Dalton Transactions

$[Cr(pincer^{2-})]_2$ as an Electron Shuttle for Reductively Promoted Hydrazine Disproportionation

Journal:	*Dalton Transactions*
Manuscript ID	DT-COM-05-2019-002300.R1
Article Type:	Communication
Date Submitted by the Author:	08-Jul-2019
Complete List of Authors:	Labrum, Nicholas; Indiana University, Department of Chemistry Caulton, Kenneth; Indiana University, Department of Chemistry

COMMUNICATION

$[Cr(pincer^{2-})]_2$ as an Electron Shuttle for Reductively Promoted Hydrazine Disproportionation

Nicholas S. Labrum,[a] and Kenneth G. Caulton *[a]

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

We describe here delivery of hydrazine to a reducing, low oxidation state chromium bound to a proton responsive ligand which has already been deprotonated. Reaction of $PhHNNH_2$ at a 4:1 mole ratio with the *bis*-(pyrazolate)pyridyl pincer ligated reducing agent $[Cr^{II}L]_2$ gives prompt conversion to $[Cr^{III}{}_2L_2(PhNH_2)_2(\mu\text{–}PhHNN)]$, with release of NH_3 and C_6H_6, a new disproportionation of the hydrazine, with trapping of PhHNN as its dianion, bridging the two chromium centers. The redox balance of the reaction is discussed, and participation by Bronsted basic sites on the *bis*-(pyrazolate)pyridyl pincer ligand L^{2-} is suggested, but no hydrazine protons remain on the pincer in the product.

Reported here is an effort to better understand the reactivity of hydrazines under reducing conditions, and also in the presence of a proton responsive ligand. Hydrazines are candidate intermediates in nitrogen fixation, based on the expectation that there will come a stage where the initial N≡N triple bond becomes a N-N single bond.[1] The next step in nitrogen fixation is qualitatively different from the proton coupled electronic transfer which delivers the hydrazine redox level, because it involves full cleavage of a N-N single bond. Besides its *reductive* conversion to ammonia and amide ligands, one can also envision another important conversion of hydrazine: *disproportionation*. This N-N scission is redox neutral (i.e. no external electron source) and thus involves hydrogen transfer between two hydrazines. Disproportionation has seen considerable research, both in stoichiometric as well as catalytic conversions.[2] Hydrazine is an especially versatile ligand, because it can bind monodentate, bidentate or bridging, and each of these forms is subject to deprotonation to make anionic hydrazides (Figure 1, a). Much of the precedent work has used ancillary ligands without pendant Bronsted *basic* sites or available Bronsted *acidic* functionality, so the topic of proton responsive ligands offers new opportunities.[3] Finally, synthesis of hydrazine and hydrazide complexes has generally involved deprotonated hydrazide with metal halide, or silyl hydrazine with metal halides, and we report here a *reductive* approach.[4]

We have developed a molecule containing two divalent chromium centers in a compact package composed of a proton responsive pincer ligand, *bis*-(pyrazolate)pyridine (Figure 1, b). We have shown earlier that this complex is both a Lewis acid and a Bronsted base.[5] We now attempt to exploit the two functionalities to direct its reductive character towards the hydrazine N-N bond. We sought two-electron reducing power and Bronsted basicity, in some bond cleavage transformations.

