JACS JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication

pubs.acs.org/JACS

Generation of Powerful Tungsten Reductants by Visible Light Excitation

Wesley Sattler,[†] Maraia E. Ener,[†] James D. Blakemore,[†] Aaron A. Rachford,*[,‡] Paul J. LaBeaume,[§] James W. Thackeray,[§] James F. Cameron,[§] Jay R. Winkler,[†] and Harry B. Gray*[,†]

[†]Beckman Institute, California Institute of Technology, Pasadena, California 91125, United States

[‡]The Dow Chemical Company, Analytical Sciences, 1897 Building, Midland, Michigan 48667, United States

[§]The Dow Chemical Company, Dow Electronic Materials, 455 Forest Street, Marlborough, Massachusetts 01752, United States

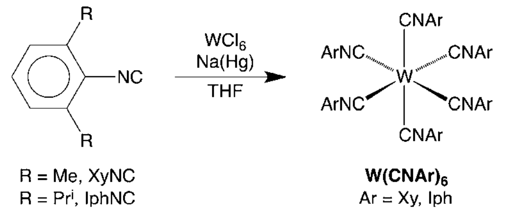
Ⓢ *Supporting Information*

ABSTRACT: The homoleptic arylisocyanide tungsten complexes, $W(CNXy)_6$ and $W(CNIph)_6$ (Xy = 2,6-dimethylphenyl, Iph = 2,6-diisopropylphenyl), display intense metal to ligand charge transfer (MLCT) absorptions in the visible region (400−550 nm). MLCT emission ($\lambda_{max} \approx 580$ nm) in tetrahydrofuran (THF) solution at rt is observed for $W(CNXy)_6$ and $W(CNIph)_6$ with lifetimes of 17 and 73 ns, respectively. Diffusion-controlled energy transfer from electronically excited $W(CNIph)_6$ (*W) to the lowest energy triplet excited state of anthracene (anth) is the dominant quenching pathway in THF solution. Introduction of tetrabutylammonium hexafluorophosphate, $[Bu^n{}_4N][PF_6]$, to the THF solution promotes formation of electron transfer (ET) quenching products, $[W(CNIph)_6]^+$ and $[anth]^{\bullet-}$. ET from *W to benzophenone and cobalticenium also is observed in $[Bu^n{}_4N][PF_6]$/THF solutions. The estimated reduction potential for the $[W(CNIph)_6]^+$/*W couple is −2.8 V vs $Cp_2Fe^{+/0}$, establishing $W(CNIph)_6$ as one of the most powerful photoreductants that has been generated with visible light.

The development of photosensitizers that can serve as powerful photoreductants is of great interest, as such reagents are used in many organic transformations and as key components in devices for the production of solar fuels.[1−3] Very promising photosensitizers are the hexakis phenylisocyanide complexes of the group six transition metals,[4,5] which absorb strongly in the visible region and emit with lifetimes (τ) ranging from ps to ns, according to Cr < Mo < W.[5] One problem is that ligand loss competes with excited state redox decay pathways, most especially in Cr(0) and Mo(0) complexes. Less prone to photosubstitution is the tungsten complex containing a bulkier[6] ligand, IphNC (IphNC = 2,6-diisopropylphenyl isocyanide), whose photosubstitution quantum yield ($\phi = 0.0003$) is much lower than that ($\phi = 0.011$) for $W(CNPh)_6$ in pyridine solution.[5] We have now extended this work on W(0) photosensitizers to include exploration of the rich photoredox chemistry of $W(CNAr)_6$ (Ar = Xy and Iph, Xy = 2,6-dimethylphenyl) complexes.

Methods for preparing M(0) isocyanide complexes[7] include:[8] (*i*) substitution of isocyanides in metal carbonyls;[9] (*ii*) substitution for other ligands,[10] (*e.g.*, acetate, acetonitrile) where excess isocyanide can also act as a reducing agent;[11] and (*iii*) reduction of metal halides by metallic reducing agents (*e.g.*, Na(Hg), Mg) in the presence of free isocyanide.[4,12] We obtained red, crystalline $W(CNAr)_6$ by Na(Hg) reduction of WCl_6 in the presence of arylisocyanide in THF (Scheme 1).[13]

