

# Cr(0), Mo(0) and W(0) isocyanide complexes as luminophores and photosensitizers with long-lived excited states

Laura A. Büldt,<sup>[b]</sup> and Oliver S. Wenger\*<sup>[a]</sup>

**Abstract:** Group 6 d<sup>6</sup> metal complexes with arylisocyanide ligands are earth-abundant alternatives to photoactive complexes made from precious metals such as Ru(II), Re(I), Os(II), or Ir(III). Some of them have long-lived <sup>3</sup>MLCT excited states that exhibit luminescence with good quantum yields combined with nano- to microsecond lifetimes, and they are very strongly reducing. Recent studies have demonstrated that Cr(0), Mo(0), and W(0) arylisocyanides have great potential for application in luminescent devices, photoredox catalysis, and dye-sensitized solar cells.

## 1. Introduction

The Ru(bpy)<sub>3</sub><sup>2+</sup> (bpy = 2,2'-bipyridine) complex is the fruit fly of inorganic photophysics and photochemistry. Owing to its favorable excited-state properties, its advantageous electrochemical behavior, and its chemical robustness Ru(bpy)<sub>3</sub><sup>2+</sup> has become one of the most widely used chemical compounds. Initially mostly a subject of interest for inorganic and physical chemists, Ru(bpy)<sub>3</sub><sup>2+</sup> and its isoelectronic d<sup>6</sup> congeners made from Re(I), Os(II), and Ir(III) have found application in lighting devices,<sup>[1]</sup> solar cells,<sup>[2]</sup> sensors, and photoredox catalysis,<sup>[3]</sup> just to name a few examples. There is a long-standing interest in replacing these precious metals by more earth-abundant elements,<sup>[4]</sup> and this has triggered much research on Fe(II) polypyridines.<sup>[5]</sup> Unfortunately, the ligand field is quite weak in these Fe(II) complexes, leading to ultrafast relaxation in most cases, since MLCT excited states depopulate very efficiently via energetically lower-lying d-d states. The current record MLCT excited state lifetime for Fe(II) complexes is 37 ps on Al<sub>2</sub>O<sub>3</sub> nanofilms,<sup>[5a, 6]</sup> which compares to 855 ns for Ru(bpy)<sub>3</sub><sup>2+</sup> in de-aerated CH<sub>3</sub>CN at 25 °C.<sup>[7]</sup> Isocyanide complexes of Cr(0), Mo(0), and W(0) are isoelectronic to Fe(bpy)<sub>3</sub><sup>2+</sup>, Ru(bpy)<sub>3</sub><sup>2+</sup>, and Os(bpy)<sub>3</sub><sup>2+</sup>, but until recently they have received orders of magnitude less attention. However, zero-valent metal complexes containing only isocyanide ligands have been known for more than 60 years,<sup>[8]</sup> and the optical spectroscopic and luminescence properties of hexakis(arylisocyanide) complexes with Cr(0), Mo(0) and W(0) were first explored more than 40 years ago.<sup>[9]</sup> It was found that they have low-lying MLCT excited states, analogous to the

abovementioned precious metal complexes, and some of the Mo(0) and W(0) complexes were even reported to luminesce in fluid solution at room temperature.<sup>[9b]</sup> From then on, the field of group 6 d<sup>6</sup> isocyanides was dormant until 2013, when new reports on highly emissive W(0) isocyanide complexes appeared.<sup>[10]</sup> More recently, we found that chelating diisocyanide ligands give access to luminescent Cr(0) and Mo(0) complexes which are analogues of Fe(bpy)<sub>3</sub><sup>2+</sup> and Ru(bpy)<sub>3</sub><sup>2+</sup>,<sup>[11]</sup> and we could demonstrate that they are amenable to applications such as triplet-triplet annihilation upconversion or photoredox catalysis.

Laura A. Büldt performed her undergraduate studies in chemistry at the Ruhr-University Bochum (Germany). In 2012 she joined the group of Oliver S. Wenger in Basel (Switzerland) as a Ph.D. student. After receiving her Ph.D. degree in 2016, she started a postdoc position with Michael Seitz at the Eberhard Karls Universität Tübingen (Germany).



Oliver S. Wenger received a Ph. D. degree after work with Hans U. Güdel at University of Bern (Switzerland) in 2002. Following postdoctoral stays with Harry B. Gray at Caltech, and with Jean-Pierre Sauvage in Strasbourg, he started independent research as an assistant professor at University of Geneva in 2006. In 2009, he became W2 professor (with tenure) at Georg-August-Universität Göttingen (Germany), and in 2012 he moved with his group to the University of Basel (Switzerland).

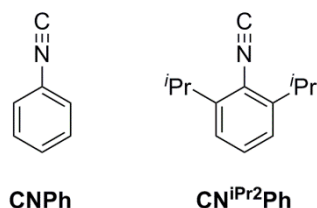


## 2. Early studies of Cr(0), Mo(0) and W(0) isocyanides

Research on isocyanide complexes with zero-valent metals emerged from studies of isoelectronic carbonyl complexes,<sup>[12]</sup> and consequently many early photochemical investigations of this compound class focused on photoinduced ligand dissociation and photo-substitution reactions.<sup>[13]</sup> This is particularly true for Cr(0) isocyanides,<sup>[14]</sup> which are analogues of Cr(CO)<sub>6</sub>, one of most thoroughly investigated carbonyl complexes with regard to photoinduced ligand dissociation.

