Inorg. Chem. **2009**, *48*, 1796−1798

Inorganic Chemistry
Communication

Synthesis of Fluorinated ReCl(4,4′-R_2-2,2′-bipyridine)$(CO)_3$ Complexes and Their Photophysical Characterization in CH_3CN and Supercritical CO_2

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Received October 14, 2008

Two new CO_2-soluble rhenium(I) bipyridine complexes bearing the fluorinated alkyl ligands 4,4′-$(C_6F_{13}CH_2CH_2CH_2)_2$-2,2′-bipyridine (**1a**), and 4,4′-$(C_8F_{17}CH_2CH_2CH_2)_2$-2,2′-bipyridine (**1b**) have been prepared and their photophysical properties investigated in CH_3CN and supercritical CO_2. Electrochemical and spectroscopic characterization of these complexes in CH_3CN suggests that the three methylene units effectively insulate the bipyridyl rings and the rhenium center from the electron-withdrawing effect of the fluorinated alkyl chains. Reductive quenching of the metal-to-ligand charge-transfer excited states with triethylamine reveals quenching rate constants in supercritical CO_2 that are only 6 times slower than those in CH_3CN.

Photochemical CO_2 reduction using tricarbonylrhenium(I) complexes with 2,2′-bipyridine (bpy) or a similar ligand has grown into an intense area of research, in large part because of the demand for renewable alternative fuel sources.[1,2] In particular, the *fac*-ReX(bpy)$(CO)_3^n$ family of complexes ($n = 0$, X = Cl^-, Br^-; $n = +1$, X = PR_3) have been demonstrated to catalyze the reduction of CO_2 to CO under near-UV irradiation in *N*,*N*-dimethylformamide (DMF) in the presence of a sacrificial electron donor such as triethanolamine.[1,3−9] While the quantum yield for formation of CO has been reported to be as high as 0.59,[10] the turnover frequency of the catalyst is still too low for efficient photocatalytic conversion of CO_2.

Photoexcitation within the metal-to-ligand charge-transfer (MLCT) absorption band of the $Re^ICl(bpy)(CO)_3$ complex, followed by reductive quenching with amine and Cl^- loss, generates a $17e^-$ metal-based radical species [i.e., Re(bpy)$(CO)_3$], which is often proposed as a key catalytic species. Kinetic studies indicate that loss of Cl^- is slow, as is the reaction with CO_2 in ordinary organic solvents such as DMF, tetrahydrofuran, and CH_3CN because the metal-based radical forms a more stable solvated $18e^-$ ligand-based radical species, Re$(bpy^{\bullet-})(CO)_3$(solv).[11] Experimental and theoretical studies[11,12] have shown that solvent coordination to the Re(bpy)$(CO)_3$ fragment inhibits rapid coordination of CO_2 ($k = 0.003$ s^{-1} under 0.8 atm of CO_2) while also inhibiting Re−Re bond formation in the absence of CO_2 (i.e., 8 orders of magnitude slower when compared to $Re(CO)_5$). While Re(bpy)$(CO)_3(CO_2)$ or Re(dmb)$(CO)_3(CO_2)$ (dmb = 4,4′-dimethyl-2,2′-bipyridine) could not be observed using spectroscopic methods, the CO_2-bridged dimer $(CO)_3$(dmb)$Re^{13}C$(O)ORe(dmb)$(CO)_3$ was detected by ^1H and ^{13}C NMR, and this intermediate was shown to decay with a first-order dependence on $[CO_2]$ to produce CO.[11] Therefore, the low pressures of CO_2 that are typically used when studying these reactions in organic solvents contribute to the extremely slow CO_2 reduction.

In view of the above considerations, we decided to investigate the photocatalytic reduction of CO_2 in supercritical CO_2 ($scCO_2$). The first step toward this goal, reported herein, involved the synthesis and photophysical characterization of suitably substituted rhenium(I) complexes that can

