

Preliminary Note

Photoreduction and electroreduction of carbon dioxide by a novel rhenium(I) *p*-phenyl-terpyridine carbonyl complex

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(Received October 10, 1991; accepted October 16, 1991)

Abstract

Photoreduction and electrocatalytic CO₂ reduction of the novel rhenium(I) *p*-phenyl-terpyridinecarbonyl (Re(pty)(CO)₃Cl) complex is reported. Remarkable photocatalytic activity is observed in DMSO but not in DMF.

Re(bpy)(CO)₃Cl (where bpy is 2,2'-bipyridine) and its analogues are promising transition metal polypyridine complexes studied in photochemical and electrocatalytic research. These complexes have been shown to mediate the photochemical reduction of carbon dioxide in the presence of a sacrificial electron donor. They act as both chromophores to visible light and homogeneous catalysts [1]. They also accomplish the electrochemical reduction of CO₂ in solution [2] and as electrode-bound polymer films [3]. Recent efforts in the photochemical application of these complexes focus on the tuning of their MLCT excited-state energies to achieve high intramolecular energy transfer rates in polynuclear systems [4], and on the coupling of the catalyst to a regenerative oxidative half-reaction [5]. Exchanging the bipyridine ligand for a *p*-phenyl-substituted terpyridine derivative holds out the prospect of a symmetrical link to an adjacent member of the electron or an energy transfer chain — a conceptual advantage in view of the intended directionality of this transfer [5, 6].

We synthesized the complex Re(pty)(CO)₃Cl (where pty is *p*-(2,6-di-2-pyridyl-4-pyridyl)phenol). In Table 1 we report its photochemical and in Fig. 1 its electrochemical activity regarding the reduction of CO₂. The photochemical experiments revealed a remarkable catalytic activity in DMSO but not in DMF solution and confirmed the stabilizing effect of a chloride additive already observed on Re(bpy)(CO)₃Cl. Although the molar absorptivities of the pty complex are slightly higher than those of its bpy-analogue, non-radiative deactivation is more effective in the former compound. Its emission is two peaked at 520 nm and 550 nm, and we have determined emission quantum yields in EtOH–MeOH(4:1) glasses to be 0.07/0.14 at 113 K and 0.13/0.25 at 77 K for 334/378 nm excitation. Taking into account the similarity of the cyclic

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TABLE 1

Generation of CO by the photoreduction of CO₂ in solutions containing 9.4×10^{-4} M *fac*-Re(L)(CO)₃Cl, CO₂ and solvent-(HOCH₂CH₂)₃N (5:1)

Experiment	Irradiation time (h)	CO produced (ml)	Turnover number
1	2	0.7	1
1	4	1.3	2
2	2.5	1.8	3
2	4	3.1	5
3	4	0	0
4	4	0.4	~0
5	4	15.3	23

Experiment 1, L≡ptpy, solvent DMSO; experiment 2, L≡ptpy, solvent DMSO, 0.03 M NEt₄Cl; experiment 3, no complex, solvent DMSO, 0.03 M NEt₄Cl; experiment 4, L≡ptpy, solvent DMF, 0.03 M NEt₄Cl; experiment 5, L≡2,2'-bipyridine (complex concentration 1×10^{-3} M), solvent DMF, 0.02 M NEt₄Cl.

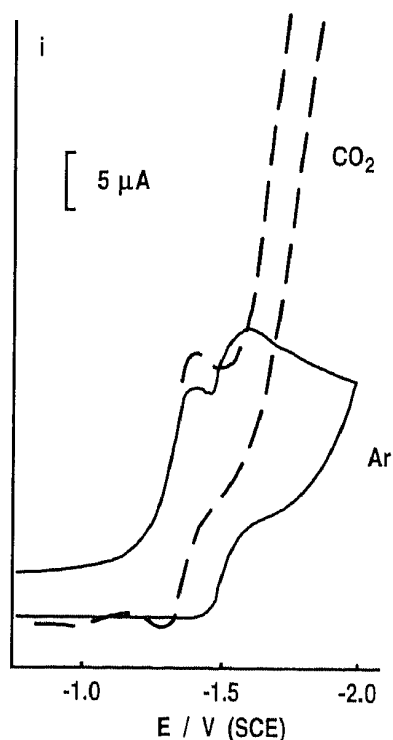


Fig. 1. Cyclic voltammogram of Re(pty)(CO)₃Cl in MeCN in the absence and presence of CO₂.