[a] Prof. Dr. O. S. Wenger  
Department of Chemistry  
University of Basel  
St. Johannis-Ring 19, 4056 Basel (Switzerland)  
E-mail: [oliver.wenger@unibas.ch](mailto:oliver.wenger@unibas.ch)

[b] Dr. L. A. Büldt  
Institute of Inorganic Chemistry  
University of Tübingen  
Auf der Morgenstelle 18, 72076 Tübingen (Germany)



**Scheme 1.** Chemical structures of the CNPh and CN<sup>iPr</sup><sub>2</sub>Ph ligands.<sup>[9]</sup>

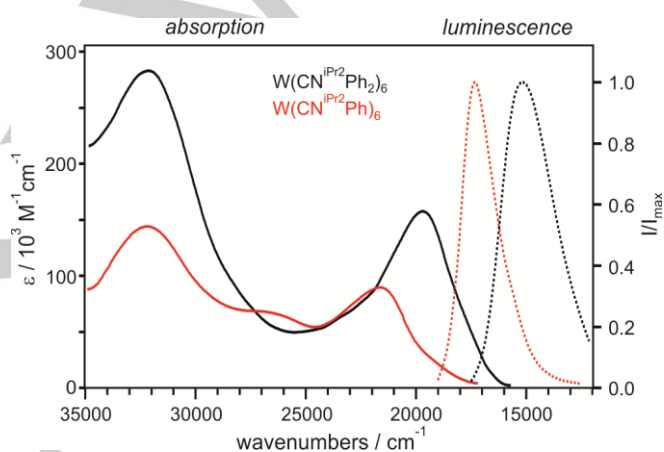
An early key study reported on homoleptic complexes of Cr(0), Mo(0), and W(0) with phenylisocyanide (CNPh) and 2,6-diisopropylphenylisocyanide (CN<sup>iPr</sup><sub>2</sub>Ph) ligands (Scheme 1).<sup>[9b]</sup> The respective Mo(0) and W(0) complexes showed luminescence in fluid solution at room temperature, whereas the Cr(0) complexes seemed to be essentially non-emissive under these conditions. In frozen 2-methylpentane matrices at 77 K, luminescence quantum yields of 0.78 and 0.93 were found for Mo(CNPh)<sub>6</sub> and W(CNPh)<sub>6</sub>, respectively, and some emission was detectable even from the Cr(CN<sup>iPr</sup><sub>2</sub>Ph)<sub>6</sub> complex. At room temperature, the excited-state lifetimes of Mo(CN<sup>iPr</sup><sub>2</sub>Ph)<sub>6</sub> and W(CN<sup>iPr</sup><sub>2</sub>Ph)<sub>6</sub> in 2-methylpentane and THF are on the order of a few dozens of nanoseconds (Table 1), while at 77 K they are in the microsecond regime, compatible with <sup>3</sup>MLCT emission. By contrast, the Cr(CN<sup>iPr</sup><sub>2</sub>Ph)<sub>6</sub> complex exhibits a luminescence lifetime below 10 ns even at 77 K, and this was interpreted in terms of spin-allowed emission from a <sup>1</sup>MLCT state.<sup>[9b]</sup> Thus it seemed that intersystem crossing from the initially excited singlet state to the <sup>3</sup>MLCT state is comparatively slow in this first-row transition metal complex.

**Table 1.** Luminescence quantum yields ( $\phi$ ), MLCT excited-state lifetimes ( $\tau$ ), and redox-potentials in the emissive excited states ( $E^0$ ).

complex	$\phi$ <sup>[a]</sup>	$\tau$ [ns] <sup>[a]</sup>	$E^0$ (M <sup>+/0</sup> /M <sup>0</sup> ) [V] <sup>[b]</sup>	solvent
Cr(CN <sup>iPr</sup> <sub>2</sub> Ph) <sub>6</sub> <sup>[c]</sup>		< 10 <sup>[d]</sup>		2-MP
Cr(CNtBuAr <sub>3</sub> NC) <sub>3</sub> <sup>[e]</sup>	~10 <sup>-5</sup>	2.2	-2.4	THF
Mo(CN <sup>iPr</sup> <sub>2</sub> Ph) <sub>6</sub> <sup>[c]</sup>		43		2-MP
Mo(CNAr <sub>3</sub> NC) <sub>3</sub> <sup>[f]</sup>	0.045	225	-2.6 <sup>[g]</sup>	<i>n</i> -hexane
W(CN <sup>iPr</sup> <sub>2</sub> Ph) <sub>6</sub> <sup>[h,i]</sup>	0.01	73	-2.8	THF
W(CN <sup>iPr</sup> <sub>2</sub> Ph <sub>2</sub> ) <sub>6</sub> <sup>[i]</sup>	0.44	15300	-2.6 <sup>[g]</sup>	toluene
W(CN <sup>iPr</sup> <sub>2</sub> Ph <sub>2</sub> OMe <sub>3</sub> ) <sub>6</sub> <sup>[i]</sup>	0.41	18300	-2.8 <sup>[g]</sup>	toluene

[a] In de-aerated solution at 298 K unless otherwise noted. [b] In Volts vs. Fc<sup>+</sup>/Fc. [c] From ref. <sup>[9b]</sup>. [d] In frozen glass at 77 K. [e] From ref. <sup>[11a]</sup>. [f] From ref. <sup>[11b]</sup>. [g] In THF. [h] From ref. <sup>[10a]</sup>. [i] From ref. <sup>[10b]</sup>. 2-MP is 2-methylpentane.

In pyridine solution, photo-substitution of the isocyanide ligands by pyridine was observed, with quantum yields decreasing from Cr(0) to Mo(0) and W(0), as well as with increased steric hindrance of the isocyanide ligands.<sup>[9b]</sup> These observations are compatible with an associative mechanism for ligand substitution, much in contrast to the dissociative photo-substitutions observed for many carbonyl complexes. Thus, it seemed that direct nucleophilic attack on the positively charged metal centers in the MLCT excited state is the initial step of photo-substitution, at least in the Mo and W cases. In chloroform solution, the seven-coordinate, two-electron oxidation products [M(CNPh)<sub>6</sub>Cl]<sup>+</sup> (M = Mo, W) were readily isolated after photo-irradiation at 436 nm.<sup>[9b]</sup> For the Cr(0) complexes, the observation of identical pyridine photo-substitution quantum yields for CNPh and CN<sup>iPr</sup><sub>2</sub>Ph ligands is consistent with a dissociative pathway. Later it was argued that Mo(0) isocyanide complexes do also react through dissociative mechanisms.<sup>[13]</sup>

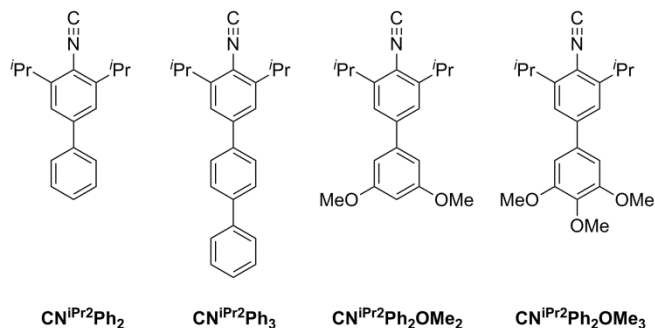


**Figure 1.** UV-Vis absorption (solid lines) and luminescence spectra (dotted traces) of W(CN<sup>iPr</sup><sub>2</sub>Ph)<sub>6</sub> (red) and W(CN<sup>iPr</sup><sub>2</sub>Ph<sub>2</sub>)<sub>6</sub> (black). Adapted with permission from ref. <sup>[10b]</sup>. Copyright 2015 American Chemical Society.

