance of NaNO₂.

We attempted a DFT geometry optimization (B3LYP/6-311G(d) level of theory) of a simplified version of this species, [(PNNH)ClCoNO₂CoCl(PNNH)]⁺, which is expected to be accessible due to the rapid substitution rate of Co(II). Both the nitrito and nitro bridge isomers were studied (1 and 2 respectively, Figure 2a). These calculations were used to establish if either species is a minimum or a transition state, to learn whether the reducing power of two d⁷ Co^{II} has already been transferred to NO_2^- , and learn about charge transfer from bond lengths and population analysis in the [CoNO₂Co]³⁺ unit. To simplify the computation, we discuss here the singlet state for this species, thus evaluating the spin state of the final, separated products. Optimization of neither species leads to spontaneous N/O bond cleavage; each is a stationary state. Full discussion is available in the Supporting information. Bond lengths in these structures show no major lengthening of N-O bonds, consistent with minimal redox or back donation from Co^{II}.



structure of bridged species containing an extra proton, with yellow circles showing the origin of intramolecular proton

We next considered whether a proton on the nitro oxygen bonded to Co in this species would trigger N/O bond scission. We considered either an external proton, giving a species with the formula [(PNNH)ClCo(HONO)CoCl(PNNH)]²⁺ (3a, Figure 2b) along with the possibility of an intramolecular proton from either PNNH ligand (3b and 3c, Figure 2b). In each case the DFT geometry optimization calculations use a bridge composed of HONO as initial geometry. In all three cases, geometry optimization of the singlet species does indeed show cleavage of the N/O bond between the protonated oxygen and nitrogen. Here, we only discuss 3a but a full analysis for 3b and 3c and higher spin states is available in the Supporting Information. The optimized structure for species 3a (Figure 3) is held together by two hydrogen bonds, one from hydroxyl oxygen to a proton of PNNH on the second cobalt, and a second from pyrazole NH to chloride of the other cobalt; Co-Cl distance is lengthened by nearly 0.2 Å compared to the second chloride in this species. The (PNNH)Co(NO)Cl⁺ moiety in 3a has not relaxed fully to the ground state geometry of its conjugate base, and the nitrosyl has \angle O1-N1-Co1 = 163.5° but a short Co1-N1 bond at 1.64 Å. It needs to be deprotonated at pyrazole NH to give the experimentally observed product.



Figure 3. Optimized structure of 3a. with selected bond lengths and atom labels.

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The other component in **3a**, (PNNH)Co(OH)Cl⁺, has square pyramidal geometry for trivalent cobalt, with chloride as the apical ligand. Overall, this shows that N/O bond scission needs an electrophile at the nitro oxygen even though it bridges two d⁷ metal reducing agents; proton assist to electron transfer is an essential component of nitrogen deoxygenation even in this reducing environment. Following diffusive separation of these two complexes, forming the observed products will be completed by ligand substitution, converting (PNNH)Co(OH)Cl⁺ to (PNNH)Co(NO₂)₃.

Evidence for CoNO₂Co participation

We sought experimental evidence of intermediate bridging nitro species. Reaction of (PNNH)CoCl₂ with 5 NaNO₂ in CD₂Cl₂ was monitored by ¹H NMR to attempt detection of any paramagnetic intermediates. Stirring for 2 h at room temperature showed no reaction. Addition of 18-crown-6 to solubilize NaNO₂ caused a color change within 10 minutes, with new signals growing only in the diamagnetic chemical shift region; no new paramagnetic species is observed to reach detectable concentration. The 0-10 ppm region showed the formation of the two species, (PNN)Co(NO₂)(NO) and (PNNH)Co(NO₂)₃ without any detectable intermediates (Figure S6). The reaction was repeated at low-temperature to detect any paramagnetic intermediates. Performing the reaction at -45 °C in acetonitrile gave red crystals within 30 min, which were studied by single crystal X-ray diffraction. This revealed a species with the formula (PNN)₂Co₃(NO₂)₆ (Figure 4) containing deprotonated pincers and three 6-coordinate Co; the absence of pyrazole NH protons is established because each ring bridges the central to a terminal Co.



