Coordination Chemistry Reviews, 132 (1994) 195–200

Toward Photochemical Carbon Dioxide Activation by Transition Metal Complexes

Etsuko Fujita,*,[a] Bruce S. Brunschwig,[a] Tomoyuki Ogata,[a,b] and Shozo Yanagida[b]

[a] *Chemistry Department, Brookhaven National Laboratory, Upton, NY 11973, USA*

[b] *Chemical Process Engineering, Faculty of Engineering, Osaka University, Osaka, Japan*

Abstract

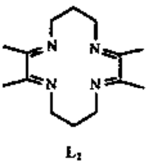
Nickel and cobalt complexes of 14-membered tetraazamacrocycles mediate electron transfer and produce CO in the photochemical reduction of CO_2. Two integrated systems for the CO_2 reduction are discussed: (1) photophysical properties of bifunctional supramolecules, $Ru(bpy)_2(bpy\text{-}L_{10}M)^{4+}$ (bpy = 2,2'-bipyridine, bpy-L_{10} = 1-(2,2'-bipyridin-6-ylmethyl)-1,4,8,11-tetraazacyclotetradecane, M = H_2, Ni) and its limitation as a photocatalyst; (2) advantages of multimolecular system with *p*-terphenyl as a photosensitizer, a cobalt macrocycle as an electron mediator, and a tertiary amine as a sacrificial electron donor.

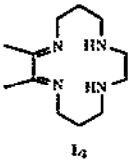
Introduction

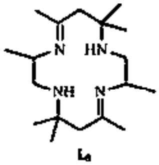
Considerable effort has been devoted to searching for effective catalysts for photochemical and electrochemical reduction of CO_2. Metal complexes with 14-membered tetraazamacrocyclic ligands, $[CoL_5(H_2O)]^{2+}$ (L_5 = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene) and NiL_{10}^{2+} (L_{10} = 1,4,8,11-tetraazacyclotetradecane), have been used as successful electrocatalysts [1-3] for the reduction of CO_2 in H_2O or aqueous CH_3CN. The total yields of CO and H_2 are ~1 in most cases and the CO/H_2 production ratio is ~1 for $[CoL_5(H_2O)]^{2+}$ [1, 2] and >100 for NiL_{10}^{2+} [3]. Beley et al. [3] suggested that the large selectivity for the electroreduction of CO_2 compared with water is related to the size of the macrocyclic ligand and to the presence of N-H groups in NiL_{10}^{2+}. Despite the successful electrochemical reduction of CO_2 by metal macrocycles, photochemical reduction of CO_2 by these macrocycles showed a very low quantum yield for CO_2 reduction and the undesired competitive evolution of H_2, along with HCO_2^- and CO production. Tinnermans et al. [2] have reported the use of cobalt macrocyclic complexes as electron mediators for the Ru(2,2'-bipyridine)$_3^{2+}$-catalyzed photochemical reduction of CO_2 to yield a CO/H_2 ratio of ~0.3. Grant et al. [4] investigated the electron mediation of a NiL_{10}

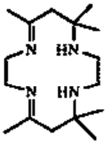
0010-8545/94/$26.00
SSDI 0010-8545 (94) 02023–C

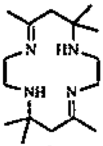
complex for the same photosensitized CO_2 reduction and found quantum yields of 10^{-4} to 10^{-3} and a CO/H_2 ratio of ~0.2. Both groups proposed the insertion of CO_2 into the M-H bond in the reaction mechanisms.