Scheme 1



While several homoleptic $W(CNAr)_6$ complexes are known,[4,5,12] inspection of the Cambridge Structural Database[13] suggests that only $W(CNXy)_6$ has been structurally characterized.[14,15] We determined the structure of $W(CNIph)_6$[16] by single-crystal X-ray diffraction (Figure 1) from large red crystals

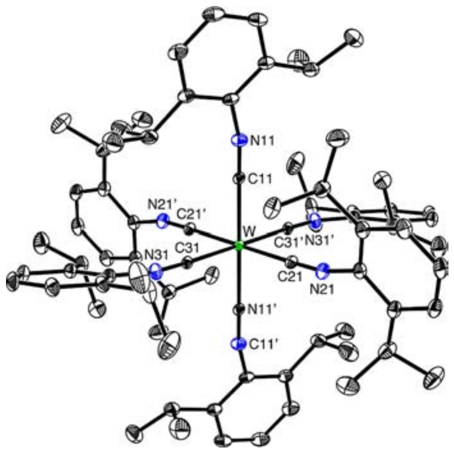


Figure 1. Molecular structure of $W(CNIph)_6$ (H-atoms omitted for clarity).

Received: May 10, 2013
Published: July 15, 2013

dx.doi.org/10.1021/ja4047119 | *J. Am. Chem. Soc.* 2013, 135, 10614−10617

of W(CNIph)$_6$ obtained by slow evaporation from benzene (triclinic, space group $P\bar{1}$, with two benzene molecules per unit cell). The average W−C and WC−N bond lengths are 2.062 and 1.176 Å, respectively, with an average WC−N−Iph angle of 164.4°.

The solid-state IR spectrum of W(CNIph)$_6$ features a single, broad CN stretch at 1944 cm^{-1}, which is 10 cm^{-1} higher than the corresponding CN stretching frequency for W(CNXy)$_6$.

Both W(CNXy)$_6$ and W(CNIph)$_6$ absorb strongly between 400 and 550 nm (Figure 2). Interestingly, the lowest energy absorption maximum of W(CNIph)$_6$ (ε_{465} = 9.09 × 10^4 M^{-1} cm^{-1}) is substantially more intense than that of W(CNXy)$_6$ (ε_{455} = 6.04 × 10^4 M^{-1} cm^{-1}), a finding that could be related to differences in the orientation of the π-systems on the isocyanide ligands. Specifically, the *trans* XyNC ligands of W(CNXy)$_6$ are approximately orthogonal to each other,[14] while the *trans* IphNC ligands of W(CNIph)$_6$ are roughly coplanar. Both complexes are luminescent, emitting yellow-to-red light with maxima at *ca.* 580 nm (Figure 2). The energy of the E_{00} transition is estimated to be 18 350 cm^{-1} above the ground state, as judged by the 77 K emission spectrum (Supporting Information (SI), Figure S3). The lifetime of electronically excited W(CNXy)$_6$, *W(CNXy)$_6$, is *ca.* 17 ns in THF solution at rt, whereas that of *W(CNIph)$_6$ (*W) is *ca.* 73 ns under the same conditions (SI, Figure S4). In accord with previous literature reports, we suggest that the isopropyl groups of the IphNC ligand provide greater steric protection of the metal center than the methyl groups of the XyNC ligand, disfavoring excited state decay that would occur by collisions of the metal center with solvent molecules.[5]

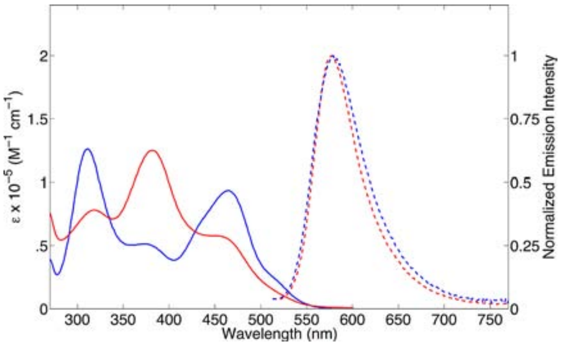


Figure 2. Absorption and emission spectra of W(CNXy)$_6$ (red) and W(CNIph)$_6$ (blue) in THF solutions.