voltammograms of Re(pty)(CO)₃Cl in the absence and presence of CO₂ to those of the bpy complex [2] we find no evidence of mechanistic differences in the photoreduction and electroreduction of CO₂ mediated by the two polypyridine complexes.

Based on the reportedly failed synthesis of complexes of the composition $M(\text{py})_n\text{CO}_{(5-n)}\text{X}$ with $n > 2$, where $M \equiv \{\text{Mn}, \text{Re}\}$ and $X \equiv \{\text{Cl}, \text{Br}, \text{I}\}$ [7] and on previous reports of bidentate terpyridine coordination [8] one would rather expect a two-coordinate ptpy ligand than a three-coordinate ligand. In fact neither of the two spectra in Fig. 2 is in agreement with a three-coordinate ptpy ligand (nor is the

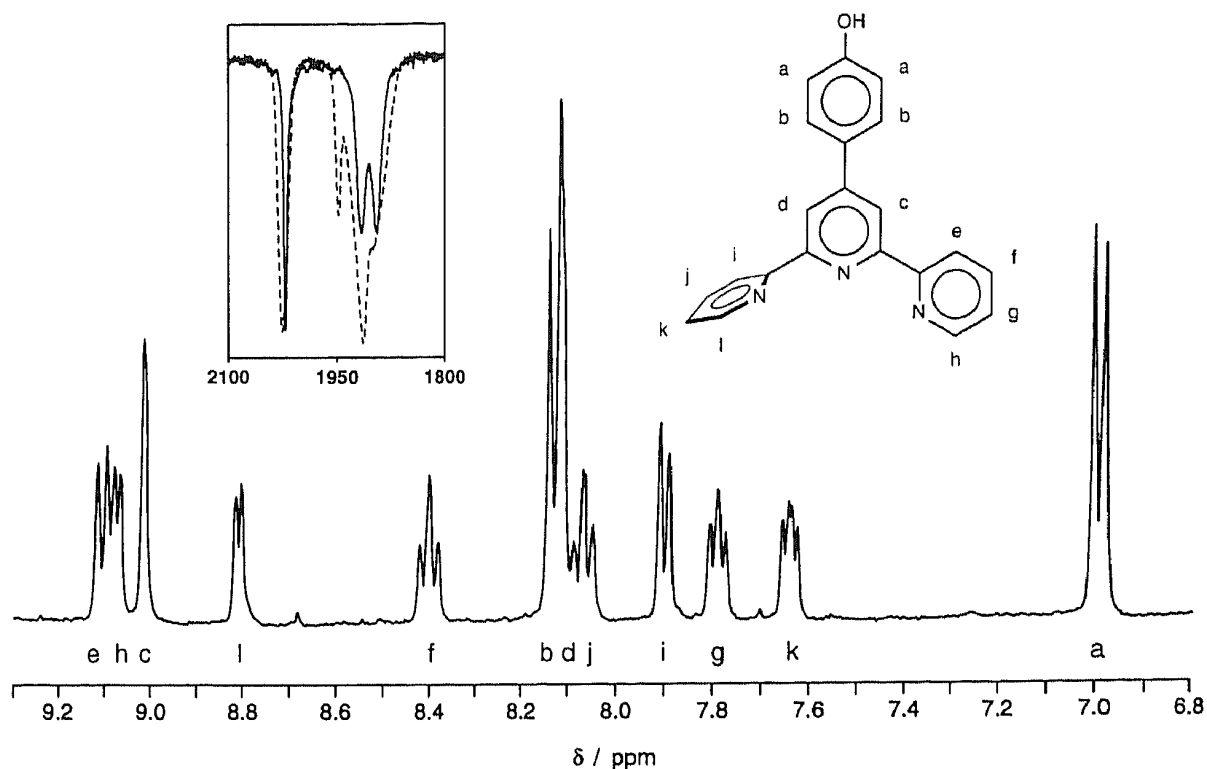


Fig. 2. 400 MHz ^1H NMR spectrum of $\text{Re}(\text{pty})(\text{CO})_3\text{Cl}$ in $\text{DMSO}-d_6$ at room temperature. Chemical shifts δ in ppm, coupling constants in Hz, 7.02 (d, 2H_a , $J_{ab}=9$), 7.66 (dd, 1H_k , $J_{k(jl)}=7$), 7.81 (dd, 1H_g , $J_{g(hn)}=6$), 7.93 (d, 1H_i , $J_{ij}=8$), 8.09 (dd, 1H_j , $J_{j(ik)}=7$), 8.14 (m, sh, 1H_d), 8.15 (d, 2H_b , $J_{ba}=9$), 8.43 (dd, 1H_f , $J_{f(eg)}=8$), 8.83 (d, br, 1H_l , $J_{lk}=4$), 9.04 (s, 1H_c), 9.10 (d, br, 1H_h , $J_{hg}=6$), 9.14 (d, 1H_e , $J_{ef}=9$); inset, Fourier transform IR spectrum as MeCN solution (solid line, 2022, 1917, 1896 cm^{-1}) and KBr pellet (dashed line, 2027, 1948, 1921 cm^{-1} , solution peaks superimposed).

