Photoredox Catalysis

International Edition: DOI: 10.1002/anie.201605571
German Edition: DOI: 10.1002/ange.201605571

A Molybdenum(0) Isocyanide Analogue of Ru(2,2′-Bipyridine)$_3^{2+}$: A Strong Reductant for Photoredox Catalysis

*Laura A. Büldt, Xingwei Guo, Alessandro Prescimone, and Oliver S. Wenger**

Abstract: *We report the first homoleptic Mo^0 complex with bidentate isocyanide ligands, which exhibits metal-to-ligand charge transfer (^{3}MLCT) luminescence with quantum yields and lifetimes similar to Ru(bpy)$_3^{2+}$ (bpy = 2,2′-bipyridine). This Mo^0 complex is a very strong photoreductant, which manifests in its capability to reduce acetophenone with essentially diffusion-limited kinetics as shown by time-resolved laser spectroscopy. The application potential of this complex for photoredox catalysis was demonstrated by the rearrangement of an acyl cyclopropane to a 2,3-dihydrofuran, which is a reaction that requires a reduction potential so negative that even the well-known and strongly reducing Ir(2-phenylpyridine)$_3$ photosensitizer cannot catalyze it. Our study thus provides the proof-of-concept for the use of chelating isocyanides to obtain Mo^0 complexes with long-lived ^{3}MLCT excited states that are applicable to unusually challenging photoredox chemistry.*

Ru(bpy)$_3^{2+}$ is the prototype of a very large class of metal complexes with long-lived metal-to-ligand charge transfer (^{3}MLCT) excited states,[1] which comprises many examples based on the precious metals Ru^{II},[2] Os^{II},[3] Re^{I},[4] and Ir^{III}.[5] Aside from such d^6 metal diimines, many Pt^{II} and Au$^{I/III}$ complexes have favorable luminescence properties,[6] but emissive complexes made from earth-abundant metals are more difficult to obtain.[7] Notable exceptions are complexes based on Zn^{II} or Cu^{I},[8] but their MLCT excited states usually undergo strong geometrical distortion,[9] and nonradiative relaxation to the ground state is rapid.

Many of the above-mentioned metal complexes have found applications, for example, as triplet harvesters in organic light emitting diodes (OLEDs),[10] photosensitizers in dye-sensitized solar cells (DSSCs),[11] or sensitizers of electron- and energy-transfer processes in artificial and biological systems.[12] In recent years, photoredox catalysis has received much attention in organic synthesis,[13] with Ru^{II} and Ir^{III} complexes playing a particularly prominent role. Furthermore, Ru(bpy)$_3^{2+}$ and related complexes are now frequently used for the production of solar fuels, for example, in the light-driven reduction of CO$_2$ or H$_2$O.[14] However, ruthenium is a precious metal with a natural abundance of approximately 10^{-3} ppm in the earth's crust, and even though the luminescence and photoredox properties of Ru(bpy)$_3^{2+}$-type complexes are tunable through ligand variation, there are limitations to this approach. In view of the continued great interest in the above-mentioned research areas ranging from synthetic organic chemistry to materials applications and solar-energy conversion, the development of new photosensitizers is highly desirable.

The photophysical and photochemical properties of Mo^0 complexes with monodentate arylisocyanide ligands were first explored nearly 40 years ago.[15] Some ^{3}MLCT luminescence was indeed observed, but these complexes become substitutionally labile upon photoexcitation, thus making them unsuitable for most applications.[15,16] Recently, W^0 complexes with monodentate arylisocyanides were found to be strong emitters and photoreductants, but as a 5d metal, W^0 is inherently more inert to substitution than the 4d metal Mo^0.[17] We hypothesized that by using chelating arylisocyanides rather than monodentate ligands, it might be possible to obtain robust Mo^0 complexes with long-lived ^{3}MLCT excited states and high reducing power.