As W(CNIph)$_6$ is relatively robust, we investigated its electrochemistry[11,17] and photochemistry in more depth; importantly, we have found that this W(0) complex is among the most powerful photoreductants generated with visible light. Cyclic voltammograms of W(CNIph)$_6$ at a basal-plane graphite electrode (electrode area = 0.09 cm^2) in a 0.1 M THF solution of [Bu$^n_4$N][PF$_6$] exhibit reversible waves at $E_{1/2}$ = −0.53(2) V (all potentials are reported relative to ferricenium/ferrocene, Cp$_2$Fe$^{+/0}$) assigned to the W(+1/0) couple (Figure 3, top). This couple exhibits a scan rate dependence consistent with a diffusional process (SI, Figures S7 and S8). Additional oxidation events ($E_{p,a}$ = 0.42(3) V and 0.72(3) V, $E_{p,a}$ = anodic peak potential) are only partially reversible at a scan rate of 100 mV/s (reductions occur at $E_{p,c}$ = 0.45(3) and −1.93(3) V, $E_{p,c}$ = cathodic peak potential) (Figure 3, bottom). No sign of the W(0/−1) couple was observed at E > −2.5 V.

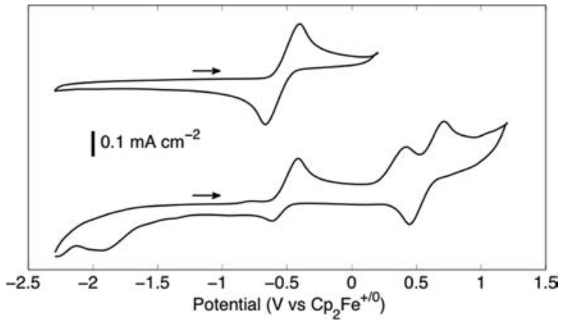
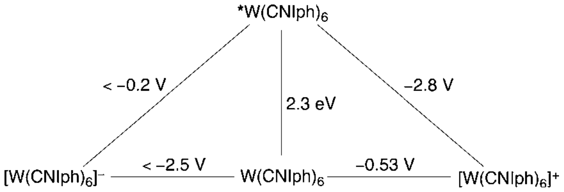


Figure 3. Cyclic voltammograms of W(CNIph)$_6$ (*ca.* 1 mM) in THF with 0.1 M [Bu$^n_4$N][PF$_6$] supporting electrolyte: scan rate 100 mV/s.

By performing a controlled-potential electrolysis at −0.15 V in a spectroelectrochemical cell, we have obtained a rough estimate for the absorption spectrum of [W(CNIph)$_6$]$^+$ (SI, Figure S9), which also can be formed by ET from *W to an acceptor. However, the spectrum obtained by the controlled-potential electrolysis is slightly different from that obtained by photochemical generation of [W(CNIph)$_6$]$^+$; we believe that decomposition of [W(CNIph)$_6$]$^+$ could occur during the electrolysis, as this happens on a much longer time scale (many minutes) compared to the photochemistry (<10 ms, *vide infra*).

These electrochemical and photophysical data suggest that *W is an extremely powerful reductant, with an estimated potential of −2.80(4) V (Scheme 2).[18] For comparison, data for inorganic photosensitizers that have been used for reductions are set out in Table 1.

Scheme 2



We have studied the reactions of *W with anthracene (anth), benzophenone, and cobalticenium (Cp$_2$Co$^+$). Following excitation of W(CNIph)$_6$, transient absorption (TA) spectroscopy was used to characterize the reaction products. For anth$^{0/-1}$ in glyme, $E_{1/2}$ = −2.47 V,[38,19] so we estimate that the driving force (−Δ$G°$) for its reduction by *W is 0.3 eV. Quenching of *W ($\lambda_{\text{excitation}}$ = 488 nm) by anth is diffusion controlled (Stern−Volmer analysis, k_q = 1.1 × 10^{10} M^{-1} s^{-1}, SI, Figure S10). However, TA spectroscopy clearly demonstrates that the photoproducts are primarily due to excitation energy transfer (EET) and not ET (Figure 4, top and inset).[20,11] This outcome is not unexpected, as the lowest triplet excited state of anth, ^{3}anth, is 14,850 cm^{-1} above its ground state (Δ$G°_{\text{EET}}$ ≈ −0.5 eV).[21] TA spectra recorded after excitation of W(CNIph)$_6$ in the presence of anth (>10 mM) exhibit large absorbance increases at 400 and 424 nm (Figure 4), consistent with production of ^{3}anth.[22,23] A small TA signal (negative ΔOD with a peak around 460−470 nm, and increased ΔOD peaking at 390 nm) is attributable to the production of [W(CNIph)$_6$]$^+$. The decay kinetics of ^{3}anth, monitored at *ca.* 424 nm, are dominated by a second-order reaction, consistent with a prior report.[24]