### 3. New tungsten(0) luminophores and photoreductants

Given these early fundamental insights, it seems logical that studies geared at obtaining strongly emissive group 6 d<sup>6</sup> metal complexes initially concentrated on W(0) rather than on the lighter homologues Mo(0) and Cr(0). Particular focus was on 2,6-disubstituted phenylisocyanides,<sup>[10a]</sup> because isocyanide ligands with this substitution pattern were the most robust ones in the abovementioned early studies and because such ligands had been used very successfully for stabilization of other (non-emissive) metals in low oxidation states.<sup>[15]</sup> The homoleptic W(CN<sup>iPr</sup><sub>2</sub>Ph)<sub>6</sub> complex exhibits <sup>3</sup>MLCT luminescence (dotted red trace in Figure 1) with nanosecond lifetimes in solution at room temperature (Table 1). The metal center in W(CN<sup>iPr</sup><sub>2</sub>Ph)<sub>6</sub> is oxidized at a potential of -0.53 V vs. Fc<sup>+</sup>/Fc in THF, and given an energy of 2.3 eV for the long-lived <sup>3</sup>MLCT state, an excited-state oxidation potential of -2.8 V vs. Fc<sup>+</sup>/Fc results. Thus, W(CN<sup>iPr</sup><sub>2</sub>Ph)<sub>6</sub> is one of the strongest photoreductants operating

on the basis of visible light absorption, and it was demonstrated by transient UV-Vis absorption spectroscopy that upon photoexcitation this complex is able to reduce benzophenone and anthracene to their radical anionic forms.<sup>[10a]</sup>

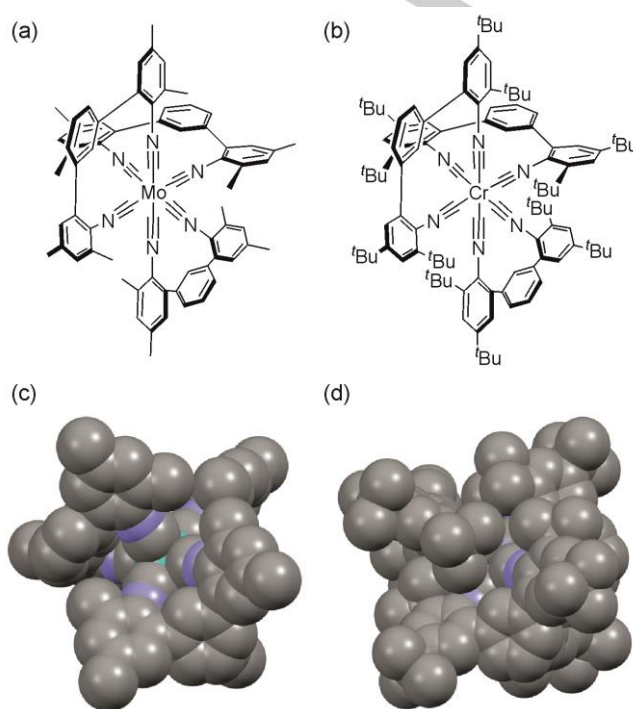


**Scheme 2.** Chemical structures of monodentate isocyanide ligands for  $W(0)$  complexes.<sup>[10]</sup>

Subsequent further studies concentrated on arylisocyanides made from biphenyl or terphenyl moieties (Scheme 2), leading to further enhancement of the absorption and luminescence properties while maintaining the favorable electrochemical behavior.<sup>[10b]</sup> Homoleptic  $W(0)$  complexes with the ligands from Scheme 2 exhibit MLCT absorptions in the visible spectral range with extinction coefficients up to  $1.6 \cdot 10^5 \text{ M}^{-1} \text{ cm}^{-1}$  (solid black trace in Figure 1), roughly an order of magnitude higher than for  $\text{Ru}(\text{bpy})_3^{2+}$ . According to DFT calculations, the most intense absorptions originate from singlet-singlet transitions that combine MLCT with intraligand  $\pi-\pi^*$  contributions.<sup>[10c]</sup> The lowest relaxed triplet excited state is largely localized along one molecular axis, and it has contributions from MLCT, intraligand  $\pi-\pi^*$ , as well as from ligand-to-ligand charge transfer (LLCT). Based on transient IR spectroscopy, intersystem crossing after  $^1\text{MLCT}$  excitation is ultrafast ( $< 200 \text{ fs}$ ), and time-dependent DFT indicates that at room temperature the lowest triplet excited state is populated almost exclusively.<sup>[10c]</sup> Large delocalization of the excited electron density over a pair of *trans*-standing ligands in the lowest  $^3\text{MLCT}$  state minimizes excited-state distortions and, in consequence, the Franck-Condon factor of nonradiative relaxation to the electronic ground state. This can account for the high luminescence quantum yields ( $\phi = 0.41 - 0.44$  in toluene at  $25 \text{ }^\circ\text{C}$ ) and long excited-state lifetimes (up to  $1.83 \text{ } \mu\text{s}$ ) observed for the  $W(0)$  complexes with the biphenyl- or terphenyl-based isocyanide ligands from Scheme 2 (Table 1). Evidently, d-d excited states are not accessible from the lowest  $^3\text{MLCT}$  state, thanks to the combination of a 5d metal with strong-field isocyanide ligands.