Except for a series of older studies,[18] there has been surprisingly little prior work on chelating isocyanide ligands, particularly with regard to luminescent metal complexes.[19] We prepared the new 2,2″-diisocyano-3,5,3″,5″-tetramethyl-1,1′:3′,1″-terphenyl (CNAr$_3$NC) ligand and reacted it with Mo(THF)$_2$Cl$_4$ in the presence of Na/Hg to obtain the Mo(CNAr$_3$NC)$_3$ complex shown in Figure 1 (pages S2–S5 in the Supporting Information). X-ray diffraction on single crystals revealed Mo–C distances of 2.051(5) and 2.056(4) Å, as well as C-Mo-C bite angles between 82.9(2) and 94.2(4)° (pages S6–S7 in the Supporting Information). In each ligand, there are torsion angles of 51.2(7) and 55.8(7)° between the central benzene ring and the two flanking aryls. *trans*-

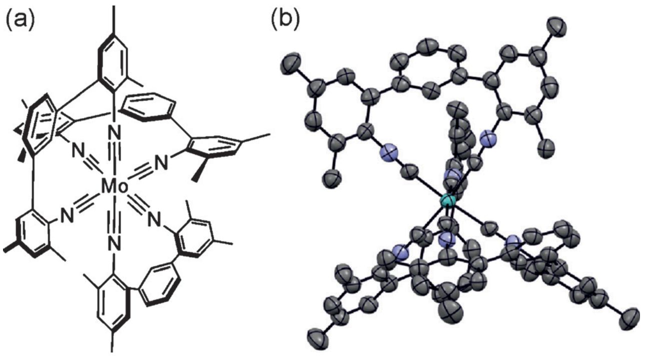


Figure 1. Molecular (a) and crystallographic (b) structures of the Mo(CNAr$_3$NC)$_3$ complex; thermal ellipsoids are drawn at the 50% probability level.[29] Hydrogen atoms are omitted for clarity.

---

[*] L. A. Büldt, Dr. X. Guo, Dr. A. Prescimone, Prof. Dr. O. S. Wenger
Department of Chemistry, University of Basel
St. Johanns-Ring 19 and Spitalstrasse 51, 4056 Basel (Switzerland)
E-mail: oliver.wenger@unibas.ch

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under http://dx.doi.org/10.1002/anie.201605571.

Standing isocyanobenzene units are nearly orthogonal to each another. The methyl substituents help shield the metal center from the environment and thus presumably contribute to the overall stability of the complex. The C≡N stretch frequency in the complex is $\tilde{\nu} = 1939\,\text{cm}^{-1}$, compared to $\tilde{\nu} = 2113\,\text{cm}^{-1}$ in the free ligand, thus indicating substantial π backbonding (page S8 in the Supporting Information).[20]

In cyclic voltammetry, the Mo^0 center is oxidized reversibly to Mo^I at a potential (E^0) of −0.40 V vs. Fc$^+$/Fc in THF (page S9 in the Supporting Information), which is in line with a prior report of Mo^0 complexes with monodentate isocyanide ligands.[15a]

The UV/Vis absorption spectrum of Mo(CNAr$_3$NC)$_3$ in THF (Figure 2a) exhibits a broad band between λ = 350 and λ = 560 nm, which is reminiscent of the MLCT absorption of Ru(bpy)$_3^{2+}$. At shorter wavelengths, there are ligand-based absorptions. The photoluminescence band maximum is blue-shifted when going from THF to toluene to *n*-hexane (Figure 2b), as expected for MLCT emission. The luminescence lifetime (τ) increases from 74 ± 7 (THF) to 166 ± 17 (toluene) to 225 ± 23 ns (*n*-hexane) in deaerated solutions at 20 °C (page S11 in the Supporting Information), and in parallel there is an increase of the luminescence quantum yield (ϕ) from 0.6 ± 0.1 to 2.3 ± 0.2 to 4.5 ± 0.4 % (page S11 in the Supporting Information). In frozen matrices at 77 K, there is a strong rigidochromic effect and emission decays are biexponential with lifetimes in the μs region (pages S12–S13 in the Supporting Information). From the 77 K emission spectra, we estimate an energy (E_{00}) of 2.2 eV for the emissive ^{3}MLCT state. The transient absorption spectra of the long-lived ^{3}MLCT excited state of Mo(CNAr$_3$NC)$_3$ in various solvents are very similar to the spectrum of the ^{3}MLCT state of Ru(bpy)$_3^{2+}$ (page S10 in the Supporting Information).