Table 1. Selected Inorganic Photosensitizers

sensitizer (D)	$E°(D^+/D)$, (V)[a]	E_{00} (eV)	τ[b]	$E°(D^+/{}^*D)$ (V)[a]	solvent	reference
$[(PNP)Cu]_2$[c]	−0.55	2.6	10.2 μs	−3.2	CH_2Cl_2[d]	27
$W(CNIph)_6$	−0.53	2.3	73 ns	−2.8	THF	this work
$[Ir(\mu\text{-}Pz)(COD)]_2$[e]	−0.15	2.06	250 ns	−2.21	CH_3CN	28
fac-$Ir(ppy)_3$[f]	+0.37	2.50	1.9 μs	−2.10	CH_3CN	29, 30
ZnTPP[g]	+0.39	2.05 (singlet)	2.7 ns	−1.66	CH_3CN	31, 32
		1.59 (triplet)	1200 μs	−1.20		
$[Cu(dmp)_2]^{+}$[h]	+0.53[i]	2.04	85 ns	−1.51	CH_2Cl_2	33, 34
$[Ru(bpy)_3]^{2+}$[j]	+0.89	2.12	855 ns	−1.23	CH_3CN	35, 36
fac-$[Re(CO)_3(bpy)(py)]^{+}$[k]	+1.41	2.38	211 ns	−0.97	CH_3CN	37

[a] Data reported at rt; redox potentials are reported vs $Cp_2Fe^{+/0}$. Literature values vs the saturated calomel electrode (SCE) are corrected according to ref 38 (i.e., in CH_3CN, $Cp_2Fe^{+/0}$ is +0.4 V vs SCE; CH_2Cl_2, $Cp_2Fe^{+/0}$ is +0.46 V vs SCE). [b] Data pertaining to the emitting state. [c] PNP^- = bis(2-(diisobutylphosphino)phenyl)amide. [d] Electrochemistry was performed in CH_2Cl_2, while the photophysics were studied in THF and cyclohexane. [e] μ-Pz = bridging pyrazolyl, COD = 1,5-cylooctadiene. [f] ppy = (2-pyridinyl-κN)phenyl-κ²C. [g] TPP = tetraphenylporphyrin. [h] dmp = 2,9-dimethyl-1,10-phenanthroline. [i] A potential of +0.64 V vs $Ag/AgNO_3$ in 0.1 M $[Bu^n_4N][PF_6]/CH_2Cl_2$ was measured for the (D^+/D) redox couple. The $Ag/AgNO_3$ redox couple was found to be +0.35 V vs SCE using ferrocene as an internal standard (see ref 34). [j] bpy = 2,2′-bipyridine. [k] py = pyridine.

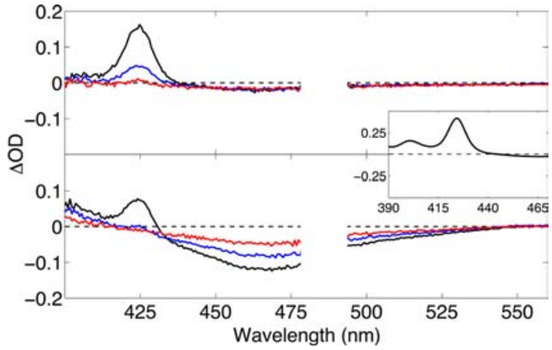


Figure 4. Transient difference spectra for quenching of *W by anthracene (*ca.* 35 mM) in THF without (top) and with (bottom) 0.1 M $[Bu^n_4N][PF_6]$ at selected time delays after laser excitation (black = 20 μs, blue = 100 μs, and red = 300 μs). Inset: Transient difference spectra at 50 ns in the absence of $[Bu^n_4N][PF_6]$. $\lambda_{excitation}$ = 488 nm. The spectra from *ca.* 478 to 493 nm are not shown due to the use of a notch filter to protect the detector from scattered laser light.