$W(I/0)$  redox potentials in the lowest  $^3\text{MLCT}$  states range from  $-2.7$  to  $-2.8 \text{ V}$  vs.  $\text{Fc}^+/\text{Fc}$  for these complexes, and consequently efficient oxidative excited-state quenching by benzophenone ( $E^0 = -2.3 \text{ V}$  vs.  $\text{Fc}^+/\text{Fc}$ ) and even acetophenone ( $E^0 = -2.5 \text{ V}$  vs.  $\text{Fc}^+/\text{Fc}$ ) occurred.<sup>[10b]</sup> With the widely used  $\text{Ir}(\text{ppy})_3$  ( $\text{ppy} = 2-$

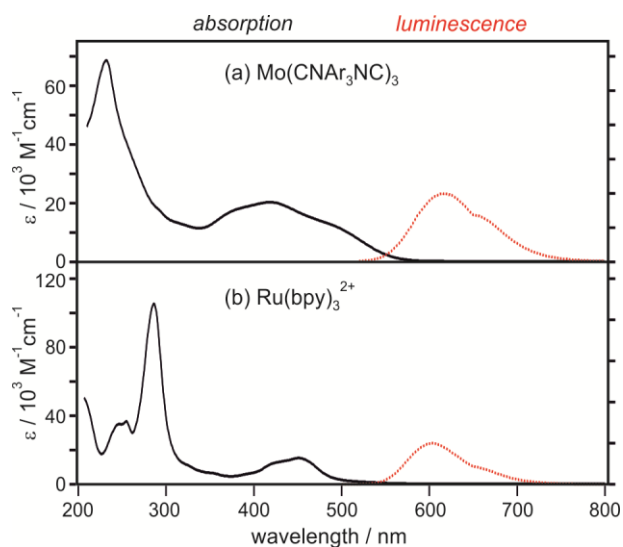
phenylpyridine) sensitizer, direct photo-reduction of acetophenone to its ketyl radical anion is unattainable.<sup>[16]</sup>



**Figure 2.** Chemical structures of the  $\text{Mo}(\text{CNAr}_3\text{NC})_3$  (a) and  $\text{Cr}(\text{CN}^{\text{tBu}}\text{Ar}_3\text{NC})_3$  complexes (b) along with space-filling representations of their X-ray crystal structures (c, d). H-atoms have been omitted.

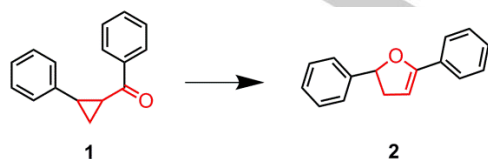
#### 4. A $\text{Mo}(0)$ isocyanide analogue of $\text{Ru}(\text{bpy})_3^{2+}$ for photoredox catalysis

As a 4d metal, molybdenum is inherently more substitution-labile than the 5d metal tungsten, and therefore it was thought that chelating diisocyanide ligands would increase chances of obtaining robust  $\text{Mo}(0)$  complexes. A *meta*-terphenyl moiety equipped with isocyanide groups at the two peripheral aryls was well suited for complexation of  $\text{Mo}(0)$ , resulting in the homoleptic tris(diisocyanide) complex  $\text{Mo}(\text{CNAr}_3\text{NC})_3$  that is not only isoelectronic to  $\text{Ru}(\text{bpy})_3^{2+}$ , but also structurally related (Figure 2a).<sup>[11b]</sup> The optical absorption and luminescence spectra of  $\text{Mo}(\text{CNAr}_3\text{NC})_3$  are remarkably similar to those of  $\text{Ru}(\text{bpy})_3^{2+}$  (Figure 3). The  $^3\text{MLCT}$  lifetime ( $\tau$ ) in de-aerated *n*-hexane is  $225 \text{ ns}$  and the luminescence quantum yield is  $0.045$ , coming reasonably close to the emission properties of  $\text{Ru}(\text{bpy})_3^{2+}$  in de-aerated  $\text{CH}_3\text{CN}$  ( $\tau = 855 \text{ ns}$ ,  $\phi = 0.095$ ).<sup>[7, 17]</sup> However, the  $\text{Mo}(0)$  center in  $\text{Mo}(\text{CNAr}_3\text{NC})_3$  is oxidized  $1.2 \text{ V}$  more easily than  $\text{Ru(II)}$  in  $\text{Ru}(\text{bpy})_3^{2+}$ , and for the emissive  $^3\text{MLCT}$  state a  $\text{Mo}(I/0)$  redox potential of  $-2.6 \text{ V}$  vs.  $\text{Fc}^+/\text{Fc}$  can be estimated. Indeed, photoinduced electron transfer from  $^3\text{MLCT}$ -excited  $\text{Mo}(\text{CNAr}_3\text{NC})_3$  to acetophenone was detectable by transient absorption spectroscopy.

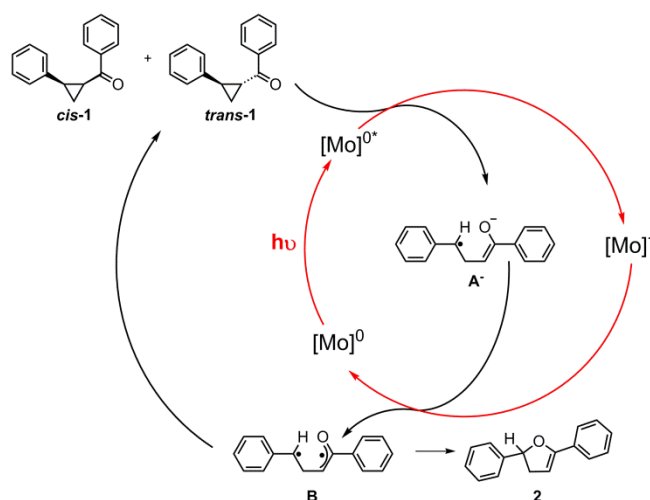


**Figure 3.** UV-Vis absorption (solid black lines) and luminescence spectra (dotted red traces) of (a)  $\text{Mo}(\text{CNAr}_3\text{NC})_3$  in THF and (b)  $\text{Ru}(\text{bpy})_3^{2+}$  in  $\text{CH}_3\text{CN}$ .