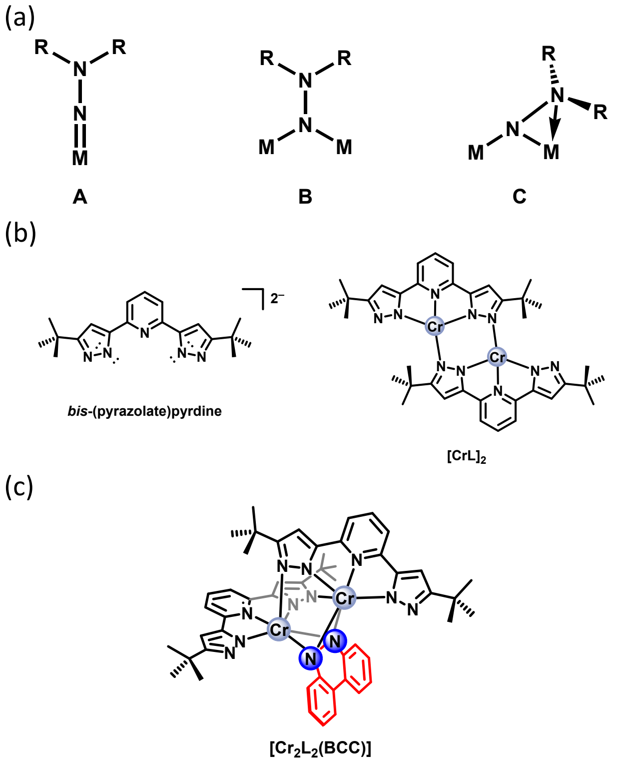


Figure 1. (a) Coordination modes of hydrazido(2−) ligand to transition metals. **(b)** Ligand and chromium reagent used in this work. **(c)** An example of benzo[*c*]cinnoline substrate binding between two $Cr^{III}L$ units.

---

[a] *Department of Chemistry, Indiana University, Bloomington IN. E-mail: Caulton@indiana.edu*

† Electronic Supplementary Information (ESI) available: [Synthetic details crystallographic data, and XPS data are included. CCDC 1906015]. See DOI: 10.1039/x0xx00000x