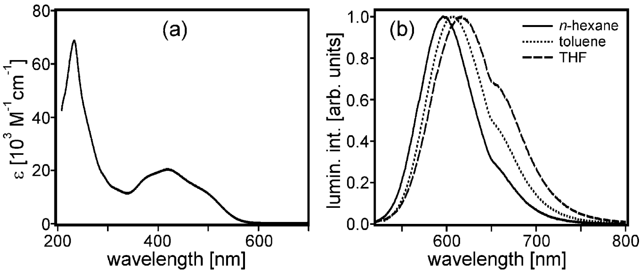


Figure 2. a) UV/Vis absorption spectrum of Mo(CNAr$_3$NC)$_3$ in THF at 20 °C. b) Luminescence spectra in different solvents at 20 °C (λ_{exc} = 500 nm).

Given a potential of −0.40 V vs. Fc$^+$/Fc in the electronic ground state and an energy (E_{00}) of 2.2 eV for the emissive excited state (see above), a potential of around −2.6 V vs. Fc$^+$/Fc can be expected for oxidation of Mo^0 to Mo^I in the long-lived ^{3}MLCT state. In order to test this estimate of the excited-state redox potential, the possibility of photoinduced electron transfer with acetophenone (ACP) was explored. The redox potential for the ACP/ACP$^-$ couple in THF is −2.5 V vs. Fc$^+$/Fc,[21] and hence ^{3}MLCT-excited Mo(CNAr$_3$NC)$_3$ should be thermodynamically competent for the reduction of ACP to ACP$^-$. Indeed the luminescence of Mo(CNAr$_3$NC)$_3$ in THF is strongly quenched upon addition of ACP (page S14 in the Supporting Information), and a Stern–Volmer plot (Figure 3a) yields a quenching constant of $(3.1 \pm 0.4) \times 10^9\,\text{M}^{-1}\,\text{s}^{-1}$, which is near the diffusion limit.

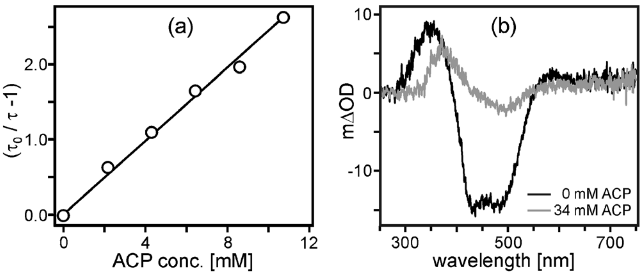
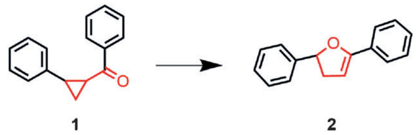


Figure 3. Stern–Volmer plot based on luminescence lifetimes (λ_{det} = 615 nm) of ca. 10^{-5} M Mo(CNAr$_3$NC)$_3$ in deaerated THF at 20 °C in presence of increasing concentrations of acetophenone (ACP). b) Transient absorption of ca. 10^{-5} M Mo(CNAr$_3$NC)$_3$ in the absence (black) and presence (gray) of 34 mM ACP. Excitation and detection was as described above. The disappearance of the bleach between 400 and 520 nm is caused by formation of the ACP radical anion (ACP$^-$); see text and pages S14–S16 in the Supporting Information.

The transient absorption data in Figure 3b are fully compatible with the formation of ACP$^-$ and Mo(CNAr$_3$NC)$_3^+$ (see pages S14–S16 in the Supporting Information for further details).