The very high reducing power of electronically excited  $\text{Mo}(\text{CNAr}_3\text{NC})_3$  was exploited for photoredox catalysis of the rearrangement reaction of an acyl cyclopropane to a 2,3-dihydrofuran (Scheme 3).<sup>[11b]</sup> Thermal rearrangement of this type usually requires high temperatures or activating groups, but with  $\text{Mo}(\text{CNAr}_3\text{NC})_3$  it can readily be performed at room temperature in benzene. Mechanistically, this can be considered an electron-catalyzed reaction in which the substrate is reduced by photoexcited  $\text{Mo}(\text{CNAr}_3\text{NC})_3$  to radical intermediate  $\text{A}^\cdot$  (Scheme 4), which is then re-oxidized by the  $\text{Mo}(\text{I})$  species to yield diradical B. The latter can either form the 2,3-dihydrofuran product or revert to the starting material, thereby leading to a mixture of *cis*- and *trans*-isomers. The pericyclic rearrangement in Scheme 3 was performed in 86% yield at 25 °C at a catalyst loading of 5%, corresponding to a turnover number (TON) of 17, but no optimization was performed.<sup>[11b]</sup> The  $\text{Ir}(\text{ppy})_3$  photoredox catalyst gave no turnover at all, because it is a weaker reductant.



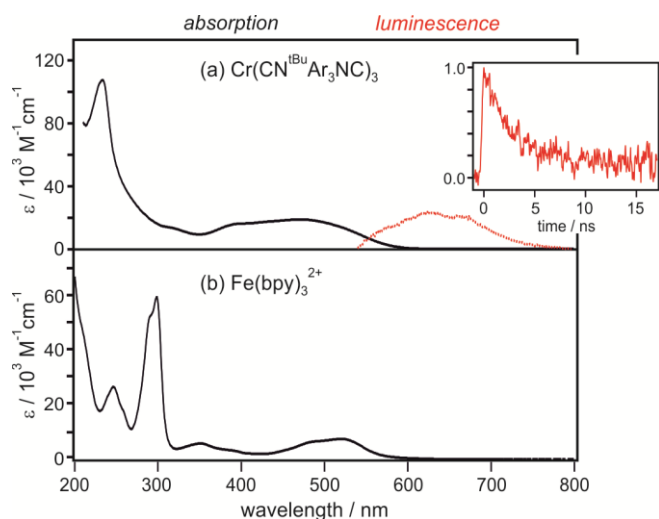
**Scheme 3.** Pericyclic rearrangement reaction performed by photoredox catalysis with  $\text{Mo}(\text{CNAr}_3\text{NC})_3$ . Reproduced with permission from ref. <sup>[11b]</sup>. Copyright 2016 Wiley-VCH Verlag GmbH & Co. KGaA.



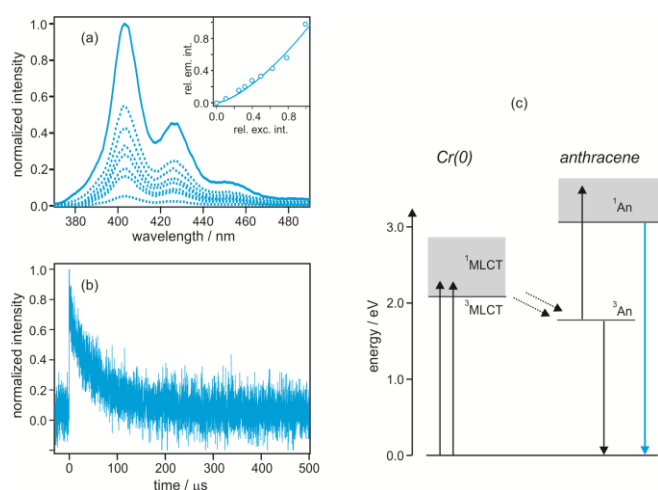
**Scheme 4.** Proposed mechanism for the electron-catalyzed rearrangement reaction from Scheme 3. Reproduced with permission from ref. <sup>[11b]</sup>. Copyright 2016 Wiley-VCH Verlag GmbH & Co. KGaA.

## 5. A luminescent Cr(0) isocyanide analogue of $\text{Fe}(\text{bpy})_3^{2+}$

In recent years, much progress on the photophysics of  $\text{Fe}(\text{II})$  complexes has been made.<sup>[5a, 5b, 18]</sup> New guiding principles for obtaining complexes with long-lived excited states have been developed, resulting in a current record <sup>3</sup>MLCT lifetime of 37 ps on  $\text{Al}_2\text{O}_3$  nanofilm.<sup>[6, 19]</sup> Many of these studies were motivated by the idea to replace  $\text{Ru}(\text{II})$  by  $\text{Fe}(\text{II})$  in dyes for solar cells.  $\text{Cr}(\text{0})$  is isoelectronic with  $\text{Fe}(\text{II})$ , and by using diisocyanide ligands it was anticipated that emissive  $\text{Cr}(\text{0})$  complexes could be obtained. With  $\text{CN}^{\text{tBu}}\text{Ar}_3\text{NC}$  as a ligand, this is indeed the case.<sup>[11a]</sup> This chelating agent is a sterically more demanding congener of the previously used  $\text{CNAr}_3\text{NC}$  ligand (Figure 2a/b), which shields the metal center more effectively from its chemical environment. This becomes directly visible when comparing space-filling representations of the crystal structures of  $\text{Mo}(\text{CNAr}_3\text{NC})_3$  and  $\text{Cr}(\text{CN}^{\text{tBu}}\text{Ar}_3\text{NC})_3$  (Figure 2c/d).<sup>[11a]</sup> The  $\text{Cr}(\text{CN}^{\text{tBu}}\text{Ar}_3\text{NC})_3$  complex exhibits quasi-reversible redox chemistry for all oxidation states ranging from  $\text{Cr}(\text{0})$  to  $\text{Cr}(\text{III})$ , and all potentials are shifted anodically by ca. 0.4 V compared to homoleptic  $\text{Cr}(\text{0})$  complexes with monodentate arylisocyanides.<sup>[11a]</sup> Presumably, this reflects a destabilization of the higher oxidation states in  $\text{Cr}(\text{CN}^{\text{tBu}}\text{Ar}_3\text{NC})_3$ , because the bite angle of the diisocyanide ligand becomes less favorable due to decreasing Cr-C bond distances.