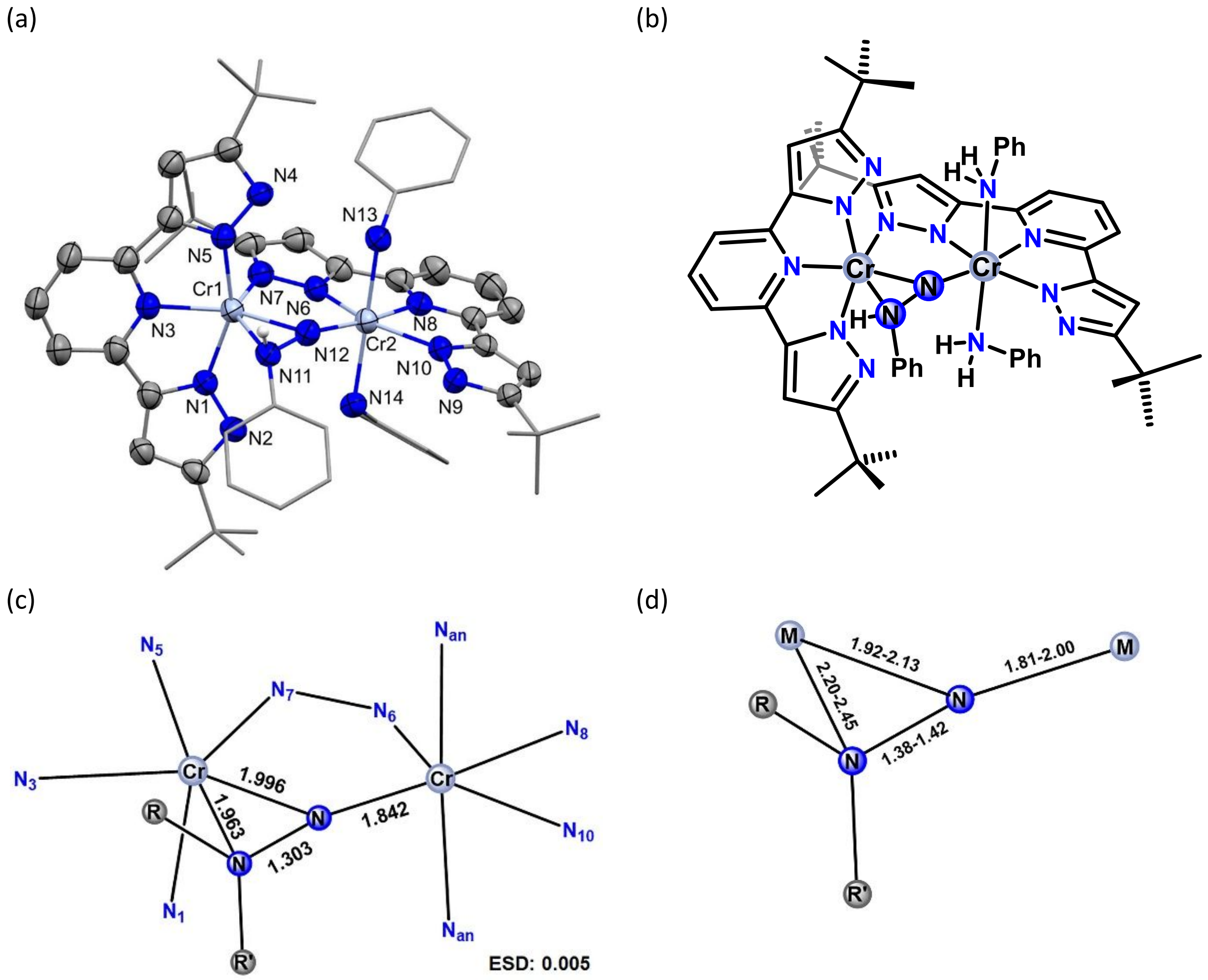


Figure 2. (a) Solid-state structure (50% probability) of $[Cr^{III}_2L_2(PhNH_2)_2(PhHNN)]$. Ligand carbon atoms (unlabeled) are shown in grey. Hydrogen atoms and solvent molecules are omitted for clarity; ^{t}Bu and phenyl are shown as a wireframe. The aniline aryl ring on N14 is nearly edge-on and thus hard to see. Selected structural parameters (Å, °): Cr1-N11: 1.963(5); Cr1-N12: 1.996(5); Cr2-N12: 1.842(5); N11-N12: 1.303(6); Cr2-N13, 2.135(5); Cr2-N14, 2.147(5); N13-Cr2-N14, 178.02(19), Cr1-N12-Cr2: 115.5(2). **(b)** Line drawing of $[Cr^{III}_2L_2(PhNH_2)_2(PhHNN)]$. **(c)** Bond lengths in $[Cr^{III}_2L_2(PhNH_2)_2(PhHNN)]$; **(d)** bond lengths in comparison Ti, Zr, and Mo compounds

We have shown earlier that $[CrL]_2$ has the reducing power to convert ArN=NAr bonds to hydrazide, found bridging two CrL units in the product (Figure 1, c); subsequent delivery of KC_8 effects full cleavage of the N-N bond.[6] In pursuing NN bond transformations, we were drawn next to disproportionation since this has the simplicity of not needing any external reagents, neither electrophiles (e.g. H^+) nor electrons. In addition, our metal complex offers product stabilization by the availability of two metal centers if the dimeric character is retained. While 3d metals often undergo one-electron redox change, a *di*metal 3d species can accommodate the two-electron changes generally preferred by small molecule redox products. Due to the hazards associated with anhydrous hydrazine, we explore a substituted hydrazine, phenylhydrazine, and we value the possibility that N-C bonds will be kinetically persistent, and thus enable detection of relevant intermediates, in addition to the crystal growth benefit of the phenyl ring. The electronic character of phenyl substituents may also play a significant role.

The paramagnetic, generally Cr^{III} character of the products reported here, together with the absence of symmetry which might simplify establishing product structure, means that crystallographic structure determination is the only way to *definitively* establish product identity, so characterization here will rely mainly on that technique. As will be seen, protons of the tBu substituents, because of their relative insulation from spin transmission, are the most diagnostic spectral features.

A 1:2 $[CrL]_2$:PhHNNH$_2$ mole ratio was chosen in anticipation of the disproportionation in eq 1, but anticipating that the $[CrL]_2$ would trap some of the products shown.

$$2\ PhHN\text{-}NH_2 \rightarrow PhN{=}NH + PhNH_2 + NH_3 \qquad (1)$$

The reaction of $[CrL]_2$ with PhHNNH$_2$ in a 1:2 mole ratio in THF proceeds in time of mixing with color change to brown-yellow. Assay of the reaction mixture after 5 minutes of reaction time shows a paramagnetic product with low symmetry and 26 resonances ranging from +37 to – 104 ppm with four tBu resonances in the 3 to 0 ppm range.