spectroscopic characterization given by Juris *et al.* [9] for their closely related terpyridine complex). A ^1H nuclear magnetic resonance (NMR) spectrum of an authenticated three-coordinate terpyridine complex, namely $[\text{Ru}(\text{II})(\text{pty})_2]^{2+}$, has been reported recently [6]. The ^1H NMR spectrum (and its ^{13}C counterpart and H,H-COSY data not shown here) of $\text{Re}(\text{pty})(\text{CO})_3\text{Cl}$ is assignable to a two-coordinate pty ligand with one "dangling" pyridyl substituent, leaving three coordination sites for carbonyls. The IR spectrum of the ν_{CO} stretching region shows the familiar $2A' + A''$ pattern of the *facial* CO arrangement in an octahedron of approximate C_s symmetry. Our assignments are also in accordance with the observation that, in contrast to the $\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}$ spectrum, the $\text{Re}(\text{pty})(\text{CO})_3\text{Cl}$ absorption spectrum in MeOH changes with the addition of $(\text{HOCH}_2\text{CH}_2)_3\text{N}$.

Experimental details

Syntheses: *p*-(2,6-di-2-pyridyl-4-pyridyl)phenol (pty) was synthesized according to Spahni *et al.* [10]; yield after recrystallization from EtOH, 8.5%. To pty (600 mg, 1.84 mmol) in 6 ml of DMF at 120 $^\circ\text{C}$ was added in small portions 500 mg of $\text{Re}(\text{CO})_5\text{Cl}$ (1.38 mmol); CO evolution ceased after 10 min; the reaction was complete after an additional 20 min; the reaction mixture was cooled in ice-water and 9 ml of Et_2O were added; after 1 h of cooling orange crystals were collected by filtration and were recrystallized from hot EtOH with two drops of concentrated HCl added; the product was dried at 100 $^\circ\text{C}$ (350 mg, 0.55 mmol, 40.1% yield). Analysis: calculated, 45.7% C, 2.4% H, 6.7% N, 5.6% Cl; found, 44.0% C, 3.7% H, 7.8% N, 4.8% Cl. UV-visible,

MeOH (room temperature), ϵ ($l \text{ mol}^{-1} \text{ cm}^{-1}$), 21400 (308 nm), 20200 (334 nm), 10800 (378 nm).

