A New Pathway for Photobleaching of [*fac*-Re(bpy)$(CO)_3Br$] (bpy = 2,2′-bipyridine) by Triethylamine: Ethylation of the Bipyridine Ligand

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Irradiation of [*fac*-Re(bpy)$(CO)_3Br$] and triethylamine in *N,N*-dimethylformamide resulted in photobleaching of the complex to give the 5-ethyl-2,2′-bipyridine complex (**2**), the formation of which was affected by either Br^- or water.

The redox chemistry of [*fac*-Re(bpy)$(CO)_3Br$] (**1**) (bpy = 2,2′-bipyridine; X = Cl or Br) is of interest because of the capability of (**1**) to photocatalyse the reduction of CO_2 to CO by tertiary aliphatic amines.[1] Interestingly, the photocatalysis is accompanied by a photobleaching of the rhenium complexes,[1,2] which is attributed to the formation of a hydride complex,[1] a metalloformate complex,[1,3] and/or dinuclear complexes,[4] though the mechanistic details are still unclear. We have found another pathway for the photobleaching of [*fac*-Re(bpy)$(CO)_3Br$] by triethylamine (TEA), the ethylation of the bipyridine ligand.

Irradiation of an Ar-purged solution of (**1**) and TEA in *N,N*-dimethylformamide at $>\lambda$ 400 nm gave the 5-ethyl-2,2′-bipyridine complex (**2**) in 10—43% yields based on the quantity of (**1**) consumed, depending on reaction conditions, while very little evolution of H_2 or CO was observed as reported previously.[1] Diethylamine was also detected by g.l.c. Prolonged irradiation resulted in consumption of the (**2**) formed, accompanied by the formation of an unknown secondary product. As is shown in Table 1, the yield of (**2**) depends on the quantity of either water or Bu_4NBr added, reaching a maximum value in the presence of both water at 0.6—2.0 mol dm^{-3} and Bu_4NBr at 20—40 mmol dm^{-3}. Higher concentrations of either resulted in a decrease of the yield. When Bu_4NClO_4 was used in place of the ammonium bromide, the yield of (**2**) was essentially identical with that in the absence of the ammonium salt.

The structure of (**2**) was deduced from its spectroscopic properties.† This complex shows a u.v. absorption maximum at 386 nm in CH_2Cl_2 and i.r. absorption of the CO ligands at 2030, 1920, and 1900 cm^{-1} in tetrahydrofuran, which are almost identical with those of (**1**). The ^1H n.m.r. spectrum of (**2**) in $CDCl_3$ at 270 MHz shows signals for the ethyl protons at δ 1.38 (t), 2.83 (q), with *J* 7.6 Hz, and the seven aromatic protons at δ 7.51 (ddd, *J* 1.2, 5.5, 7.9 Hz, 5′-H), 7.89 (dd, *J* 1.8, 8.6 Hz, 4-H), 8.04 (dt, *J* 1.8, 7.9 Hz, 4′-H), 8.11 (d, *J* 8.5 Hz, 3-H), 8.15 (d, *J* 7.9 Hz, 3′-H), 8.89 (d, *J* 1.9 Hz, 6-H), and 9.06 (dd, *J ca.* 0.5, 5.5 Hz, 6′-H). The assignments are based on comparisons with the ^1H n.m.r. spectra of the free bipyridine ligand and (**1**) and with those of Os^{II} and Ir^{III} bipyridine complexes.[5] The ^{13}C n.m.r. spectrum of (**2**) reveals resonances for the three quarternary carbons at δ 144.01, 153.03, and 155.87 and for the CO resonances at δ 189.02 and 196.87 in a 1 : 2 intensity ratio.

The photoethylation of (**1**) by TEA can be interpreted in terms of Scheme 1. The proposed mechanism is similar to that suggested for the photosubstitution reactions of *p*-dicyano-

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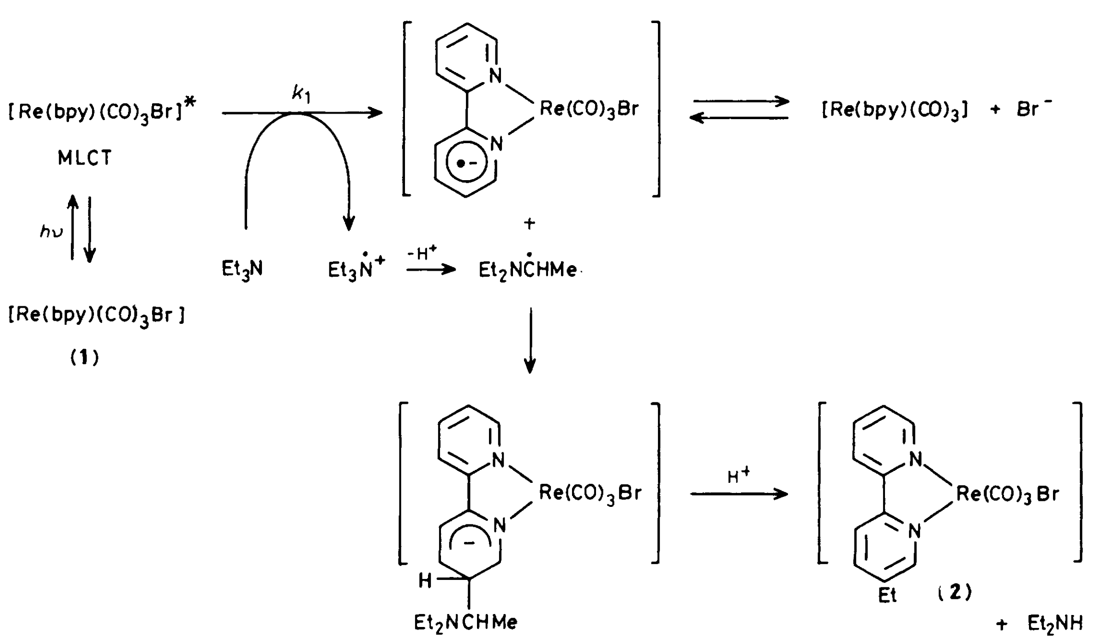
† Satisfactory elemental analyses were obtained.