Single crystal X-ray diffraction of a sample grown by pentane diffusion into a concentrated THF solution revealed (Figure 2) a composition $[Cr_2L_2(PhNH_2)_2(PhHNN)]$ containing two 6-

coordinate octahedral Cr linked by two bridges, pyrazolate and PhHNN. One L^{2-} ligand is tridentate to Cr1, and the second L^{2-} is tridentate to Cr2 but bridges also to Cr1 using one Nβ; the two pincers are mutually perpendicular. The molecule might have a mirror plane containing the Cr_2NNHPh unit, except for the H and phenyl substituents on four coordinate N11, which render that N chiral, and destroys mirror symmetry. Since the molecule has no symmetry, four tBu chemical shifts are anticipated and observed. None of the hydrazine protons are on pyrazolate nitrogen atoms: the absence of protons on L^{2-} βN is established by the small angles CNN, 105.8 - 107.2°, compressed due to repulsion by the nitrogen lone pairs.[5, 7] Lattice guest THF forms one hydrogen bond with one aniline proton, and two βN (N2 and N4) on L^{2-} bound to Cr1 form hydrogen bonds (2.929 and 3.152 Å) to different aniline protons on Cr2. Cr-N(pincer) distances fall in the narrow range 2.019 – 2.034 Å and are normal, and Cr-N(aniline) distances are longest, at 2.135 and 2.147 Å, these being much longer than to the other hydrazine-derived nitrogen atoms.

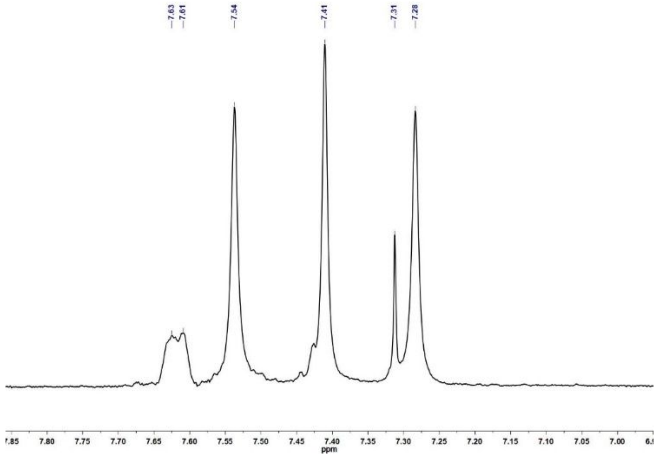


Figure 3. ^1H NMR spectrum of acid-quenched volatile products from $[Cr_2L_2(PhNH_2)_2(PhHNN)]$ synthesis, showing NH_4^+ triplet, and benzene singlet (7.31 ppm); $BArF_{24}$ signals at 7.62 ppm.

The PhHNN ligand (2-) forms two comparable interactions with Cr1 (1.996 and 1.963), and a shorter bond to Cr2, 1.842 Å. Overall this gives charge balance based on two Cr^{III}. Consistent with this, chromium shows no "long bond axis," as typically shown by Jahn-Teller distorted Cr^{II}, and four Cr/Nα(pyrazolate) distances range only from 2.015 to 2.029 Å. The Cr2N12N11 angle is 165.6 °; that NN distance is 1.303 Å, thus between a single and a double bond. N12 is essentially coplanar with Cr1, Cr2 and N11 (out of plane distance 0.17 Å, sum of angles 350.6°). The bond lengths in the bridging hydrazide unit (Figure 2, b) mimic those found in other examples, involving Ti, Zr or Mo (Figure 2, c), but are to be compared to the N-N distance (there 1.380 – 1.424 Å) with the N12 to Cr2 distance being among the shortest (*vs.* 1.808 – 1.996 Å).[8] For comparison, the N=N distance in the very different substituent placement in M(κ^1-HN=NPh) examples are 1.218 – 1.330 Å for M = Ru, Os, Re and Fe.[3a, 9]

The composition of this product establishes the *minimum* number of N-phenyl groups needed for a balanced reaction 2a, which however lacks two H on the reactant side. If this is supplied by removal of the geminal hydrogens from one *additional* $PhHNNH_2$, we arrive at eq 2b to explain this disproportionation reaction.

$$3\ PhHNNH_2 \not\rightarrow\ PhHNN + 2\ PhNH_2 + 2\ NH_3 \quad (2a)$$
$$4\ PhHNNH_2 \rightarrow PhHNN + 2\ PhNH_2 + 2\ NH_3 + PhN{=}NH \quad (2b)$$
$$\ldots\text{then } PhN{=}NH \rightarrow C_6H_6 + N_2 \quad (2c)$$