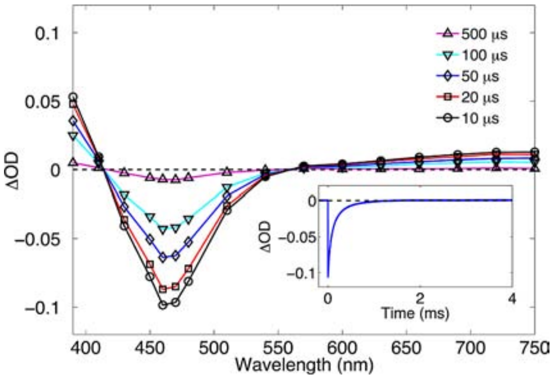


Figure 5. Transient difference spectra (points taken from single-wavelength data) for quenching of *W by benzophenone (*ca.* 50 mM) in THF with 0.1 M $[Bu^n_4N][PF_6]$ at selected time delays after laser excitation. Inset: Single-wavelength TA (460 nm) for the decay of $[W(CNIph)_6]^+$. $\lambda_{excitation}$ = 488 nm.

We suggest that the lack of observable ET reactivity between *W and anth is due to limited cage escape.[20] Addition of electrolyte ($[Bu^n_4N][PF_6]$, 0.1 M in THF) promotes[25] ET from *W to anth, as observed by TA spectroscopy (Figure 4, bottom).[26] The lifetime of *W in the presence of $[Bu^n_4N][PF_6]$ is unaffected, and Stern−Volmer analysis confirms that quenching by anth is still diffusion-controlled (1.0×10^{10} M^{-1} s^{-1}, SI, Figure S11). These experiments illustrate that the ratio of EET to ET quenching products can be tuned by variations in the concentration of $[Bu^n_4N][PF_6]$ in THF.

ET from *W to benzophenone in THF ($E_{1/2}$ = −2.30 V)[38] should be the favored reaction channel ($\Delta G°_{ET} \approx -0.5$ eV), since EET is energetically unfavorable ($\Delta G°_{EET} \approx +0.7$ eV, lowest excited state energy of ~24 000 cm^{-1}).[39] Stern−Volmer analysis of *W ($\lambda_{excitation}$ = 488 nm) quenching by benzophenone in THF solution (with and without $[Bu^n_4N][PF_6]$) confirms that the quenching reaction is diffusion-controlled ($k_q = 1.0 \times 10^{10}$ M^{-1} s^{-1}, SI, Figure S12). TA spectra obtained following excitation are consistent with the production of $[W(CNIph)_6]^+$ and $[\text{benzophenone}]^{\bullet-}$, indicated by positive TA between *ca.* 600 and 800 nm (Figure 5).[40] The ET reaction between $[W(CNIph)_6]^+$ and $[\text{benzophenone}]^{\bullet-}$ proceeds on the millisecond time scale with concentration dependent kinetics indicative of a second-order process (Figure 5, inset; SI, Figures S14−S16).

We also investigated the ET quenching of *W with Cp_2Co^+ ($Cp_2Co^{+/0}$ in THF, $E_{1/2}$ = −1.35 V).[38,41] As expected, ET is diffusion-controlled (SI, Figure S13) and produces $[W(CNIph)_6]^+$ and cobaltocene (Cp_2Co), as detected by TA spectroscopy. The second-order back ET reaction also is diffusion-controlled (*ca.* 2×10^{10} M^{-1} s^{-1}, SI, Figures S17−S19). It is of special interest that $W(CNIph)_6$ can generate Cp_2Co efficiently upon visible light excitation, as the latter has been used as a homogeneous reducing agent for the reduction of protons to dihydrogen[42] and dinitrogen to ammonia.[43]

Interest in photosensitizers continues to be driven by the desire to carry out challenging inorganic and organic reactions by exposure to visible light. Our work confirms that arylisocyanide metal complexes are among the most powerful photoreductants to date. The lowest energy excited states of these molecules can potentially be active in a very large range of ET reaction cycles.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details and crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

hbgray@caltech.edu; raaaron@dow.com

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Dedicated to the memory of Nicholas J. Turro. The authors thank Jeffrey J. Warren, James R. McKone, and Oliver S. Shafaat for helpful discussions. Our work is supported by the National Science Foundation Center for Chemical Innovation in Solar Fuels (CHE-0802907); CCI postdoctoral fellowship to W.S.; and the Dow Chemical Company through the university partnership program (Agreement No. 227027AH).