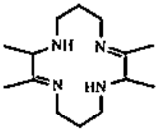

L_1

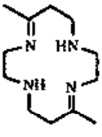

L_2

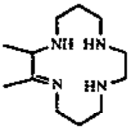

L_3

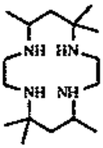

L_4


L_5

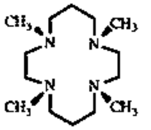

L_6

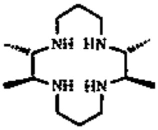

L_7

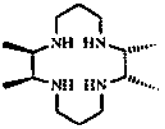

L_8


L_9


L_{10}


L_{11}

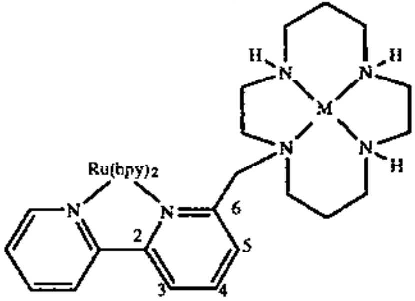

L_{12}


L_{13}

In order to find an effective and selective photochemical CO_2 reduction system, we are studying the factors controlling excited-state lifetimes, electron- or hole-transfer rates to mediators/catalysts, the binding of small molecules to reduced or oxidized mediators, and the reactivity of the mediators with small molecules to yield the desired products. Since some of metal macrocycles shown above have been used as catalysts for photochemical CO_2 reduction, we studied the nature of reduced nickel and cobalt mediators, and the binding of H^+, CO and CO_2 to the mediators in acetonitrile and water in order to understand the mechanism of CO_2 reduction [5]. We also studied two integrated systems for photochemical CO_2 reduction because the multimolecular systems studied previously show low yield due to a competing process in the catalytic cycle. Here we describe our results on covalently attached $Ru(bpy)_3{}^{2+}$ and $ML_{10}{}^{2+}$ (M = Ni, H_2) [6] and terphenyl-catalyzed CO_2 reduction with various metal macrocycles as mediators [7].

Photophysical Properties of Covalently Attached $Ru(bpy)_3^{2+}$ and ML_{10}^{2+} ($M = Ni, H_2$) Complexes

Combining the sensitizer and reduction catalyst in a single molecule [8, 9] by covalently attaching a macrocycle to a polypyridyl sensitizer may yield a complex that will be useful in CO_2 reduction. Complexes in which a macrocycle is bound to several polypyridyl metal complexes have been produced, and their potential multiredox and catalytic features have been studied [8]. $Ru(bpy)_2(bpy\text{-}L_{10}M)^{4+}$ ($M = H_2$, Ni) complexes have been prepared and characterized by Kimura et al. [9]. They suggested that the lowered emission yields of both pendant complexes are due to intramolecular quenching. In order to determine if this is the case, the photophysical properties of these complexes, including the temperature dependence of their emission lifetimes, were studied. As a basis for comparison, $Ru(bpy)_2(6\text{-}Mebpy)^{2+}$ was also prepared and studied. A pictorial representation of the pendant complexes, with $M = Ni^{2+}$ or $2H^+$, is shown below:

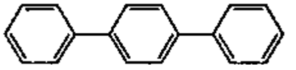


The spectroscopy and photophysics of the metal-to-ligand charge-transfer (MLCT) excited state(s) of $Ru(bpy)_2(6\text{-}Mebpy)^{2+}$, $Ru(bpy)_2(bpy\text{-}L_{10}H_2)^{4+}$, and $Ru(bpy)_2(bpy\text{-}L_{10}Ni)^{4+}$ were examined. The absorption and emission spectra of these complexes are similar to those of $Ru(bpy)_3^{2+}$ in H_2O at 25 °C. The emission lifetime decreases by a factor of about 80 for 6-Mebpy and the emission quantum yield decreases by a factor of about 300 for the bpy-cyclam pendant complexes compared to the parent $Ru(bpy)_3^{2+}$ complex at 25 °C. Decay of the ^{3}MLCT excited state takes place by two independent channels: a temperature-independent pathway to the ground state and a thermally-activated pathway *via* a ligand-field excited state. Activation free-energies, E_a, for the latter pathway were obtained from fits of the temperature-dependent emission lifetime data. Smaller E_a were observed for the 6-substituted complexes (1500-2300 cm^{-1}) than for $Ru(bpy)_3^{2+}$ (3000-3910 cm^{-1}) in EtOH and CH_3CN. The smaller E_a can be attributed to the increased Ru-N bond distance in the 6-substituted complexes caused by steric hindrance that decreases the ligand-field strength and lowers the energy and/or reorganization parameter of the ligand-field excited state. For the bpy-cyclamNi^{2+} pendant complex, an energy-transfer pathway may also provide a deactivation channel, since the rate constant for the bimolecular quenching, k_q, of $Ru(bpy)_3^{2+}$ by NiL_{10}^{2+} is 1.5×10^8 $M^{-1}s^{-1}$ at 20 °C.

Our recent studies [5b, 10] of metal macrocycles indicate that the Co-N bond distances are not significantly changed by reduction, but the Ni-N distances of nickel(I) complexes (NiL_5, NiL_{10}, and NiL_{13}) increase quite dramatically compared to the nickel(II) complexes. Although the coordination geometry varies from square planar to elongated octahedral, and the spin varies from low to high in these nickel(II) complexes, the bond length differences between the Ni(II) and Ni(I) complexes remain about 0.11 Å. Such a bond length difference may cause a 2- or 3-order-of-magnitude slower electron transfer between the Ni(II) and Ni(I) species than that between the Co(II) and Co(I). A complex such as $Ru(phen)_2(phen\text{-}L_{10}Co)^{4+}$ (phen-L_{10} = 1-(1,10-phenanthrolin-5-ylmethyl)-1,4,8,11-tetraazacyclotetradecane) may exhibit a faster electron transfer to the intramolecularly attached CoL_{10}^{2+}, compared to $Ru(phen)_2(phen\text{-}L_{10}Ni)^{4+}$ [11], but we still cannot eliminate the possibility of energy transfer because the cobalt unit has a d-d transition near the MLCT band of the $Ru(bpy)_3^{2+}$ unit. It is also worth mentioning that the chemical CO_2 reduction process is much slower than the photo-absorption or electron-transfer process. Therefore a bifunctional supramolecule with one sensitizer and one catalyst may not be the best choice.