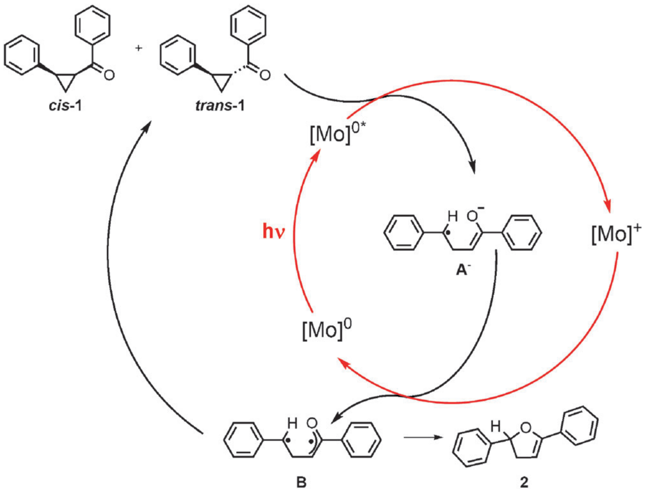
To assess the potential applicability of Mo(CNAr$_3$NC)$_3$ as a photoredox catalyst, we attempted to perform a rearrangement of an acyl cyclopropane (**1**) to a 2,3-dihydrofuran (**2**; Scheme 1), a reaction related to vinylcyclopropane-cyclopentene rearrangements that are important for organic synthesis.[22] 2,3-Dihydrofurans play key roles as structural elements of biologically active compounds such as aflatoxin B$_1$, and they are considered very useful synthetic intermediates.[23] We used the reaction in Scheme 1 as a benchmark for the utility of our complex. Thermally, the conversion of **1** into **2** is very difficult to perform because very harsh conditions or activating groups are necessary.[24]



Scheme 1. Rearrangement of acyl cyclopropane (**1**) to 2,3-dihydrofuran (**2**) accomplished in 84 % yield through photoirradiation (λ_{exc} = 455 nm) of 5 % Mo(CNAr$_3$NC)$_3$ in dry [D$_6$]benzene (TON = 17).

When irradiating a mixture of substrate **1** and 5 % Mo(CNAr$_3$NC)$_3$ in dry [D$_6$]benzene with a blue LED at λ = 455 nm in an evacuated sealed NMR tube, product **2** is formed in 84 % yield (at room temperature). When attempting to perform the same reaction with the well-known Ir(ppy)$_3$ (ppy = 2-phenylpyridine) photosensitizer, no conversion is observed. We attribute this to the very negative potential required for one-electron reduction of **1**, which is necessary to initiate pericyclic rearrangement through a diradical mechanism. This potential can reasonably be assumed to be similar to that of acetophenone (−2.5 V vs. Fc^+/Fc), and our Mo^0 complex has sufficient reducing power (−2.6 V vs. Fc^+/Fc) to undergo photoinduced electron transfer with nearly diffusion-limited kinetics (see above). By contrast, the $Ir(ppy)_3$ photosensitizer has an excited-state reduction potential of only −2.1 V vs. Fc^+/Fc[13c] and is therefore unable to reduce **1** efficiently.

The proposed reaction mechanism for the conversion of **1** into **2** with $Mo(CNAr_3NC)_3$ is shown in Scheme 2. Initially only the *trans* isomer of **1** is present.[25] Electron transfer between photoexcited $Mo(CNAr_3NC)_3$ and *trans*-**1** produces radical intermediate $\mathbf{A}^{-\cdot}$ which can be oxidized to diradical **B** by $Mo(CNAr_3NC)_3^+$ in the electronic ground state.[26] **B** can then either undergo intramolecular reaction to form product **2** or it can revert to substrate **1**, thereby producing a mixture of *cis* and *trans* isomers. Both diastereomers can then re-enter the catalysis cycle with photoexcited Mo^0 complex until conversion to **2** is complete. In principle, this can be considered an electron-catalyzed reaction.[27]



Scheme 2. Proposed reaction mechanism for the conversion of **1** into **2**. Mo^{0*} denotes the photoexcited $Mo(CNAr_3NC)_3$ complex.

Owing to the ability of diradical **B** to undergo forward and backward reactions, the irradiation time to achieve complete conversion to **2** is relatively long, at approximately 80 hours. This is evidently an inherent property of the model reaction investigated here and is clearly not a shortcoming of the Mo^0 sensitizer. We were able to follow the isomerization of **1** and conversion to **2** as a function of irradiation time by NMR spectroscopy (page S17 in the Supporting Information). The overall yield of **2** is 84 %, which corresponds to a TON of 17, which is close to the theoretical limit of 20 at a catalyst loading of 5 %.