Photochemistry. Solutions of $\text{Re}(\text{ptpy})(\text{CO})_3\text{Cl}$ at 25 °C were illuminated with a 450 W xenon high pressure arc lamp operated at 300 W through an IR water filter and a 389 nm cut-off filter; the total photoreactor volume was 126 ml; the solution volume was 30 ml, saturated with CO_2 (99.99%) for 20 min; the absence of CO_2 led to an absence of the product CO; CO concentration was determined from the photoreactor head space by gas chromatography on molecular sieve 4 Å with He as carrier gas.

Electrochemistry. Cyclic voltammograms of a $5 \times 10^{-4} \text{ M}$ $\text{Re}(\text{ptpy})(\text{CO})_3\text{Cl}$ solution in MeCN (0.1 M TBAH supporting electrolyte) were measured using a platinum disk electrode (0.13 cm^2) at 100 mV s^{-1} sweep rate vs. saturated calomel electrode (SCE); prior to measurement the analyte was either purged with argon or enriched with CO_2 .

Acknowledgments

We thank Professor M. Neuenschwander for helpful discussions of the NMR results. Financial support by the Schweizerische Bundesamt für Energiewirtschaft (grant BEW-EPA 217.307) and by the Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung (grant 20-28'528.90) is gratefully acknowledged.

- 1 J. Hawecker, J.-M. Lehn and R. Ziessel, *J. Chem. Soc., Chem. Commun.*, (1983) 536.
 - B. P. Sullivan and T. J. Meyer, *J. Chem. Soc., Chem. Commun.*, (1984) 1244.
 - 2 J. Hawecker, J.-M. Lehn and R. Ziessel, *J. Chem. Soc., Chem. Commun.*, (1984) 328.
 - B. P. Sullivan, C. M. Bolinger, D. Conrad, W. J. Vining and T. J. Meyer, *J. Chem. Soc., Chem. Commun.*, (1985) 1414.
 - 3 C. R. Cabrera and H. D. Abruña, *J. Electroanal. Chem.*, 209 (1986) 101.
 - T. R. O'Toole, B. P. Sullivan, M. R.-M. Bruce, L. D. Margerum, R. W. Murray and T. J. Meyer, *J. Electroanal. Chem.*, 259 (1989) 217.
 - 4 M. Furue, M. Naiki, Y. Kanematsu, T. Kushida and M. Kamachi, *Coord. Chem. Rev.*, in the press.
 - 5 R. Beer, G. Calzaferri, N. Gfeller, J. Li and B. Waldeck, *Proc. 44th Ann. Conf. IS&T, May 12-17, 1991, St. Paul, MN*, in the press.
 - R. Beer, G. Calzaferri, J. Li and B. Waldeck, *Coord. Chem. Rev.*, 111 (1991) 193.
 - 6 E. Amouyal, M. Moullem-Bahout and G. Calzaferri, *J. Phys. Chem.*, 95 (1991) 7641.
 - 7 E. W. Abel, G. B. Hargreaves and G. Wilkinson, *J. Chem. Soc.* (1958) 3149.
 - E. W. Abel and G. Wilkinson, *J. Chem. Soc.* (1959) 1501.
 - F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Interscience, New York, 1972, p. 708, 3rd edn.
 - 8 E. C. Constable, *Adv. Inorg. Chem. Radiochem.*, 30 (1986) 69, refs. 4, 79, 110, 162, 205 and 349.
 - 9 A. Juris, S. Campagna, I. Bidd, J.-M. Lehn and R. Ziessel, *Inorg. Chem.*, 27 (1988) 4007.
 - 10 W. Spahni and G. Calzaferri, *Helv. Chim. Acta*, 67 (1984) 450.
- Sadtler Handbook of Proton NMR Spectra (entry no. 44477M), and Sadtler Handbook of Infrared Spectra (entry no. 71498K), Sadtler Research Laboratories, Philadelphia, PA, 1987.