Figure 4. Molecular structure of $(PNN)_2Co_3(NO_2)_6$ showing selected atom labelling. Ellipsoids are plotted at the 50% probability level. Gray atoms are carbon. Hydrogen atoms, solvent molecules and phenyl rings on pyrazole have been omitted for clarity. Selected structural parameters (Å): N14-Co1, 1.914(4); O16-N17, 1.265(4); N17-O18, 1.225(5); N17-Co1, 1.927(4); O19-N20, 1.318(5); O19-Co1, 1.916(3); N20-O21, 1.219(5); N22-Co1, 1.945(3); N23-Co1, 1.933(3); Co1-P2, 2.3200(12); O13-N14, 1.256(5); N14-O15 1.231(5); N24-Co10, 2.115(4); O16-Co10, 2.135(3); O13-Co10, 2.149(3).

The structure has an idealized C₂ axis bisecting the O9-Co10-O13 angle. The Co-Co-Co angle is 170.5°. The central Co carries two pyrazolate N and four bridging nitrite O; the terminal Co carry tridentate PNN⁻, two bridging nitrite N, and O of one nitrito ligand. This gives metal charge Co_3^{8+} and we assign the unique central metal as Co^{II} due to its longer bond lengths, consistent with lower oxidation state. It has previously been shown that monovalent cobalt, augmented by Mg²⁺ forms a product with nitrite bridging in this same way via the four atom unit CoNOMg.¹¹

In (PNN)₂Co₃(NO₂)₆, all protons are transferred, less likely to NO_2^- (pK_a of HONO is 3.16)¹² so probably to oxo removed from nitrogen, forming hydroxide. Consistent with our DFT work, NO_2^- on one Co^{II} in this species is unable to break these N/O bonds. This Co38+ unit is not the final product because it contains unused reducing equivalents, but it cannot proceed further unimolecularly because it lacks a second reducing equivalent, as well as the needed proton. In summary, this molecule is composed of Co²⁺ and two (PNN)Co(NO₂)₃-, the latter the conjugate base of the observed product (PNNH)Co(NO₂)₃. This is a product where two divalent metals have expended their reducing power (to nitrogen in another product), but one cobalt has not. It is surprising that one Co has lost its pincer ligand (Co^{II} is labile), but mixed valent M₃ compounds like this have been seen before.¹³ It is detected here because of its low solubility based on no dipole moment and its larger size. Although it is not an intermediate to products observed in the room temperature execution of this reaction, it does confirm the possibility of a CoNO₂Co binding motif.

Independent synthesis of (PNNH)Co(NO₂)₃ and (PNN)Co(NO₂)(NO)

Separation of $(PNNH)Co(NO_2)_3$ and $(PNN)Co(NO_2)(NO)$ after synthesis from (PNNH)CoCl₂ and NaNO₂, was difficult due to the similar solubilities of the two Co(III) products. We therefore sought independent synthesis of both species. (PNNH)Co(NO₂)₃ can be synthesized by the reaction of PNNH with sodium hexanitrocobaltate in THF (Scheme 2a). We then used the $(PNNH)Co(NO_2)_3$ as the precursor to $(PNN)Co(NO_2)(NO)$. We and others have previously reported deoxygenation of nitrogen oxyanions with the bis-silylated heterocycle 1.4-Bis(trimethylsilyl)-1,4-diaza-2,5-cyclohexadiene.14 We therefore envisioned that deoxygenation of (PNNH)Co(NO₂)₃ with this reagent would give $(PNNH)Co(NO_2)_2(NO)$, which upon subsequent deprotonation would give rise to our other product, (PNN)Co(NO)(NO₂). (Scheme 2b). In this execution, the tetramethyl bis-silylated heterocycle, 2,3,4,6-tetramethyl-1,4bis(trimethylsilyl)-1,4-diaza-2,5-cyclohexadiene (Me₄TMSPz) was used to prevent coordination of byproduct pyrazine.¹⁵