In summary, we have synthesized and characterized the first homoleptic Mo^0 complex with bidendate isocyanide ligands. Photoexcited $Mo(CNAr_3NC)_3$ has roughly 1.3 V more reducing power than ^{3}MLCT-excited $Ru(bpy)_3^{2+}$,[1a,2a,13c] and it is about 0.5 V more reducing than photoexcited $Ir(ppy)_3$,[13c,17a,28] thus making it one of the most potent visible-light absorbing photoreductants known to date. The application potential of Mo^0 complexes with chelating isocyanides for photoredox catalysis was illustrated in this study by using the example of a pericyclic rearrangement, which is a very challenging benchmark reaction because its initiation requires exceptionally strong reductants. The $Mo(CNAr_3NC)_3$ complex is able to act as a robust and efficient photoredox sensitizer for this reaction, clearly outperforming the widely used $Ir(ppy)_3$ complex.

In conclusion, our study provides a proof-of-concept for the use of chelating isocyanides to obtain Mo^0 complexes with long-lived ^{3}MLCT excited states, which emit visible light and are applicable to unusually challenging photoredox chemistry.

Acknowledgements

This research was supported by the Swiss National Science Foundation through grant number 200021_156063/1 and through the NCCR Molecular Systems Engineering.

Keywords: electron transfer · isocyanide ligands · luminescence · photocatalysis · photochemistry

---

[1] a) C. R. Bock, T. J. Meyer, D. G. Whitten, *J. Am. Chem. Soc.* **1974**, *96*, 4710–4712; b) R. Bensasson, C. Salet, V. Balzani, *J. Am. Chem. Soc.* **1976**, *98*, 3722–3724.
[2] a) A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser, A. Von Zelewsky, *Coord. Chem. Rev.* **1988**, *84*, 85–277; b) J. K. McCusker, *Acc. Chem. Res.* **2003**, *36*, 876–887; c) J. England, C. C. Scarborough, T. Weyhermüller, S. Sproules, K. Wieghardt, *Eur. J. Inorg. Chem.* **2012**, 4605–4621.
[3] J.-P. Sauvage, J.-P. Collin, J.-C. Chambron, S. Guillerez, C. Coudret, V. Balzani, F. Barigelletti, L. De Cola, L. Flamigni, *Chem. Rev.* **1994**, *94*, 993–1019.
[4] a) K. S. Schanze, D. B. MacQueen, T. A. Perkins, L. A. Cabana, *Coord. Chem. Rev.* **1993**, *122*, 63–89; b) D. J. Stufkens, A. Vlcek, *Coord. Chem. Rev.* **1998**, *177*, 127–179.
[5] a) M. S. Lowry, S. Bernhard, *Chem. Eur. J.* **2006**, *12*, 7970–7977; b) J. Li, P. I. Djurovich, B. D. Alleyne, M. Yousufuddin, N. N. Ho, J. C. Thomas, J. C. Peters, R. Bau, M. E. Thompson, *Inorg. Chem.* **2005**, *44*, 1713–1727; c) K. N. Swanick, S. Ladouceur, E. Zysman-Colman, Z. F. Ding, *Angew. Chem. Int. Ed.* **2012**, *51*, 11079–11082; *Angew. Chem.* **2012**, *124*, 11241–11244; d) R. D. Costa, E. Orti, H. J. Bolink, F. Monti, G. Accorsi, N. Armaroli, *Angew. Chem. Int. Ed.* **2012**, *51*, 8178–8211; *Angew. Chem.* **2012**, *124*, 8300–8334.
[6] a) M. Hissler, J. E. McGarrah, W. B. Connick, D. K. Geiger, S. D. Cummings, R. Eisenberg, *Coord. Chem. Rev.* **2000**, *208*, 115–137; b) V. W. W. Yam, *Acc. Chem. Res.* **2002**, *35*, 555–563; c) T. T. Zou, C. T. Lum, C. N. Lok, J. J. Zhang, C. M. Che, *Chem. Soc. Rev.* **2015**, *44*, 8786–8801; d) F. N. Castellano, I. E. Pomestchenko, E. Shikhova, F. Hua, M. L. Muro, N. Rajapakse, *Coord. Chem. Rev.* **2006**, *250*, 1819–1828; e) M. A. Malwitz, S. H. Lim, R. L. White-Morris, D. M. Pham, M. M. Olmstead, A. L. Balch, *J. Am. Chem. Soc.* **2012**, *134*, 10885–10893; f) M. J. Irwin, J. J. Vittal, R. J. Puddephatt, *Organometallics* **1997**, *16*, 3541–3547.
[7] a) S. Otto, M. Grabolle, C. Förster, C. Kreitner, U. Resch-Genger, K. Heinze, *Angew. Chem. Int. Ed.* **2015**, *54*, 11572–11576; *Angew. Chem.* **2015**, *127*, 11735–11739; b) A. Vogler, H.