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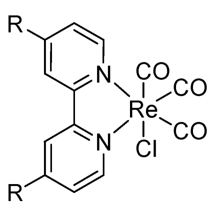
(1) Fujita, E.; Brunschwig, B. S. Homogeneous Redox Catalysis in CO_2 Fixation. In *Electron Transfer in Chemistry*; Balzani, V., Ed.; Wiley-VCH: New York, 2001; Vol. *4*, pp 88−126.
(2) Arakawa, H.; Aresta, M.; Armor, J. N.; Barteau, M. A.; Beckman, E. J.; Bell, A. T.; Bercaw, J. E.; Creutz, C.; Dinjus, E.; Dixon, D. A.; Domen, K.; DuBois, D. L.; Eckert, J.; Fujita, E.; Gibson, D. H.; Goddard, W. A.; Goodman, D. W.; Keller, J.; Kubas, G. J.; Kung, H. H.; Lyons, J. E.; Manzer, L. E.; Marks, T. J.; Morokuma, K.; Nicholas, K. M.; Periana, R.; Que, L.; Rostrup-Nielson, J.; Sachtler, W. M. H.; Schmidt, L. D.; Sen, A.; Somorjai, G. A.; Stair, P. C.; Stults, B. R.; Tumas, W. *Chem. Rev.* **2001**, *101*, 953–996.
(3) Koike, K.; Hori, H.; Ishizuka, M.; Westwell, J. R.; Takeuchi, K.; Ibusuki, T.; Enjouji, K.; Konno, H.; Sakamoto, K.; Ishitani, O. *Organometallics* **1997**, *16*, 5724–5729.
(4) Hori, H.; Johnson, F. P. A.; Koike, K.; Ishitani, O.; Ibusuki, T. *J. Photochem. Photobiol. A: Chem.* **1996**, *96*, 171–174.
(5) Ishitani, O.; George, M. W.; Ibusuki, T.; Johnson, F. P. A.; Koike, K.; Nozaki, K.; Pac, C.; Turner, J. J.; Westwell, J. R. *Inorg. Chem.* **1994**, *33*, 4712–4717.
(6) Kutal, C.; Corbin, A. J.; Ferraudi, G. *Organometallics* **1987**, *6*, 553–557.
(7) Hawecker, J.; Lehn, J.-M.; Ziessel, R. *Helv. Chim. Acta* **1986**, *69*, 1990–2012.
(8) Kutal, C.; Weber, M. A.; Ferraudi, G.; Geiger, D. *Organometallics* **1985**, 2161–2166.
(9) Hawecker, J.; Lehn, J.-M.; Ziessel, R. *J. Chem. Soc., Chem. Commun.* **1983**, 536–538.
(10) Takeda, H.; Koike, K.; Inoue, H.; Ishitani, O. *J. Am. Chem. Soc.* **2008**, *130*, 2023–2031.
(11) Hayashi, Y.; Kita, S.; Brunschwig, B. S.; Fujita, E. *J. Am. Chem. Soc.* **2003**, *125*, 11976–11987.
(12) Fujita, E.; Muckerman, J. T. *Inorg. Chem.* **2004**, *43*, 7636–7647.

10.1021/ic8019556 CCC: $40.75

Chart 1. *fac*-ReCl(4,4′-R$_2$-2,2′-bpy)(CO)$_3$ Complexes **2a**−**c**



Complex	R
2a	(CH$_2$)$_3$C$_6$F$_{13}$
2b	(CH$_2$)$_3$C$_8$F$_{17}$
2c	H

be dissolved in scCO$_2$. Using CO$_2$ as both the solvent *and* reactant offers several potential advantages. In particular, it eliminates the possibility of solvent coordination to the metal center, and the [CO$_2$] can be extremely high (ca. 22 M at 35 MPa). Furthermore, the physical properties of scCO$_2$ are easily tuned as a function of the temperature and pressure, and the whole process is more environmentally friendly.[13] In an effort to investigate the effect of high CO$_2$ pressures on photochemical CO$_2$ reduction, Hori et al. prepared CO$_2$-soluble cationic rhenium phosphite complexes incorporating a fluorinated counteranion, such as [Re(bpy)(CO)$_3${P(OC$_6$H$_{13}$)$_3$}][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$].[14] This complex was reported to reduce CO$_2$ to CO in liquid CO$_2$ under 365 nm irradiation in the presence of triethylamine (TEA) as an electron donor (T = 28 °C, p = 7 MPa, ρ = 0.70 g cm^{-3}) with 2.2 total turnovers after 2 h (TOF = 1.1 h^{-1}). Under more conventional high-pressure two-phase conditions (high-pressure CO$_2$ gas/DMF liquid), the related [Re(bpy)(CO)$_3${P(O^{i}Pr)$_3$}][SbF$_6$] complex reduced CO$_2$ to CO under 365 nm irradiation in the presence of TEA with up to 3.4 total turnovers after 24 h (TOF = 0.14 h^{-1}).[15]