Scheme 1. MLCT = metal to ligand charge transfer. $k_1 = 8 \times 10^7$ dm^3 mol^{-1} s^{-1}.

Table 1. Photoethylation of [*fac*-Re(bpy)$_3$(CO)$_3$Br] by TEA.[a]

Additive	Conversion/%	Yield of (2)[b]/%
None	51	22
[Bu_4NBr]/mmol dm^{-3}		
10	48	30
20	47	37
40	40	43
100	32	31
200	20	28
[H_2O]/mol dm^{-3} [c]		
0.6	53	43
1.8	60	40
3.0	64	39
6.0	40	32
12.0	20	11

[a] For 5 cm^3 solutions of *N,N*-dimethylformamide containing (1) (0.8—1.0 mmol dm^{-3}) and TEA (1.0 mol dm^{-3}) in the presence or absence of H_2O and Bu_4NBr irradiated through an $NaNO_2$ filter solution with a tungsten-halogen lamp (300 W) for 40—50 min at 20 ± 2 °C. [b] H.p.l.c. yields based on the quantity of (1) consumed. [c] [Bu_4NBr] 20 mmol dm^{-3}.

benzene[6] and methyl 4-phenylbenzoate[7] by TEA. Electron transfer from TEA to the luminescent state of (**1**) certainly occurs, since the luminescence of (**1**) is quenched by TEA at 8×10^7 dm^3 mol^{-1} s^{-1}, a rate constant very similar to that for electron transfer from triethanolamine.[2] The loss of a proton from TEA$^{\bullet+}$ is a known process to give $Et_2N\dot{C}HMe$, which then adds to the bpy ligand of (**1**$^{\bullet-}$). The final products, (**2**) and diethylamine, are readily formed by a proton-coupling reaction of the Meisenheimer-type adduct. The effect of Bu_4NBr on the formation of (**2**) may be due to inhibition of another competitive route from (**1**$^{\bullet-}$), Br$^-$ loss.[1,3,4]

The photoethylation is probably a consequence of the localisation of an odd electron of (**1**$^{\bullet-}$) on the bpy ligand. Therefore, a similar alkylation reaction should be involved in the photobleaching of (**1**) by triethanolamine, which is as efficient as that by TEA. No photobleaching of (**1**) occurred at all with either *N,N*-dimethylaniline or 1,4-diazabicyclo[2.2.2]octane, probably because of the stabilities of the cation radicals, which might favour charge recombination with (**1**$^{\bullet-}$) over deprotonation.

Finally, it should be noted that the formation of (**2**) decreased in a CO_2-saturated solution to one-third that in an Ar-purged solution, though the photobleaching of (**1**) was not affected by CO_2 saturation. This suggests that the photoethylation and the CO_2 photoreduction involve at least one common intermediate.

This work was supported by Grant-in-Aid for Special Project Research (No. 61123001) from the Ministry of Education, Science and Culture (Japan).

Received, 26th March 1987; Com. 383

References

1 J. Hawecker, J.-M. Lehn, and R. Ziessel, *J. Chem. Soc., Chem. Commun.*, 1983, 536.
2 C. Kutal, M. A. Weber, G. Ferraudi, and D. Geiger, *Organometallics*, 1985, **4**, 2161.
3 B. P. Sullivan and T. J. Meyer, *J. Chem. Soc., Chem. Commun.*, 1984, 1244.
4 B. P. Sullivan, C. M. Bolinger, D. Conrad, W. J. Vining, and T. J. Meyer, *J. Chem. Soc., Chem. Commun.*, 1985, 1414.
5 J. L. Kahl, K. Hanck, and K. DeArmond, *J. Inorg. Nucl. Chem.*, 1979, **41**, 495; R. E. DeSimone and R. S. Drago, *Inorg. Chem.*, 1969, **8**, 2517.
6 M. Ohashi, K. Miyake, and K. Tsujimoto, *Bull. Chem. Soc. Jpn.*, 1980, **53**, 1685.
7 K. Tsujimoto, Y. Inaba, and M. Ohashi, *Chem. Lett.*, 1983, 1113.