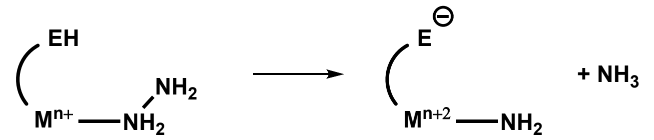
The decay of PhN=NH (eq. 2c) has been characterized,[10] and has a half-life of only minutes at room temperature. Whether *free* PhN=NH is a mechanistic participant is beyond what our observations establish. The two reducing equivalents supplied by the $[Cr^{II}]_2$ reagent convert PhHNN to its dianion, the aminoimide $(PhHN)N^{2-}$. With the exception of $[(C_5H_5)Mo(NO)I(N_2HPh)]_2$, μ_2:η^2,η^1-hydrazido(2−) (Figure 1, C) is unknown for group 6 metals.[11] While $[Cr_2L_2(PhNH_2)_2(PhHNN)]$ has no protons on pyrazolate nitrogens, but instead on aniline, proton transfer *mediated by* those nitrogen atoms can be hypothesized in the N/N bond scission reported here. Overall, this material balance suggests the liberated products NH_3, benzene, and N_2. The first two of these have been identified by ^1H NMR of volatile material vacuum transferred away from $[Cr_2L_2(PhNH_2)_2(PhHNN)]$ (See ESI for details). The complete reaction (eq. 3) is appropriately termed reductively promoted hydrazine disproportionation. The observed reaction is noteworthy for cleaving *some* but not all of the NN bonds present in the available hydrazine reagent (eq. 3). The two electrons in $[CrL]_2$ trap the product where the NN bond is *not* cleaved, as the aminoimide, $[PhHN]N^{2-}$.

$$[CrL]_2 + 4\ PhHNNH_2 \rightarrow [Cr_2L_2(PhNH_2)_2(PhHNN)] + 2\ NH_3 + C_6H_6 + N_2 \quad (3)$$

Repeating the reaction with an optimized 4:1 mole ratio of $PhHNNH_2$ to $[CrL]_2$ (eq. 3) to quantify the amount of NH_3 and benzene liberated by ^1H NMR against an internal standard, $NaBArF_{24}$, gives an NMR yield of 60% for NH_3 and 20% for benzene (Figure 3; See ESI for additional details). At this stoichiometry, all $[CrL]_2$ is consumed and $[Cr_2L_2(PhNH_2)_2(PhHNN)]$ yield is 60%.

Some mechanistic speculation is appropriate. The key event, NN bond scission, has been illustrated previously[3a] (Scheme 1) to involve proton transfer from ligand to the pendant hydrazine nitrogen lone pair and NN bond scission, the latter a 2-electron oxidation step at M. If there are two Cr involved, this would be the redox event which produces *two* Cr^{III}, as in the characterized product. Also noteworthy is that ammonia is *liberated* in the chromium example reported here; because Cr^{III} is kinetically inert, this suggests N-N bond scission occurs from a Cr-κ^1-$NHPh$-NH_2 connectivity, with NN bond scission never involving coordinated NH_3, but instead via pendant NH_2.

In summary, $[CrL]_2$ offers two attractive features in a compact molecule: two low-valent chromium and two proton-responsive pincer ligands. In particular, $[CrL]_2$ can facilitate the N-N bond cleavage of phenylhydrazine under mild conditions and, due to the persistence of the N-C bond, an uncommon isomer of phenyldiazene, PhHNN, is captured at chromium. Previous examples of RHNN complexes are mainly monometallic, and were made either by insertion of PhN_2^+ into MH bonds or by proton transfer to Bronsted basic MR or MNR_2 from phenylhydrazine; another approach is reaction of MCl with a silylhydrazine.[9c, 12] Our advances involve using an earth-abundant dimetal reagent, and a redox process, in addition to the availability of a proton responsive ligand for intramolecular proton transfer. While our work was in review, N_2H_4 disproportionation was shown to be efficiently catalyzed by a $V^{III}Fe^{II}$ species, but mechanistic detail of substrate bond scission, and catalyst speciation were not discussed; it is interesting that this unit contains eight d electrons as do two Cr^{II}.[13]



Scheme 1.

Overall, the reactivity of phenylhydrazine shown here is best described as reductively promoted hydrazine disproportionation. This process is distinguished from many other transformations of hydrazine in that it avoids loss of H_2 and it is retention of those reducing equivalents which is responsible for maximal cleavage of NN bonds here. By the isolobal analogy, replacement of one hydrazine $-NH_2$ by $-OH$ yields hydroxylamine which is a key molecule along the nitrate-to-ammonia nitrogen cycle. Here, N-O bond scission may be favorable due to the π/π repulsion, as it is in hydrazine. The ideas described here may, therefore, advance hydroxylamine chemistry.