While the addition of a fluorinated counteranion imparts CO$_2$ solubility to the corresponding rhenium complex, this approach does not extend to the neutral, and perhaps most thoroughly studied, ReCl(bpy)(CO)$_3$ complex. Furthermore, the low catalytic activity of Hori's catalyst in liquid CO$_2$ might be due to precipitation of the photogenerated reduced neutral intermediate. Here we describe the synthesis and characterization of neutral CO$_2$-soluble rhenium bipyridine complexes bearing fluorinated alkyl substituents. Such substituents are well-known to impart enhanced solubility to otherwise insoluble metal complexes in scCO$_2$.[13] The photophysical and photochemical properties of the complexes in CH$_3$CN and scCO$_2$ have also been determined and are compared with those of the unsubstituted bipyridine complex.

Fluorinated bipyridine ligands (N^N) **1a** and **1b** were prepared as reported,[16,17] followed by metalation with ReCl(CO)$_5$ in refluxing toluene to give the corresponding *fac*-ReCl(N^N)(CO)$_3$ complexes **2a** and **2b** (Chart 1).[18] The ^{1}H, ^{13}C{^{1}H}, and ^{19}F NMR, IR spectroscopy, and elemental analysis results are consistent with the expected facial geometry of the carbonyl ligands around a rhenium(I) center coordinated to chloride and 4,4′-disubstituted bipyridine ligands.[19] The three methylene units separating the fluorinated alkyl chains from the bipyridine π system serve to insulate the bipyridine rings, and by extension the rhenium center, from the electron-withdrawing effect of the F atoms. This is reflected in the ν_{CO} IR stretching frequencies, which do not change upon replacement of the 4,4′-H atoms in ReCl(bpy)(CO)$_3$ (**2c**) with either −(CH$_2$)$_3$C$_6$F$_{13}$ or −(CH$_2$)$_3$C$_8$F$_{17}$ in **2a** and **2b**, respectively (Table 1). In addition, cyclic voltammograms for complexes **2a** and **2b** recorded in CH$_3$CN indicate that the irreversible rhenium(I) oxidation peak at 1.35 V and the reversible N^N reduction to form the N^N radical anion at −1.40 V are virtually unchanged from those reported for **2c**.[20] UV−vis absorption spectra in CH$_3$CN exhibit characteristic MLCT absorption bands at 368 nm for both **2a** and **2b** and corresponding emission maxima at 625 nm with emission lifetimes, τ_{em}, of 30 ns. The photophysical characteristics of complexes **2a** and **2b** are practically identical. Therefore, only complex **2a** will be discussed further.

Dissolution of complex **2a** in scCO$_2$ (T = 35 °C, p = 13.8 MPa) gives an intense yellow solution exhibiting ν_{CO} stretching frequencies at 2028, 1933, and 1909 cm^{-1}, which are shifted to higher energy with respect to those recorded in CH$_3$CN. The corresponding UV−vis absorption spectrum displays a +26 nm solvatochromic shift of the MLCT absorption band to 394 nm and a −15 nm shift of the emission maximum to 610 nm, with τ_{em} = 34 ns. This slightly longer emission lifetime relative to that in CH$_3$CN[21] can be attributed to the lower polarity of scCO$_2$, which serves to raise the energy of the excited state, consistent with the blue shift of the emission in scCO$_2$ and the energy-gap law.[18]

UV−vis transient absorption spectroscopy of a degassed CH$_3$CN solution of complex **2a** after pulsed 410 nm laser excitation produces a spectrum within the experimental time resolution (<10 ns) with absorption bands at 375 and 475 nm.[19] These bands, which together decay with a lifetime of 30 ns, are characteristic of an MLCT excited state and agree with those reported for **2c**.[20] Consistent with these results, the UV−vis transient absorption spectrum in scCO$_2$ exhibits absorption bands at 370 and 470 nm, which decay with a lifetime of 34 ns.[19] Time-resolved IR (TRIR) spectra of the MLCT excited state of **2a**, formed after 410 nm laser excitation in a CH$_3$CN solution, exhibit three new ν_{CO} bands at 2066, 1990, and 1956 cm^{-1}, which are shifted to higher energy relative to the ground state.[19] These bands, which agree with those reported for **2c**,[11,22] are characteristic of an MLCT triplet excited state and reflect an increase in the C−O bond strengths, as a result of less back-bonding due to reduced electron density at the rhenium center in the excited state. The TRIR spectrum of **2a** in scCO$_2$ is shown in Figure 1 and exhibits similar excited-state bands at 2065, 1991, and 1964 cm^{-1}.