Kunkely, *Transition Metal and Rare Earth Compounds: Excited States, Transition, Interactions I, Vol. 213*, Springer, Berlin, **2001**, pp. 143–182; c) A. J. Lees, *Chem. Rev.* **1987**, *87*, 711–743.

[8] a) G. Cheng, G. K. M. So, W. P. To, Y. Chen, C. C. Kwok, C. S. Ma, X. G. Guan, X. Chang, W. M. Kwok, C. M. Che, *Chem. Sci.* **2015**, *6*, 4623–4635; b) D. G. Cuttell, S. M. Kuang, P. E. Fanwick, D. R. McMillin, R. A. Walton, *J. Am. Chem. Soc.* **2002**, *124*, 6–7.

[9] L. X. Chen, G. B. Shaw, I. Novozhilova, T. Liu, G. Jennings, K. Attenkofer, G. J. Meyer, P. Coppens, *J. Am. Chem. Soc.* **2003**, *125*, 7022–7034.

[10] a) A. Tsuboyama, H. Iwawaki, M. Furugori, T. Mukaide, J. Kamatani, S. Igawa, T. Moriyama, S. Miura, T. Takiguchi, S. Okada, M. Hoshino, K. Ueno, *J. Am. Chem. Soc.* **2003**, *125*, 12971–12979; b) H. Yersin, A. F. Rausch, R. Czerwieniec, T. Hofbeck, T. Fischer, *Coord. Chem. Rev.* **2011**, *255*, 2622–2652.

[11] A. Hagfeldt, G. Boschloo, L. C. Sun, L. Kloo, H. Pettersson, *Chem. Rev.* **2010**, *110*, 6595–6663.

[12] a) B. Geiss, C. Lambert, *Chem. Commun.* **2009**, 1670–1672; b) A. Magnuson, M. Anderlund, O. Johansson, P. Lindblad, R. Lomoth, T. Polivka, S. Ott, K. Stensjö, S. Styring, V. Sundström, L. Hammarström, *Acc. Chem. Res.* **2009**, *42*, 1899–1909; c) J. R. Winkler, H. B. Gray, *Chem. Rev.* **1992**, *92*, 369–379; d) L. De Cola, P. Belser, *Coord. Chem. Rev.* **1998**, *177*, 301–346; e) D. G. Brown, N. Sanguantrakun, B. Schulze, U. S. Schubert, C. P. Berlinguette, *J. Am. Chem. Soc.* **2012**, *134*, 12354–12357; f) A. J. Howarth, M. B. Majewski, M. O. Wolf, *Coord. Chem. Rev.* **2015**, *282*, 139–149; g) M. Goez, C. Kerzig, R. Naumann, *Angew. Chem. Int. Ed.* **2014**, *53*, 9914–9916; *Angew. Chem.* **2014**, *126*, 10072–10074.

[13] a) J. Svoboda, B. König, *Chem. Rev.* **2006**, *106*, 5413–5430; b) J. M. R. Narayanam, C. R. J. Stephenson, *Chem. Soc. Rev.* **2011**, *40*, 102–113; c) C. K. Prier, D. A. Rankic, D. W. C. MacMillan, *Chem. Rev.* **2013**, *113*, 5322–5363; d) T. P. Yoon, M. A. Ischay, J. N. Du, *Nat. Chem.* **2010**, *2*, 527–532; e) T. Bach, J. P. Hehn, *Angew. Chem. Int. Ed.* **2011**, *50*, 1000–1045; *Angew. Chem.* **2011**, *123*, 1032–1077; f) D. B. Bagal, G. Kachkovskyi, M. Knorn, T. Rawner, B. M. Bhanage, O. Reiser, *Angew. Chem. Int. Ed.* **2015**, *54*, 6999–7002; *Angew. Chem.* **2015**, *127*, 7105–7108; g) H. H. Huo, X. D. Shen, C. Y. Wang, L. L. Zhang, P. Rose, L. A. Chen, K. Harms, M. Marsch, G. Hilt, E. Meggers, *Nature* **2014**, *515*, 100–103; h) K. T. Tarantino, P. Liu, R. R. Knowles, *J. Am. Chem. Soc.* **2013**, *135*, 10022–10025; i) O. Gutierrez, J. C. Tellis, D. N. Primer, G. A. Molander, M. C. Kozlowski, *J. Am. Chem. Soc.* **2015**, *137*, 4896–4899; j) A. C. Bissember, R. J. Lundgren, S. E. Creutz, J. C. Peters, G. C. Fu, *Angew. Chem. Int. Ed.* **2013**, *52*, 5129–5133; *Angew. Chem.* **2013**, *125*, 5233–5237.