REFERENCES

(1) (a) Gray, H. B.; Maverick, A. W. *Science* **1981**, *214*, 1201−1205. (b) Cano-Yelo, H.; Deronzier, A. *J. Chem. Soc., Perkin Trans. 2* **1984**, 1093−1098. (c) Nicewicz, D. A.; MacMillan, D. W. C. *Science* **2008**, *322*, 77−80. (d) Narayanam, J. M. R.; Stephenson, C. R. J. *Chem. Soc. Rev.* **2011**, *40*, 102−113. (e) Du, J.; Espelt, L. R.; Guzei, I. A.; Yoon, T. P. *Chem. Sci.* **2011**, *2*, 2115−2119. (f) Tucker, J. W.; Stephenson, C. R. J. *J. Org. Chem.* **2012**, *77*, 1617−1622.

(2) Concepcion, J. J.; House, R. L.; Papanikolas, J. M.; Meyer, T. J. *Proc. Natl. Acad. Sci. U.S.A.* **2012**, *109*, 15560−15564.

(3) (a) Creutz, S. E.; Lotito, K. J.; Fu, G. C.; Peters, J. C. *Science* **2012**, *338*, 647−651. (b) Bissember, A. C.; Lundgren, R. J.; Creutz, S. E.; Peters, J. C.; Fu, G. C. *Angew. Chem., Int. Ed. Engl.* **2013**, *52*, 5129−5133.

(4) Mann, K. R.; Cimolino, M.; Geoffroy, G. L.; Hammond, G. S.; Orio, A. A.; Albertin, G.; Gray, H. B. *Inorg. Chim. Acta* **1976**, *16*, 97−101.

(5) Mann, K. R.; Gray, H. B.; Hammond, G. S. *J. Am. Chem. Soc.* **1977**, *99*, 306−307.

(6) (a) Stewart, M. A.; Moore, C. E.; Ditri, T. B.; Labios, L. A.; Rheingold, A. L.; Figueroa, J. S. *Chem. Commun.* **2011**, *47*, 406−408. (b) Labios, L. A.; Millard, M. D.; Rheingold, A. L.; Figueroa, J. S. *J. Am. Chem. Soc.* **2009**, *131*, 11318−11319. (c) Ditri, T. B.; Fox, B. J.; Moore, C. E.; Rheingold, A. L.; Figueroa, J. S. *Inorg. Chem.* **2009**, *48*, 8362−8375.

(7) Yamamoto, Y. *Coord. Chem. Rev.* **1980**, *32*, 193−233.

(8) (a) Fehlhammer, W. P.; Mayr, A. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 757−758. (b) Luart, D.; Salaün, J.-Y.; Patinec, V.; Rumin, R.; des Abbayes, H. *Inorg. Chim. Acta* **2003**, *350*, 656−660. (c) Dombek, B. D.; Angelici, R. J. *J. Am. Chem. Soc.* **1973**, *95*, 7516−7518. (d) Sattler, W.; Parkin, G. *Chem. Commun.* **2009**, 7566−7568.

(9) Coville, N. J.; Albers, M. O. *Inorg. Chim. Acta* **1982**, *65*, L7−L8.

(10) Ditri, T. B.; Moore, C. E.; Rheingold, A. L.; Figueroa, J. S. *Inorg. Chem.* **2011**, *50*, 10448−10459.

(11) Klendworth, D. D.; Welters, W. W., III; Walton, R. A. *Organometallics* **1982**, *1*, 336−343.

(12) Yamamoto, Y.; Yamazaki, H. *J. Organomet. Chem.* **1985**, *282*, 191−200.

(13) Cambridge Structural Database (Version 5.34). Search performed on April 17, 2013. 3D Search and Research Using the Cambridge Structural Database. Allen, F. H.; Kennard, O. *Chemical Design Automation News* **1993**, *8* (1), 1−31−37.

(14) Lockwood, M. A.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1997**, *16*, 3574−3575.

(15) CSD deposition code: NEVSIQ.

(16) The structure of $\mathrm{Cr(CNIph)_6}$ has been determined: Anderson, K. A.; Scott, B.; Wherland, S.; Willett, R. D. *Acta Crystallogr.* **1991**, *C47*, 2337−2339.

(17) Bohling, D. A.; Mann, K. R.; Enger, S.; Gennett, T.; Weaver, M. J.; Walton, R. A. *Inorg. Chim. Acta* **1985**, *97*, L51−L53.

(18) Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; Von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85−277.