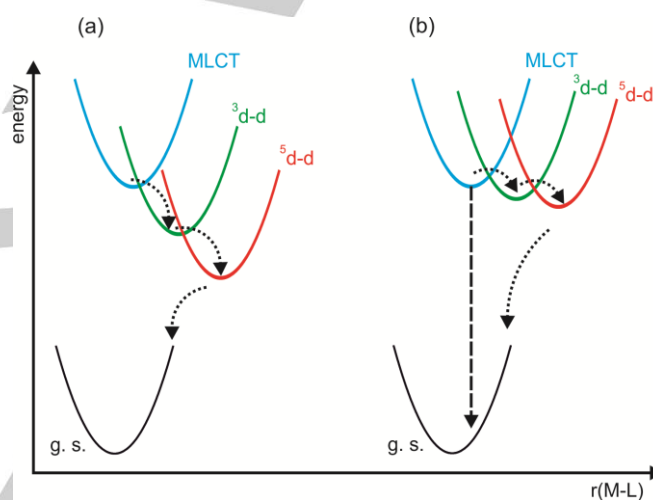
**Figure 4.** UV-Vis absorption (solid black lines) and luminescence spectra (dotted red trace) of (a)  $\text{Cr}(\text{CN}^{\text{tBu}}\text{Ar}_3\text{NC})_3$  in THF and (b)  $\text{Fe}(\text{bpy})_3^{2+}$  in  $\text{CH}_3\text{CN}$ . Inset: Luminescence decay of  $\text{Cr}(\text{CN}^{\text{tBu}}\text{Ar}_3\text{NC})_3$  at 630 nm in de-aerated THF, following excitation at 532 nm with laser pulses of  $\sim 30$  ps duration.



**Figure 5.** (a) Upconversion luminescence after triplet-triplet annihilation of anthracene sensitized by  $\text{Cr}(\text{CN}^{\text{tBu}}\text{Ar}_3\text{NC})_3$ . Inset: dependence of the relative upconversion luminescence intensity at 405 nm on the relative excitation intensity at 530 nm. (b) Decay of the upconversion luminescence intensity at 405 nm after excitation at 532 nm with pulses of  $\sim 10$  ns duration. (c) Energy-level scheme for the upconversion process.

The UV-Vis spectrum of  $\text{Cr}(\text{CN}^{\text{tBu}}\text{Ar}_3\text{NC})_3$  in THF is reminiscent of that of  $\text{Fe}(\text{bpy})_3^{2+}$  in  $\text{CH}_3\text{CN}$  (Figure 4) with MLCT absorption bands in the visible spectral range and ligand-centered  $\pi-\pi^*$  absorptions in the UV.<sup>[11a]</sup> Excitation at 500 nm induces weak luminescence ( $\phi \approx 10^{-5}$ ) attributable to MLCT emission. The transient absorption spectrum of the excited  $\text{Cr}(\text{CN}^{\text{tBu}}\text{Ar}_3\text{NC})_3$  complex shows a bleach of the MLCT absorption band between 400 and 580 nm, and this bleach recovers with a time constant identical to the luminescence lifetime. In de-aerated THF, the MLCT excited-state lifetime is 2.2 ns, whereas in toluene and *n*-

hexane somewhat shorter bi-exponential decays are observed, presumably due to some conformational heterogeneity. Thus, in de-aerated THF the MLCT lifetime (2.2 ns) is nearly two orders of magnitude longer than the current record excited-state lifetime of Fe(II) complexes on solid support (37 ps).<sup>[5a]</sup> The emissive MLCT state in  $\text{Cr}(\text{CN}^{\text{tBu}}\text{Ar}_3\text{NC})_3$  has triplet spin multiplicity, as becomes evident when excess anthracene is added to a dilute solution of this complex. Transient absorption spectroscopy then provides clear evidence for rapid population of the lowest triplet state on anthracene.<sup>[11a]</sup> Moreover, subsequent triplet-triplet annihilation between individual anthracene molecules leads to population of the fluorescent singlet excited state of anthracene, manifesting in upconversion luminescence at 430 nm following excitation at 532 nm (Figure 5). Some of this upconverted population re-feeds the MLCT manifold on the Cr(0) complex via Förster energy transfer, presumably due to favorable spectral overlaps and the comparatively high concentration of anthracene.



**Figure 6.** Potential energy diagram with some key electronic states involved in excited-state relaxation of  $3d^6$  metal complexes: (a) Fe(II) polypyridines; (b)  $\text{Cr}(\text{CN}^{\text{tBu}}\text{Ar}_3\text{NC})_3$ . Reproduced with permission from ref. <sup>[11a]</sup>. Copyright 2017 American Chemical Society.

However, the key finding is that  $\text{Cr}(\text{CN}^{\text{tBu}}\text{Ar}_3\text{NC})_3$  is an emissive analogue of non-luminescent  $\text{Fe}(\text{bpy})_3^{2+}$ , and in terms of  $^3\text{MLCT}$  lifetime it clearly outperforms currently known Fe(II) polypyridines, including recently developed NHC-based Fe(II) complexes.<sup>[5a, 6, 19a, 19b]</sup> The lowest  $^3\text{MLCT}$  states of Fe(II) polypyridines usually depopulate very rapidly via energetically lower-lying  $^3d-d$  and  $^5d-d$  states (Figure 6a), but in  $\text{Cr}(\text{CN}^{\text{tBu}}\text{Ar}_3\text{NC})_3$  the ligand field seems sufficiently strong to lead to a significant barrier associated with crossing into these non-emissive states (Figure 6b). The resulting  $^3\text{MLCT}$  lifetime of  $\text{Cr}(\text{CN}^{\text{tBu}}\text{Ar}_3\text{NC})_3$  should be long enough for efficient photo-injection of electrons into semiconductors of solar cells. Given the very high reducing power of photoexcited  $\text{Cr}(\text{CN}^{\text{tBu}}\text{Ar}_3\text{NC})_3$  ( $-2.4$  V vs.  $\text{Fc}^+/\text{Fc}$ ),<sup>[11a]</sup> semiconductors other than  $\text{TiO}_2$  can potentially be used to achieve good energy matching between

the sensitizer LUMO and the conduction band of the semiconductor.