[14] a) J. L. Dempsey, B. S. Brunschwig, J. R. Winkler, H. B. Gray, *Acc. Chem. Res.* **2009**, *42*, 1995–2004; b) M. G. Pfeffer, B. Schäfer, G. Smolentsev, J. Uhlig, E. Nazarenko, J. Guthmüller, C. Kuhnt, M. Wachtler, B. Dietzek, V. Sundström, S. Rau, *Angew. Chem. Int. Ed.* **2015**, *54*, 5044–5048; *Angew. Chem.* **2015**, *127*, 5132–5136; c) D. J. Boston, C. D. Xu, D. W. Armstrong, F. M. MacDonnell, *J. Am. Chem. Soc.* **2013**, *135*, 16252–16255; d) A. Fihri, V. Artero, M. Razavet, C. Baffert, W. Leibl, M. Fontecave, *Angew. Chem. Int. Ed.* **2008**, *47*, 564–567; *Angew. Chem.* **2008**, *120*, 574–577; e) E. Reisner, D. J. Powell, C. Cavazza, J. C. Fontecilla-Camps, F. A. Armstrong, *J. Am. Chem. Soc.* **2009**, *131*, 18457–18466; f) J. F. Hull, Y. Himeda, W. H. Wang, B. Hashiguchi, R. Periana, D. J. Szalda, J. T. Muckerman, E. Fujita, *Nat. Chem.* **2012**, *4*, 383–388; g) S. Kato, J. U. Jung, T. Suenobu, S. Fukuzumi, *Energy Environ. Sci.* **2013**, *6*, 3756–3764; h) C. D. Windle, M. W. George, R. N. Perutz, P. A. Summers, X. Z. Sun, A. C. Whitwood, *Chem. Sci.* **2015**, *6*, 6847–6864; i) H. Takeda, O. Ishitani, *Coord. Chem. Rev.* **2010**, *254*, 346–354; j) J. H. Alstrum-Acevedo, M. K. Brennaman, T. J. Meyer, *Inorg. Chem.* **2005**, *44*, 6802–6827; k) C. Herrero, A. Quaranta, S. El Ghachtouli, B. Vauzeilles, W. Leibl, A. Aukauloo, *Phys. Chem. Chem. Phys.* **2014**, *16*, 12067–12072.

[15] a) K. R. Mann, H. B. Gray, *J. Am. Chem. Soc.* **1977**, *99*, 306–307; b) K. R. Mann, M. Cimolino, G. L. Geoffroy, G. S. Hammond, A. A. Orio, G. Albertin, H. B. Gray, *Inorg. Chim. Acta* **1976**, *16*, 97–101.

[16] L. E. Shaw, C. H. Langford, *Coord. Chem. Rev.* **2002**, *230*, 165–169.

[17] a) W. Sattler, M. E. Ener, J. D. Blakemore, A. A. Rachford, P. J. LaBeaume, J. W. Thackeray, J. F. Cameron, J. R. Winkler, H. B. Gray, *J. Am. Chem. Soc.* **2013**, *135*, 10614–10617; b) W. Sattler, L. M. Henling, J. R. Winkler, H. B. Gray, *J. Am. Chem. Soc.* **2015**, *137*, 1198–1205; c) H. Kvapilová, W. Sattler, A. Sattler, I. V. Sazanovich, I. P. Clark, M. Towrie, H. B. Gray, S. Zalis, A. Vlcek, *Inorg. Chem.* **2015**, *54*, 8518–8528.