This work was supported by the Indiana University Office of Vice President for Research and the National Science Foundation, Chemical Synthesis Program (SYN), by grant CHE-1362127. NSF's ChemMatCARS Sector 15 is principally supported by the Divisions of Chemistry (CHE) and Materials Research (DMR), National Science Foundation, under grant number NSF/CHE-1346572. Use of the Advanced Photon Source, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science by Argonne National Laboratory, was supported by the U.S. DOE under Contract No. DE-AC02-06CH11357.

Conflicts of interest

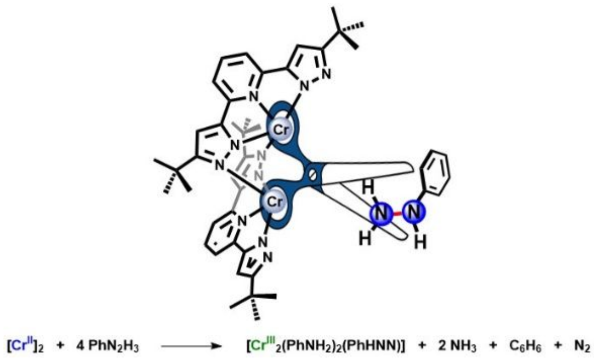
There are no conflicts to declare

Notes and references

1. (a) J. Chatt, J. R. Dilworth and R. L. Richards, *Chem. Rev.*, 1978, **78**, 589-625; (b) N. Hazari, *Chem. Soc. Rev.*, 2010, **39**, 4044-4056; (c) Y. Nishibayashi, *Inorg. Chem.*, 2015, **54**, 9234-9247; (d) J. Rittle and J. C. Peters, *J. Am. Chem. Soc.*, 2016, **138**, 4243-4248.
2. (a) N. Menashe and Y. Shvo, *Organometallics*, 1991, **10**, 3885-3891; (b) E. J. Larson and V. L. Pecoraro, *J. Am. Chem. Soc.*, 1991, **113**, 7809-7810; (c) S. Kuwata, Y. Mizobe and M. Hidai, *Inorg. Chem.*, 1994, **33**, 3619-3620; (d) J. Y. Yang and D. G. Nocera, *J. Am. Chem. Soc.*, 2007, **129**, 8192-8198; (e) A. J. M. Miller, D. M. Heinekey, J. M. Mayer and K. I. Goldberg, *Angew. Chem. Int. Ed.*, 2013, **52**, 3981-3984; (f) A. Gelasco, A. Askenas and V. L. Pecoraro, *Inorg. Chem.*, 1996, **35**, 1419-1420; (g) P. B. Hitchcock, D. L. Hughes, M. J. Maguire, K. Marjani and R. L. Richards, *J. Chem. Soc., Dalton Trans.*, 1997, 4747-4752; (h) G. E. Alluisetti, A. E. Almaraz, V. T. Amorebieta, F. Doctorovich and J. A. Olabe, *J. Am. Chem. Soc.*, 2004, **126**, 13432-13442; (i) E. Block, G. Ofori-Okai, H. Kang and J. Zubieta, *J. Am. Chem. Soc.*, 1992, **114**, 758-759; (j) C. Milsmann, S. P. Semproni and P. J. Chirik, *J. Am. Chem. Soc.*, 2014, **136**, 12099-12107; (k) M. J. Zdilla, A. K. Verma and S. C. Lee, *Inorg. Chem.*, 2011, **50**, 1551-1562; (l) T. R. Porter and J. M. Mayer, *Chemical Science*, 2014, **5**, 372-380; (m) M. J. Zdilla, A. K. Verma and S. C. Lee, *Inorg. Chem.*, 2008, **47**, 11382-11390; (n) H. Yamagishi, S. Nabeya, T. Ikariya and S. Kuwata, *Inorg. Chem.*, 2015, **54**, 11584-11586; (o) C. Wegeberg, W. R. Browne and C. J. McKenzie, *ACS Catalysis*, 2018, **8**, 9980-9991.
3. (a) K. Umehara, S. Kuwata and T. Ikariya, *J. Am. Chem. Soc.*, 2013, **135**, 6754-6757; (b) H. Yamagishi, S. Nabeya, T. Ikariya and S. Kuwata, *Inorg. Chem.*, 2015, **54**, 11584-11586.
4. B. Wu, K. M. Gramigna, M. W. Bezpalko, B. M. Foxman and C. M. Thomas, *Inorg. Chem.*, 2015, **54**, 10909-10917.