In view of the fact that even  $\text{Fe}(\text{bpy})_3^{2+}$  has been amenable to photoredox catalysis,<sup>[20]</sup> this should also be possible with  $\text{Cr}(\text{CN}^{\text{tBu}}\text{Ar}_3\text{NC})_3$ .

## 6. Summary and outlook

With photoluminescence quantum yields approaching unity and luminescence lifetimes in the nano- to microsecond regime,<sup>[10b, 10c]</sup>  $\text{W}(0)$  arylisocyanides complexes are promising for application in luminescent devices. The emission color tunability seen for example for cyclometalated  $\text{Ir}(\text{III})$  complexes is missing yet,<sup>[21]</sup> and possibly this could be achieved with heteroleptic group 6  $d^6$  complexes. The use of two different types of ligands would potentially allow for relatively independent tuning of HOMO and LUMO energies, similarly to what is often possible for the abovementioned  $\text{Ir}(\text{III})$  complexes.<sup>[11]</sup>

The  $\text{Cr}(0)$ ,  $\text{Mo}(0)$  and  $\text{W}(0)$  complexes presented herein are among the strongest excited-state reductants that absorb visible light. For example, acetophenone with a reduction potential of  $-2.5$  V vs.  $\text{Fc}^+/\text{Fc}$  is readily converted to its ketyl radical anionic form by photoexcited  $\text{W}(0)$  and  $\text{Mo}(0)$  complexes.<sup>[10a, 11b]</sup> The high reducing power of the  $\text{Mo}(\text{CNAr}_3\text{NC})_3$  complex has been applied successfully for a thermodynamically demanding pericyclic rearrangement reaction,<sup>[11b]</sup> but other than that, photoredox catalysis with group 6  $d^6$  metal complexes is yet a wide open field. The use of these complexes will permit to perform redox reactions which are unattainable with commonly used precious-metal based photosensitizers such as  $\text{Ru}(\text{bpy})_3^{2+}$  or  $\text{Ir}(\text{ppy})_3$ .

Furthermore, strong photoreductants are of interest for more fundamental investigations of photoinduced electron transfer requiring high driving-forces, for example in rigid or frozen media. While it is relatively straightforward to initiate photoinduced electron transfer in fluid solution at room temperature, this can be very challenging in rigid and frozen media because outer-sphere reorganization is difficult and because activation barriers are more difficult to overcome.<sup>[22]</sup>

Every coin has two sides, and for group 6  $d^6$  metal complexes this means that their high reducing power in the MLCT-excited state makes them also susceptible to undesired oxidation in the electronic ground state. Current strategies to overcome this problem include the use of arylisocyanide ligands with bulky *ortho*-substituents and the development of chelating diisocyanides for the stabilization of the more substitution-labile  $\text{Mo}(0)$  and  $\text{Cr}(0)$  species.<sup>[9-11]</sup> The combination of the two strategies is very successful and has resulted in a  $\text{Cr}(0)$  complex with a record  $^3\text{MLCT}$  lifetime. In weakly coordinating solvents such as THF and *n*-hexane, these complexes are remarkably robust, albeit of course under de-aerated conditions.<sup>[11]</sup> As powders, the  $\text{Cr}(\text{CN}^{\text{tBu}}\text{Ar}_3\text{NC})_3$  and  $\text{Mo}(\text{CNAr}_3\text{NC})_3$  complexes can even be manipulated under air for short time periods.

Given the long-standing interest in replacing Ru by Fe in dyes for solar cells,<sup>[5a, 6]</sup> the observation that  $\text{Cr}(\text{CN}^{\text{tBu}}\text{Ar}_3\text{NC})_3$  is a luminescent analogue of  $\text{Fe}(\text{bpy})_3^{2+}$  is fundamentally interesting.

Future studies could therefore focus on grafting group 6  $d^6$  metal complexes on semiconductor surfaces and on exploring their application potential in dye-sensitized solar cells. Given the high reducing powers of  $\text{Cr}(0)$ ,  $\text{Mo}(0)$ , and  $\text{W}(0)$  arylisocyanides, it is possible that semiconductors other than  $\text{TiO}_2$  will turn out to be optimal for good energy matching between sensitizer LUMO and the conduction band of the semiconductor.

The bottom line is that group 6  $d^6$  arylisocyanide complexes are earth-abundant alternatives to precious metals for potential applications in luminescent devices, photoredox catalysis, and sensitizers for solar cells.

## Acknowledgements

Financial support by the Swiss National Science Foundation through grant numbers 200021\_156063/1 and 206021\_157687, as well as through the NCCR Molecular Systems Engineering is gratefully acknowledged.