Photochemical Reduction of CO_2

Cobalt macrocycles mediate electron transfer in the photoreduction of CO_2 with *p*-terphenyl as a photosensitizer and a tertiary or β-hydroxylated tertiary amine as a sacrificial electron donor in methanolic acetonitrile[12]. The anion radical of *p*-terphenyl has a long lifetime (8.3 μs in TEA/THF) and is a very strong reducing reagent (-2.45 V *vs* SCE) [13]. It reduces CO_2 to HCO_2^- with an apparent quantum yield of 0.072 at 313 nm in the TEA/DMF system. But *p*-terphenyl itself concurrently undergoes photo-Birch reduction within 4 turnovers of its catalytic cycle.



p-terphenyl (TP)

Mediation by cobalt macrocycles suppresses the degradative and competitive photo-Birch reduction of *p*-terphenyl, leading to efficient and selective formation of both CO and formate with little H_2 [7, 14]. The apparent combined quantum yield of CO and HCO_2^- is 0.25 at 313 nm in the $TEOA/CH_3CN/MeOH/CoL_{10}Cl_3$ system. Structural properties such as hydrogen-bonding interactions between the bound CO_2 and N-H protons and steric repulsion by the macrocycle methyl groups to axial ligation may be responsible for the observed differences in the distribution of reduction products – CO, formate and H_2.

Cobalt complexes with two or four C-methyl groups (L_2, L_6, L_7, and L_{10}) give comparable activity for the reduction of CO_2 and H_2 evolution. In the case of more extensively C-methylated macrocycles (L_3 and L_5), however, the activity of CO_2 reduction decreases by an appreciable amount, but not the H_2 evolution. Steric hindrance by the two pairs of geminate C-methyl groups reduces the accessibility of the metal center to approach by either CO_2 molecules or other ligands such as amines and solvent. The N-methylated complex, $Co(II)L_{11}^{2+}$, did not mediate the photoreduction of CO_2 and only a small quantity of H_2 was detected. This inactivity is due to the difficulty in attaining the six-coordinate structure of Co(III) and the very high $Co^{III/II}$ potential ($E_{1/2} > +1.2$ V vs SCE). For CoL_1, H_2 evolution dominated when TEA was used as electron donor with the tetraene complex. A proposed mechanism of CO_2 reduction is shown below.

$$\begin{aligned}
&TP^{\cdot-} + [Co^{III}L(TEA)_2]^{3+} \longrightarrow [Co^{II}L(TEA)]^{2+} + TP + TEA \\
&TP^{\cdot-} + [Co^{II}L(TEA)]^{2+} \longrightarrow [Co^{I}L]^{+} + TP + TEA \\
&[Co^{I}L]^{+} + CO_2 \longrightarrow [Co^{I}L\text{-}CO_2]^{+} \\
&[Co^{I}L\text{-}CO_2]^{+} + TEA \rightleftharpoons [Co^{III}L(CO_2^{2-})(TEA)]^{+} \\
&[Co^{III}L(CO_2^{2-})(TEA)]^{+} + H^{+} \rightleftharpoons [CoL(COOH)(TEA)]^{2+} \\
&[CoL(COOH)(TEA)]^{2+} + TP^{\cdot-} \longrightarrow [Co^{II}L(TEA)]^{2+} + CO + OH^{-} + TP
\end{aligned}$$

Flash photolysis experiments (transient absorption) in progress to identify intermediates and determine the kinetics.

The catalytic electron mediation studies were extended to $CoCl_2$ and Ni(II), Zn(II), Fe(II), Cu(II) complexes of L_{10}. None of these complexes functioned as electron mediators for CO_2 photoreduction. The failure in the case of the NiL_{10} complex is in marked contrast with its excellent performance as an electron mediator in the electrochemical reduction (almost 100% CO production) and with its moderate performance in photochemical reduction with $Ru(bpy)_3^{2+}$ as a sensitizer ($CO/H_2 = 1/6$ at pH 4). The failure with $Ni^{II}L_{10}$ and $[Co^{II}L_{11}Cl]$ in the catalytic electron mediation in the system may result from a very unstable trivalent oxidation state of the metal complexes under our conditions. Although trivalent nickel complexes have been reported, these complexes are stable only in acidic media. The CoL_{11} complex has an oxidation potential at > 1.2 V and cannot form six-coordinate species because of steric hindrance. The failure with $Ni^{II}L_{10}$ may also be due to slow electron transfer from *p*-terphenyl due to the large Ni-N bond distance change in the Ni(II) and Ni(I) states. Flash photolysis experiments in progress may clarify these issues.