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Scheme 2. a) Independent synthesis of $(\mathsf{PNNH})\mathsf{Co}(\mathsf{NO}_2)_3$ b) Independent synthesis of $(\mathsf{PNN})\mathsf{Co}(\mathsf{NO}_2)(\mathsf{NO})$

Reaction of (PNNH)Co(NO₂)₃ with 1 equivalent of Me₄TMSPz in THF at -78 °C resulted in a gradual color change from yellow to red over the course of 4 hours. The ¹H NMR, ³¹P NMR, and IR data confirm that this red product is (PNN)Co(NO₂)(NO). Additionally, crystals were grown and the unit cell determination unambiguously indicates formation of $(PNN)Co(NO_2)(NO).$ Therefore. deoxygenation and deprotonation were accomplished in this single step. We propose that the resultant tetramethyl pyrazine (Me₄Pz) from deoxygenation must act as a base to deprotonate $(PNNH)Co(NO)(NO_2)_{2}$ to $(PNN)Co(NO_2)(NO)$ with give byproduct HMe₄Pz⁺NO₂⁻.

Conclusions

This work initially targeted the seemingly simple compound $(PNNH)Co(NO_2)_2$. It now appears that either this compound, or some precursor to this, has the proper mix of reducing equivalents and protons to allow reactions bimolecular in cobalt to access nitrite-bridged species in which proton transfer leads to two distinct cobalt complexes, one a nitrosyl and the second a hydroxide. The latter undergoes nitrite-for-hydroxide ligand substitution to give the second observed product. The conclusion from this is that a one-electron reducing agent acting alone is not able to reduce $N^{\mbox{\tiny III}}$ but lability of d^7 cobalt here enables inner sphere delivery of two electrons to a single nitrogen. Operating under different reaction conditions (eq. 5a), a compound containing Co²⁺ linking two units of (PNN)Co(NO₂)₃⁻ is characterized. This complex illustrates the bridging nitro functionality that is suggested to be the central element of NO reductive bond cleavage. It is detected because it fails to cleave the NO bond.

Because of the large number of redox neutral nitrite/chloride substitutions here, our future work will focus on mono-nitrite complexes. Nevertheless, we feel that the present study identifies important aspects of what happens when a protic one-electron reductant encounters nitrite. A recent report shows an alternative to nitrite being reduced solely by (two) divalent cobalt: protonation of a single nitrite coordinated to a single Co^{II} yields (CoNO)²⁺, but reduction is augmented by oxide of NO₂⁻, which is oxidized to H₂O₂.¹⁶

Experimental section

For the details of the synthetic procedures and the experimental and computational methods used, see the Supporting information.

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Conflicts of interest

There are no conflicts to declare.