**Keywords:** luminescence • electron transfer • photochemistry • UV-Vis spectroscopy • photocatalysis

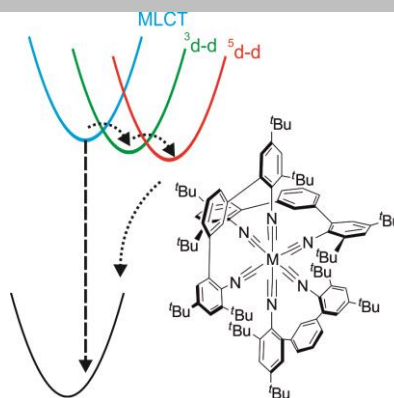
- [1] M. S. Lowry, S. Bernhard, *Chem. Eur. J.* **2006**, *12*, 7970-7977.
- [2] A. Hagfeldt, G. Boschloo, L. C. Sun, L. Kloo, H. Pettersson, *Chem. Rev.* **2010**, *110*, 6595-6663.
- [3] J. M. R. Narayanam, C. R. J. Stephenson, *Chem. Soc. Rev.* **2011**, *40*, 102-113.
- [4] H. B. Gray, A. W. Maverick, *Science* **1981**, *214*, 1201-1205.
- [5] a) Y. Z. Liu, P. Persson, V. Sundström, K. Wärnmark, *Acc. Chem. Res.* **2016**, *49*, 1477-1485; b) G. Aubock, M. Chergui, *Nature Chem.* **2015**, *7*, 629-633; c) J. K. McCusker, K. N. Walda, R. C. Dunn, J. D. Simon, D. Magde, D. N. Hendrickson, *J. Am. Chem. Soc.* **1993**, *115*, 298-307.
- [6] T. C. B. Harlang, Y. Z. Liu, O. Gordivska, L. A. Fredin, C. S. Ponseca, P. Huang, P. Chabera, K. S. Kjaer, H. Mateos, J. Uhlig, R. Lomoth, R. Wallenberg, S. Styring, P. Persson, V. Sundström, K. Wärnmark, *Nature Chem.* **2015**, *7*, 883-889.
- [7] J. V. Caspar, T. J. Meyer, *J. Am. Chem. Soc.* **1983**, *105*, 5583-5590.
- [8] a) W. Hieber, *Z. Naturforsch. B* **1950**, *5*, 129-130; b) F. Klages, K. Mönkemeyer, *Chem. Ber.* **1950**, *83*, 501-508.
- [9] a) 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; b) K. R. Mann, H. B. Gray, G. S. Hammond, *J. Am. Chem. Soc.* **1977**, *99*, 306-307.
- [10] 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. Kvapilova, 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.
- [11] a) L. A. Büldt, X. Guo, R. Vogel, A. Prescimone, O. S. Wenger, *J. Am. Chem. Soc.* **2017**, *139*, 985-992; b) L. A. Büldt, X. W. Guo, A. Prescimone, O. S. Wenger, *Angew. Chem. Int. Ed.* **2016**, *55*, 11247-11250.
- [12] Y. Yamamoto, *Coord. Chem. Rev.* **1980**, *32*, 193-233.
- [13] L. E. Shaw, C. H. Langford, *Coord. Chem. Rev.* **2002**, *230*, 165-169.
- [14] a) X. L. Xie, J. D. Simon, *J. Phys. Chem.* **1989**, *93*, 4401-4404; b) L. E. Shaw, C. H. Langford, *Inorg. Chem.* **2000**, *39*, 541-546; c) E. Maskova, A. Vlcek, *Inorg. Chim. Acta* **1996**, *242*, 17-23.

- 1 [15] a) A. E. Carpenter, G. W. Margulieux, M. D. Millard, C. E. Moore, N.  
2 Weidemann, A. L. Rheingold, J. S. Figueroa, *Angew. Chem. Int. Ed.*  
3 **2012**, *51*, 9412-9416; b) G. W. Margulieux, N. Weidemann, D. C. Lacy,  
4 C. E. Moore, A. L. Rheingold, J. S. Figueroa, *J. Am. Chem. Soc.* **2010**,  
5 *132*, 5033-5035.
- 6 [16] F. R. Petronijevic, M. Nappi, D. W. C. MacMillan, *J. Am. Chem. Soc.*  
7 **2013**, *135*, 18323-18326.
- 8 [17] K. Suzuki, A. Kobayashi, S. Kaneko, K. Takehira, T. Yoshihara, H.  
9 Ishida, Y. Shiina, S. Oishic, S. Tobita, *Phys. Chem. Chem. Phys.* **2009**,  
10 *11*, 9850-9860.
- 11 [18] a) L. L. Jamula, A. M. Brown, D. Guo, J. K. McCusker, *Inorg. Chem.*  
12 **2014**, *53*, 15-17; b) A. Hauser, C. Reber, *Struct. Bonding* **2016**, *172*,  
13 291-312.
- 14 [19] a) T. Duchanois, T. Etienne, C. Cebrian, L. Liu, A. Monari, M. Beley, X.  
15 Assfeld, S. Haacke, P. C. Gros, *Eur. J. Inorg. Chem.* **2015**, 2469-2477;  
16 b) L. Liu, T. Duchanois, T. Etienne, A. Monari, M. Beley, X. Assfeld, S.  
17 Haacke, P. C. Gros, *Phys. Chem. Chem. Phys.* **2016**, *18*, 12550-  
18 12556; c) S. G. Shepard, S. M. Fatur, A. K. Rappe, N. H. Damrauer, *J.*  
19 *Am. Chem. Soc.* **2016**, *138*, 2949-2952; d) P. Zimmer, P. Müller, L.  
20 Burkhardt, R. Schepper, A. Neuba, J. Steube, F. Dietrich, U. Flörke, S.  
21 Mangold, M. Gerhards, M. Bauer, *Eur. J. Inorg. Chem.* **2017**, doi:  
22 10.1002/ejic.201700064.
- 23 [20] A. Gualandi, M. Marchini, L. Mengozzi, M. Natali, M. Lucarini, P. Ceroni,  
24 P. G. Cozzi, *ACS Catal.* **2015**, *5*, 5927-5931.
- 25 [21] a) A. F. Henwood, E. Zysman-Colman, *Top. Curr. Chem.* **2016**, *374*; b)  
26 R. D. Costa, E. Orti, H. J. Bolink, F. Monti, G. Accorsi, N. Armadori,  
27 *Angew. Chem. Int. Ed.* **2012**, *51*, 8178-8211.
- 28 [22] a) M. R. Wasielewski, D. G. Johnson, W. A. Svec, K. M. Kersey, D. W.  
29 Minsek, *J. Am. Chem. Soc.* **1988**, *110*, 7219-7221; b) O. S. Wenger, B.  
30 S. Leigh, R. M. Villahermosa, H. B. Gray, J. R. Winkler, *Science* **2005**,  
31 *307*, 99-102; c) P. Y. Chen, T. J. Meyer, *Chem. Rev.* **1998**, *98*, 1439-  
32 1477.
- 33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65

## Entry for the Table of Contents

## MINIREVIEW

Group 6 d<sup>6</sup> metal complexes are earth-abundant alternatives to photoactive metal complexes made from precious metals such as Ru(II) or Ir(III). They are promising for applications in luminescent devices, photoredox catalysis, and dye-sensitized solar cells.



Laura A. Büldt, Oliver S. Wenger\*

Page No. – Page No.

**Cr(0), Mo(0) and W(0) isocyanide complexes as luminophores and photosensitizers with long-lived excited states**

1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65