(19) Dessy, R. E.; King, R. B.; Waldrop, M. *J. Am. Chem. Soc.* **1966**, *88*, 5112−5117.

(20) Kavarnos, G. J.; Turro, N. J. *Chem. Rev.* **1986**, *86*, 401−449.

(21) Kellogg, R. E. *J. Chem. Phys.* **1966**, *44*, 411−412.

(22) Porter, G.; Windsor, M. W. *J. Chem. Phys.* **1953**, *21*, 2088−2089.

(23) Melhuish, W. H.; Hardwick, R. *Trans. Faraday Soc.* **1962**, *58*, 1908−1911.

(24) Jackson, G.; Livingston, R. *J. Chem. Phys.* **1961**, *35*, 2182−2186.

(25) (a) Mizuno, K.; Ichinose, N.; Tamai, T.; Otsuji, Y. *Tet. Lett.* **1985**, *26*, 5823−5826. (b) Goodson, B.; Schuster, G. B. *Tet. Lett.* **1986**, *27*, 3123−3126. (c) Ruiz, J.; Lacoste, M.; Astruc, D. *J. Chem. Soc., Chem. Commun.* **1989**, 813−814. (d) Borsarelli, C. D.; Chesta, C. A.; Montejano, H. A.; Zanini, G. P.; Previtali, C. M.; Cosa, J. J. *J. Braz. Chem. Soc.* **1995**, *6*, 145−154.

(26) (a) Cox, G. S.; Whitten, D. G.; Giannotti, C. *Chem. Phys. Lett.* **1979**, *67*, 511−515. (b) Eriksen, J.; Foote, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 6083−6088.

(27) Harkins, S. B.; Peters, J. C. *J. Am. Chem. Soc.* **2005**, *127*, 2030−2031.

(28) Marshall, J. L.; Stobart, S. R.; Gray, H. B. *J. Am. Chem. Soc.* **1984**, *106*, 3027−3029.

(29) King, K. A.; Spellane, P. J.; Watts, R. J. *J. Am. Chem. Soc.* **1985**, *107*, 1431−1432.

(30) Flamigni, L.; Barbieri, A.; Sabatini, C.; Ventura, B.; Barigelletti, F. *Top. Curr. Chem.* **2007**, *281*, 143−203.

(31) Darwent, J. R.; Douglas, P.; Harriman, A.; Porter, G.; Richoux, M.-C. *Coord. Chem. Rev.* **1982**, *44*, 83−126.

(32) Aoki, K.; Goshima, T.; Kozuka, Y.; Kawamori, Y.; Ono, N.; Hisaeda, Y.; Takagi, H. D.; Inamo, M. *Dalton Trans.* **2009**, 119−125.

(33) McMillin, D. R.; Buckner, M. T.; Ahn, B. T. *Inorg. Chem.* **1977**, *16*, 943−945.

(34) Ruthkosky, M.; Castellano, F. N.; Meyer, G. J. *Inorg. Chem.* **1996**, *35*, 6406−6412.

(35) Caspar, J. V.; Meyer, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 5583−5590.

(36) Kalyanasundaram, K. *Coord. Chem. Rev.* **1982**, *46*, 159−244.

(37) Schanze, K. S.; MacQueen, D. B.; Perkins, T. A.; Cabana, L. A. *Coord. Chem. Rev.* **1993**, *122*, 63−89.

(38) Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 877−910.

(39) (a) Gilmore, E. H.; Gibson, G. E.; McClure, D. S. *J. Chem. Phys.* **1952**, *20*, 829−836. (b) Turro, N. J. *Molecular Photochemistry*; W. A. Benjamin: New York, 1967.

(40) Pedersen, S. U.; Christensen, T. B.; Thomasen, T.; Daasbjerg, K. *J. Electroanal. Chem.* **1998**, *454*, 123−143.

(41) The reduction potential of $\mathrm{Cp_2Co^{+/0}}$ was measured in 0.1 M $[\mathrm{Bu}^n{}_4\mathrm{N}][\mathrm{PF_6}]$ THF solution with $\mathrm{Cp_2Fe}$ as an internal standard using a basal-plane graphite electrode.

(42) Koelle, U.; Infelta, P. P.; Grätzel, M. *Inorg. Chem.* **1988**, *27*, 879−883.

(43) Arashiba, K.; Miyake, Y.; Nishibayashi, Y. *Nat. Chem.* **2011**, *3*, 120−125.