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(13) Jessop, P. G.; Ikariya, T.; Noyori, R. *Chem. Rev.* **1999**, *99*, 475–493.

(14) Hori, H.; Koike, K.; Takeuchi, K.; Sasaki, Y. *Chem. Lett.* **2000**, 522–523.

(15) Hori, H.; Koike, K.; Suzuki, Y.; Ishizuka, M.; Tanaka, J.; Takeuchi, K.; Sasaki, Y. *J. Mol. Catal. A: Chem* **2002**, *179*, 1–9.

(16) Bennett, B. L.; Robins, K. A.; Tennant, R.; Elwell, K.; Ferri, F.; Bashta, I.; Aguinaldo, G. *J. Fluorine Chem.* **2006**, *127*, 140–145.

(17) Xia, J.; Johnson, T.; Gaynor, S. G.; Matyjaszewski, K.; DeSimone, J. *Macromolecules* **1999**, *32*, 4802–4805.

(18) Caspar, J. V.; Meyer, T. J. *J. Phys. Chem.* **1983**, *87*, 952–957.

(19) See the Supporting Information.

(20) Kalyanasundaram, K. *J. Chem. Soc., Faraday Trans. 2* **1986**, *82*, 2401–2415.

(21) Lifetimes in CH$_3$CN at 35 °C do not change significantly with respect to those recorded at 25 °C.

(22) George, M. W.; Turner, J. J. *Coord. Chem. Rev.* **1998**, *177*, 201–217.

Table 1. Photophysical, Electrochemical and Photochemical Properties of $Re^ICl(N^\wedge N)(CO)_3$ Complexes in CH_3CN and $scCO_2$

complex	solvent	ν_{CO}, cm^{-1}	λ_{MLCT}, nm (ε, M^{-1} cm^{-1})	λ_{em}, nm (τ_0, ns)[a]	$E_{1/2}$,[b] V	TEA reductive quenching k_q, M^{-1} s^{-1}	 K_{SV}, M^{-1}
2a	CH_3CN	2022, 1916, 1897	368 (4102)	625 (30)	1.35[c], −1.40	2.5×10^7	0.76
	$scCO_2$[d]	2028, 1933, 1909	394	610[e] (34)		4.4×10^6	0.15
2b	CH_3CN	2022, 1916, 1898	368 (3794)	625 (30)	1.35[c], −1.39	2.5×10^7	0.76
	$scCO_2$[d]	2028, 1933, 1909	394	610[e] (33)		4.2×10^6	0.14
2c	CH_3CN	2023, 1917, 1899	370 (3420)[f]	625 (27)	1.36[c,f], −1.32[f]	2.6×10^7	0.71

[a] $\lambda_{ex} = 410$ nm. [b] vs SCE. [c] E_{pa} (V) with a scan rate of 50 mV s^{-1}. [d] 35 °C, 13.8 MPa. [e] Uncorrected. [f] See ref 20.

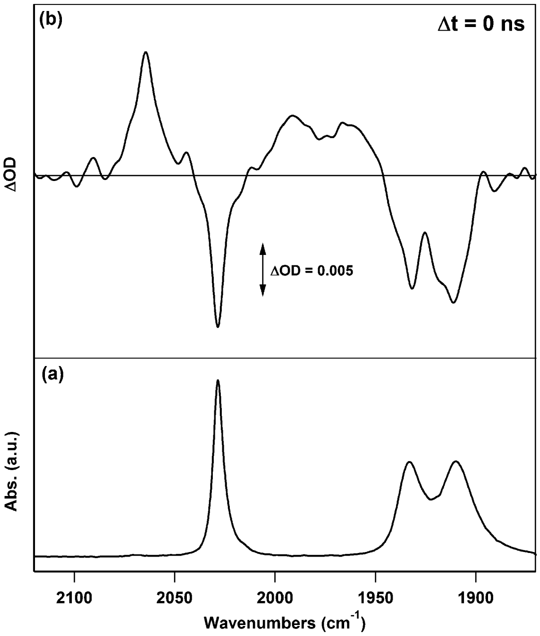

Figure 1. (a) Fourier transform IR (FTIR) spectrum of **2a** in $scCO_2$ (vs $scCO_2$ background; 35 °C, 13.8 MPa). (b) Time-resolved step-scan FTIR spectrum recorded immediately after 410 nm laser excitation of this solution. Positive bands represent the excited-state species, while negative bands represent the ground-state bleach.