5. N. S. Labrum, M. Pink, C.-H. Chen and K. G. Caulton, *Eur. J. Inorg. Chem.*, 2019, **2019**, 1932-1940.
6. N. S. Labrum and K. G. Caulton, *Submitted*, 2019.
7. (a) K. Umehara, S. Kuwata and T. Ikariya, *Inorg. Chim. Acta*, 2014, **413**, 136-142; (b) N. S. Labrum, J. Seo, C.-H. Chen, M. Pink, D. M. Beagan and K. G. Caulton, *Inorg. Chim. Acta*, 2019, **486**, 483-491.
8. (a) J. D. Selby, M. Feliz, A. D. Schwarz, E. Clot and P. Mountford, *Organometallics*, 2011, **30**, 2295-2307; (b) D. L. Hughes, I. A. Latham and G. J. Leigh, *J. Chem. Soc., Dalton Trans.*, 1986, 393-398; (c) Y. Li, Y. Shi and A. L. Odom, *J. Am. Chem. Soc.*, 2004, **126**, 1794-1803; (d) J. M. Pietryga, J. N. Jones, C. L. B. Macdonald, J. A. Moore and A. H. Cowley, *Polyhedron*, 2006, **25**, 259-265; (e) P. R. Mallinson, G. A. Sim and D. I. Woodhouse, *Acta Crystallographica Section B*, 1980, **36**, 450-452; (f) P. J. Walsh, M. J. Carney and R. G. Bergman, *J. Am. Chem. Soc.*, 1991, **113**, 6343-6345; (g) K. Weitershaus, H. Wadepohl and L. H. Gade, *Organometallics*, 2009, **28**, 3381-3389; (h) J. D. Selby, C. D. Manley, A. D. Schwarz, E. Clot and P. Mountford, *Organometallics*, 2008, **27**, 6479-6494; (i) T. B. Parsons, N. Hazari, A. R. Cowley, J. C. Green and P. Mountford, *Inorg. Chem.*, 2005, **44**, 8442-8458.
9. (a) B. L. Haymore and J. A. Ibers, *J. Am. Chem. Soc.*, 1975, **97**, 5369-5379; (b) G. Albertin, S. Antoniutti, M. Bedin, J. Castro and S. Garcia-Fontán, *Inorg. Chem.*, 2006, **45**, 3816-3825; (c) R. Melenkivitz, J. S. Southern, G. L. Hillhouse, T. E.

Concolino, L. M. Liable-Sands and A. L. Rheingold, *J. Am. Chem. Soc.*, 2002, **124**, 12068-12069.

10. M. R. Smith and G. L. Hillhouse, *J. Am. Chem. Soc.*, 1988, **110**, 4066-4068.
11. W. G. Kita, J. A. McCleverty and D. Seddon, *Journal of the Less Common Metals*, 1974, **36**, 203-206.
12. (a) L. D. Field, H. L. Li, S. J. Dalgarno and R. D. McIntosh, *Inorg. Chem.*, 2012, **51**, 3733-3742; (b) M. Yuki, Y. Miyake and Y. Nishibayashi, *Organometallics*, 2012, **31**, 2953-2956; (c) K. Kopka and R. Mattes, *Zeitschrift fur Naturforschung B A Journal for Chemical Sciences* 1996, **51**, 1675-1678; (d) C. Köthe, R. Metzinger, C. Herwig and C. Limberg, *Inorg. Chem.*, 2012, **51**, 9740-9747; (e) B. Goetze, J. Knizek, H. Nöth and W. Schnick, *Eur. J. Inorg. Chem.*, 2000, **2000**, 1849-1854.
13. N. X. Gu, G. Ung and J. C. Peters, *Chem. Commun.*, 2019, **55**, 5363-5366.



Overcoming net single-electron transfer with $[CrL]_2$, a dimeric reagent that packages two one-electron reductants, for $PhHNNH_2$ disproportionation.