[18] a) F. E. Hahn, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 650–665; *Angew. Chem.* **1993**, *105*, 681–696; b) F. E. Hahn, M. Tamm, *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 203–205; *Angew. Chem.* **1991**, *103*, 213–215; c) D. T. Plummer, G. A. Kraus, R. J. Angelici, *Inorg. Chem.* **1983**, *22*, 3492–3497; d) M. L. Winzenburg, J. A. Kargol, R. J. Angelici, *J. Organomet. Chem.* **1983**, *249*, 415–428.

[19] F. Monti, A. Baschieri, E. Matteucci, A. Mazzanti, L. Sambri, A. Barbieri, N. Armaroli, *Faraday Discuss.* **2015**, *185*, 233–248.

[20] a) G. W. Margulieux, N. Weidemann, D. C. Lacy, C. E. Moore, A. L. Rheingold, J. S. Figueroa, *J. Am. Chem. Soc.* **2010**, *132*, 5033–5035; b) C. C. Mokhtarzadeh, G. W. Margulieux, A. E. Carpenter, N. Weidemann, C. E. Moore, A. L. Rheingold, J. S. Figueroa, *Inorg. Chem.* **2015**, *54*, 5579–5587.

[21] P. J. Wagner, R. J. Truman, A. E. Puchalski, R. Wake, *J. Am. Chem. Soc.* **1986**, *108*, 7727–7738.

[22] a) J. E. Baldwin, *Chem. Rev.* **2003**, *103*, 1197–1212; b) M. Rubin, M. Rubina, V. Gevorgyan, *Chem. Rev.* **2007**, *107*, 3117–3179.

[23] a) S. Son, G. C. Fu, *J. Am. Chem. Soc.* **2007**, *129*, 1046–1047; b) T. G. Kilroy, T. P. O'Sullivan, P. J. Guiry, *Eur. J. Org. Chem.* **2005**, 4929–4949.

[24] a) C. L. Wilson, *J. Am. Chem. Soc.* **1947**, *69*, 3002–3004; b) R. K. Bowman, J. S. Johnson, *Org. Lett.* **2006**, *8*, 573–576; c) V. K. Yadav, R. Balamurugan, *Org. Lett.* **2001**, *3*, 2717–2719.

[25] K. Miyazawa, T. Koike, M. Akita, *Chem. Eur. J.* **2015**, *21*, 11677–11680.

[26] The oxidation potential of A^- is estimated to be lower than -0.8 V vs. Fc^+/Fc, given the reported values for related enolates: M. Schmittel, M. Lal, R. Lal, M. Röck, A. Langels, Z. Rappoport, A. Basheer, J. Schlirf, H. J. Deiseroth, U. Florke, G. Gescheidt, *Tetrahedron* **2009**, *65*, 10842–10855.

[27] A. Studer, D. P. Curran, *Nat. Chem.* **2014**, *6*, 765–773.

[28] K. A. King, P. J. Spellane, R. J. Watts, *J. Am. Chem. Soc.* **1985**, *107*, 1431–1432.

[29] CCDC 1446591 contains the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

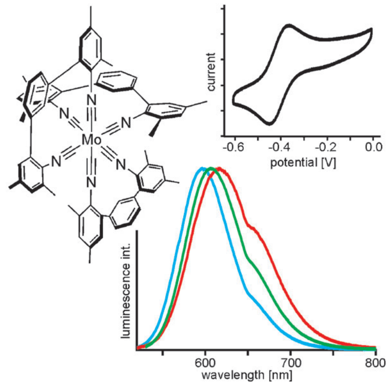
Received: June 8, 2016

Communications

Photoredox Catalysis

L. A. Büldt, X. Guo, A. Prescimone,
O. S. Wenger* ———— ▮▮▮▮–▮▮▮▮

A Molybdenum(0) Isocyanide Analogue of Ru(2,2′-Bipyridine)$_3^{2+}$: A Strong Reductant for Photoredox Catalysis



A homoleptic Mo^0 complex with chelating isocyanide ligands was investigated. This chemically robust complex exhibits long-lived ^{3}MLCT luminescence, and it is a far stronger photoreductant than d^6 metal diimines made from precious metals. The utility of this complex as a photoredox sensitizer is demonstrated by its successful application in the rearrangement of an acyl cyclopropane to a 2,3-dihydrofuran.