In order for **2a** and **2b** to act as effective photochemical CO_2 reduction catalysts, their MLCT excited states must be efficiently quenched in the presence of a suitable electron donor. Therefore, we determined the quenching rate constants with TEA by carrying out the emission lifetime measurements for **2a** and **2b** in CH_3CN and $scCO_2$ as a function of [TEA] (see Table 1).[23] A plot of τ_0/τ vs amine concentration for **2a**, as shown in Figure 2, is a straight line, the slope of which yields the Stern−Volmer constant, K_{SV}.[19] K_{SV} reflects the efficiency with which an excited state is quenched, and the quenching rate constant, k_q, can be obtained from $K_{SV} = k_q\tau_0$. Reductive quenching of the MLCT excited state of **2a** by TEA in a degassed CH_3CN solution at 25 °C occurs with a rate constant k_q of 2.5×10^7 M^{-1} s^{-1}, which corresponds to $K_{SV} = 0.76$ M^{-1}. The unsubstituted bpy analogue, **2c**, exhibits similar quenching kinetics with TEA in degassed CH_3CN, yielding a quenching rate constant of 2.6×10^7 M^{-1} s^{-1} at 25 °C and $K_{SV} = 0.71$ M^{-1}. Upon changing to a $scCO_2$ solution of **2a**, the quenching rate constant, k_q, decreases by a factor of 6 to 4.4×10^6 M^{-1} s^{-1} at 35 °C, corresponding to $K_{SV} = 0.15$ M^{-1}.[23]

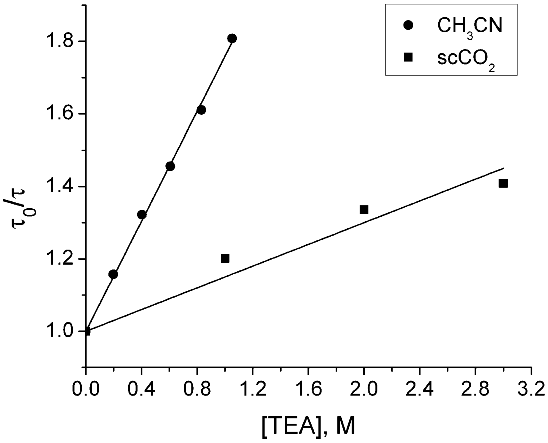

Figure 2. Stern−Volmer quenching of the emission from the MLCT excited state of **2a** by TEA in CH_3CN ($T = 25$ °C; $K_{SV} = 0.76$ M^{-1}) and $scCO_2$ ($T = 35$ °C, $p = 13.8$ MPa; $K_{SV} = 0.15$ M^{-1}). $\lambda_{ex} = 410$ nm.

In summary, we have prepared two new fluorinated *fac*-$Re^ICl(4,4'\text{-}R_2\text{-}2,2'\text{-bpy})(CO)_3$ complexes (**2a** and **2b**) and shown that their photophysical characteristics are virtually identical with those of the bpy analogue, **2c**, in CH_3CN. Reductive quenching of the MLCT excited state of **2a** and **2b** in CH_3CN and $scCO_2$ has been examined, with quenching rate constants, k_q, only 6 times slower in $scCO_2$ than in CH_3CN. Given the much lower polarity of $scCO_2$ relative to CH_3CN, this relatively small difference in k_q is quite remarkable. These results indicate that **2a** and **2b** are excellent candidates as catalysts for the photochemical reduction of CO_2 to CO in $scCO_2$. Preliminary photocatalysis experiments with these complexes show the formation of CO in both DMF and $scCO_2$, while control experiments in argon-saturated DMF show no CO formation. Detailed results, including turnover numbers and kinetic studies, will be reported soon.

Acknowledgment. We thank Prof. Mike George and Dr. Alex Cowan (University of Nottingham, Nottingham, U.K.) for the provision of the high-pressure spectroscopic cell and for valuable discussions. This work was performed at Brookhaven National Laboratory and funded under Contract DE-AC02-98CH10886 with the U.S. Department of Energy.

Supporting Information Available: Complete experimental details, transient absorption spectra, TRIR spectra, and plots of τ_0/τ vs [TEA] for complexes **2b** and **2c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[23] The $scCO_2$ solution was visually confirmed to be a single phase at all concentrations of TEA examined.