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References

- (a) R. J. Diaz and R. Rosenberg, Science, 2008, **321**, 926; (b) W.
 W. Bouska, J. L. Eitzmann, T. J. Pilger, K. L. Pitts, A. J. Riley, J. T.
 Schloesser, D. J. Thornbrugh and W. K. Dodds, Environ. Sci. Technol., 2009, **43**, 12; (c) M. A. Sutton, J. Galloway, Z. Klimont,
 W. Winiwarter and J. W. Erisman, Nat. Geosci., 2008, **1**, 636; (d)
 J. N. Galloway, J. D. Aber, J. W. Erisman, S. P. Seitzinger, R. W.
 Howarth, E. B. Cowling and B. J. Cosby, BioScience, 2003, **53**, 341.
- (a) J. A. Craig and R. H. Holm, J. Am. Chem. Soc., 1989, 111, 2111; (b) M. Delgado and J. D. Gilbertson, Chem. Commun., 2017, 53, 11249; (c) C. L. Ford, Y. J. Park, E. M. Matson, Z. Gordon and A. R. Fout, Science, 2016, 354, 741; (d) S. Xu, D. C. Ashley, H.-Y. Kwon, G. R. Ware, C.-H. Chen, Y. Losovyj, X. Gao, E. Jakubikova and J. M. Smith, Chem. Sci., 2018, 9, 4950; (e) J. Gwak, S. Ahn, M.-H. Baik and Y. Lee, Chem. Sci., 2019, 10, 4767.
- 3 (a) P. L. Damon, G. Wu, N. Kaltsoyannis and T. W. Hayton, J. Am. Chem. Soc., 2016, **138**, 12743; (b) M. K. Assefa, G. Wu and T. W. Hayton, Chem. Sci., 2017, **8**, 7873.
- (a) D. E. Richardson and H. Taube, *Coord. Chem. Rev.*, 1984, 60, 107; (b) H. Taube, *Science*, 1984, 226, 1028; (c) H. Taube, *Chem. Rev.*, 1952, 50, 69; (d) H. Myers and H. Taube, *J. Am. Chem. Soc.*, 1954, 76, 2103.
- (a) L. K. Woo, Chem. Rev., 1993, 93, 1125; (b) D. E. Over, S. C. Critchlow and J. M. Mayer, Inorg. Chem., 1992, 31, 4643; (c) D. Subedi and J. M. Smith, Dalton Trans., 2012, 41, 1423; (d) R. H. Holm, Chem. Rev., 1987, 87, 1401.
- (a) B. J. Cook, C.-H. Chen, M. Pink and K. G. Caulton, *Dalton Trans.*, 2018, 47, 2052; (b) K. Umehara, S. Kuwata and T. Ikariya, *J. Am. Chem. Soc.*, 2013, 135, 6754; (c) A. Yoshinari, A. Tazawa, S. Kuwata and T. Ikariya, *Chem. Asian J.*, 2012, 7, 1417; (d) R. H. Crabtree, *New J. Chem.*, 2011, 35, 18; (e) Y. Nakahara, T. Toda, A. Matsunami, Y. Kayaki and S. Kuwata, *Chem. Asian J.*, 2018, 13, 73.
- 7 A. V. Polezhaev, C.-H. Chen, Y. Losovyj and K. G. Caulton, *Chem. Eur. J.* **2017**, *23*, 8039-8050.
- (a) D. W. Lowman, P. D. Ellis and J. D. Odom, J. Magn. Reson., 1972, 8, 289; (b) H. Beall, C. H. Bushweller, W. J. Dewkett and M. Grace, J. Am. Chem. Soc., 1970, 92, 3484; (c) M. Grace, H. Beall and C. H. Bushweller, J. Chem. Soc. D., 1970, 701.
- 9 S. Kuwata and T. Ikariya, *Chem. Eur. J.*, 2011, **17**, 3542.

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Journal Name

- 10 M. K. Goetz, E. A. Hill, A. S. Filatov and J. S. Anderson, *J. Am. Chem. Soc.*, 2018, **140**, 13176.
- 11 C. Uyeda and J. C. Peters, J. Am. Chem. Soc., 2013, **135**, 12023.
- 12 G. Da Silva, E. M. Kennedy and B. Z. Dlugogorski, *J. Phys. Chem. A.*, 2006, **110**, 11371.
- (a) D. A. House, V. McKee and P. J. Steel, *Inorg. Chem.*, 1986, 25, 4884; (b) B. Štefane, S. Polanc and A. Golobič, *Polyhedron*, 1999, 18, 3661.
- (a) J. Seo, A. C. Cabelof, C.-H. Chen and K. G. Caulton, *Chem. Sci.*, 2019, **10**, 475; (b) H. Tsurugi and K. Mashima, *Acc. Chem. Res.*, 2019, **52**, 769.
- 15 T. Saito, H Nishiyama, H. Tanahashi, K. Kawakita, H. Tsurugi and K. Mashima, *J. Am. Chem. Soc.*, 2014, **136**, 5161.
- 16 M. A. P. Yoosaf, S. Ghosh, Y. Narayan, M. Yadav, S. C. Sahoo and P. Kumar, *Dalton Trans.*, 2019, **48**, 13916.



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