Acknowledgment

The authors would like to acknowledge many coworkers and collaborators including Prof. S. J. Milder (now at The Evergreen State College), Dr. C. Creutz, Dr. N. Sutin, Dr. L. R. Furenlid, Dr. M. W. Renner, Dr. H. A. Schwarz and Dr. J. F. Wishart of Brookhaven National Laboratory;

Dr. S. Matsuoka, Prof. M. Kusaba and Prof. N. Nakashima of Osaka University; Prof. D. J. Szalda of Baruch College; and Prof. H. Elias of Techniche Hochschule Darmstadt. This work was carried out at Brookhaven National Laboratory under contract DE-AC02-76CH00016 with the U.S. Department of Energy and supported by its Division of Chemical Sciences, Office of Basic Energy Sciences, and supported at Osaka University by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture of Japan (No. 03203119).

References

1 B. Fisher and R. Eisenberg, J. Am. Chem. Soc. 102 (1980) 7361.
2 A. T. A. Tinnermans, T. P. M. Koster, D. H. M. W. Thewissen, and A. Mackor, Recl. Trav. Chim. Pays. -Bas 103 (1984) 288-295.
3 M. Beley, J. -P. Collin, R. Ruppert, and J. -P. Sauvage, J. Am. Chem. Soc. 108 (1986) 7461.
4 (a) J. L. Grant, K. Goswami, L. O. Spreer, J. W. Otvos, and M. Calvin, J. Chem. Soc., Dalton Trans. (1987) 2105. (b) C. A. Craig, L. O. Spreer, J. W. Otvos, and M. Calvin, J. Phys. Chem. 94 (1990) 7957.
5 (a) E. Fujita, C. Creutz, D. J. Szalda, and N. Sutin, J. Am. Chem. Soc. 110 (1989) 4870. (b) E. Fujita, C. Creutz, N. Sutin, and D. J. Szalda, J. Am. Chem. Soc. 113 (1991) 343. (c) E. Fujita, C. Creutz, N. Sutin, and B. S. Brunschwig, Inorg. Chem, 32 (1993) 2657. (d) C. Creutz, H. A. Schwarz, J. F. Wishart, E. Fujita, and N. Sutin, J. Am. Chem. Soc. 113 (1991) 3361. (d) C. Creutz, H. A. Schwarz, J. F. Wishart, E. Fujita, and N. Sutin, J. Am. Chem. Soc. 111 (1989) 3361.
6 E. Fujita, S. J. Milder, B. S. Brunschwig, Inorg. Chem. 31 (1992) 2079.
7 S. Matsuoka, K. Yamada, T. Ogata, M. Kusaba, N. Nakashima, E. Fujita, and S. Yanagida, J. Am. Chem. Soc. 115 (1993) 601.
8 J. Lehn, and R. Ziessel, J. Chem. Soc., Chem. Commun. (1987) 1292.
9 E. Kimura, S. Wada, M. Shionoya, T. Takahashi, and Y. Iitaka, J. Chem. Soc., Chem. Commun. (1990) 397.
10 (a) L. R. Furenlid, M. W. Renner, D. J. Szalda, and E. Fujita, J. Am. Chem. Soc. 113 (1991) 883. (b) E. Fujita, L. R. Furenlid, and M. W. Renner, Unpublished data. (c) E. Fujita, D. J. Szalda, and H. Elias, Manuscript under preparation.
11 E. Kimura, X. Bu, M. Shionoya, S. Wada, and S. Maruyama, Inorg. Chem. 31 (1992) 4542.
12 S. Matsuoka, T. Kohzuki, C. Pac, A. Ishida, S. Takamuku, M. Kusaba, N. Nakashima, and S. Yanagida, J. Phys. Chem. 96 (1992) 4437.
13 S. Matsuoka, H. Fujii, T. Yamada, C. Pac, A. Ishida, S. Takamuku, M. Kusaba, N. Nakashima, S. Yanagida, K. Hashimoto, and T. Sakata J. Phys. Chem. 95 (1991) 5802.
14 S. Matsuoka, K. Yamamoto, C. Pac, and S. Yanagida, Chem. Lett. (1991) 2099.