A Novel Type of Photosubstitution of [*fac*-Re(bpy)(CO)$_3$Br] (bpy = 2,2′-bipyridine) with P(OR)$_3$ in the Presence of Triethylamine: Efficient Formation of [Re(bpy)(CO)$_2${P(OR)$_3$}$_2$]$^+$Br$^-$

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Photochemical ligand substitution of [*fac*-Re(bpy)(CO)$_3$Br] with P(OEt)$_3$ in the presence of triethylamine quantitatively gave [Re(bpy)(CO)$_2${P(OEt)$_3$}$_3$]$^+$Br$^-$ without the intervention of a mono-substituted product.

The photo-redox chemistry of [*fac*-Re(L)(CO)$_3$X]$^{n+}$ (n = 0 or 1; L = diimine ligand; X = neutral or anionic monodentate ligand) in the presence of an aliphatic tertiary amine is of interest associated with the photoreduction of CO$_2$ to CO in *N*,*N*-dimethylformamide (DMF),[1] the photocatalytic H$_2$ evolution in tetrahydrofuran (THF)[2] or a heterogeneous suspension of hectorite clay mineral,[3] and the photoreduction of pyridyl ketones to the corresponding alcohols.[4] A key pathway of these photoredox reactions is thought to be the loss of X or CO following electron transfer from an amine to the luminescent state of the Re$^{\rm I}$ complexes.[1–5] It is known that one-electron reduction of Re$^{\rm I}$ complexes can induce the substitution of X with another ligand, but not that of a CO ligand.[1,6,7] In the present investigation, we have found a novel type of photosubstitution of [*fac*-Re(bpy)(CO)$_3$Br] **1** with P(OR)$_3$ in the presence of triethylamine (TEA) that gives [Re(bpy)(CO)$_2${P(OEt)$_3$}$_2$]$^+$Br$^-$ **2** in high yields.

Irradiation of a deaerated solution of **1** (1–5 mmol dm^{-3}), TEA (1.0 mol dm^{-3}), and P(OEt)$_3$ (20 mmol dm^{-3}) at >400 nm gave **2** in *ca.* 90% yield along with the evolution of 0.6–0.8 equivalents of CO in each solvent of acetonitrile, DMF, methanol or THF. The formation of **2** was linear with irradiation time up to *ca.* 30% conversion, while no other substituted Re$^{\rm I}$ product was detected by HPLC at all. Therefore, **2** appears to be the exclusive primary photoproduct. It was confirmed that **2** is not formed upon refluxing of a THF or acetonitrile solution in the dark nor upon irradiation in the absence of TEA. With other P(OR)$_3$ (R = Me, Bu and Ph), the photochemical ligand substitution of **1** again occurs to give the corresponding bis(phosphito)Re$^{\rm I}$ complexes in 70–90% yields.† The quantum yields for the

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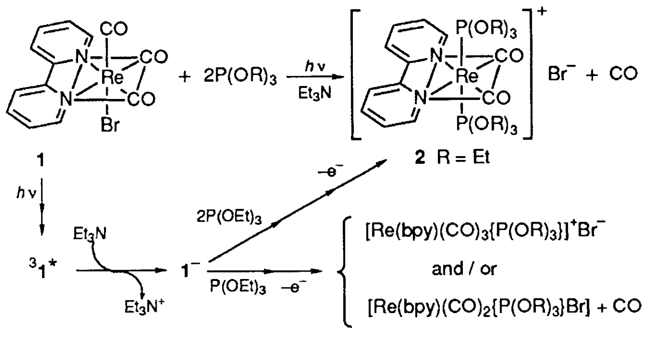
† Details of the photoproducts with other P(OR)$_3$ will be described in a full paper. Satisfactory elemental analysis of **2** was obtained.



formation of **2** at 405 nm are 0.71 for a degassed acetonitrile solution and 5.3×10^{-2} for a degassed THF solution of **1** (1.0 mmol dm^{-3}), TEA (1.0 mol dm^{-3}) and $P(OEt)_3$ (20 mmol dm^{-3}).

The structure of **2** was deduced from its spectroscopic properties;† λ_{max} (CH_2Cl_2) 378 nm (ε 4800); ν_{max}/cm^{-1} (KBr) 1945/1870 (CO ligands) and 940/780 (P–O); mass spectrum (FAB) *m/z* 731/729 (M^+ − Br); ^{1}H NMR (400 MHz; $CDCl_3$) δ 1.03 (t, 6 × CH_3), 3.77 (q, 6 × CH_2), 7.47 (ddd, 5/5′-H), 8.31 (dd, 4/4′-H), 8.31 (d, 3/3′-H) and 9.55 (d, 6/6′-H); ^{13}C NMR (400 MHz; $CDCl_3$) δ 15.95 (CH_3), 61.47 (CH_2), 126.27 (3/3′-C), 126.57 (5/5′-C), 139.90 (4/4′-C), 152.17 (6/6′-C), 156.51 (3/3′-C) and 199.30 (CO); ^{31}P NMR (160 MHz; $CDCl_3$) δ (*vs.* D_3PO_4) 116.99. The NMR data clearly indicate that **2** has a structure of C_{2v} symmetry, *i.e.* the axial *trans* configuration of the two $P(OEt)_3$ ligands.

The present photosubstitution reaction should be initiated by electron transfer from TEA to the luminescent state of **1**,[4] since the luminescence of **1** is quenched by TEA at 1×10^8 dm^3 mol^{-1} s^{-1} in acetonitrile and 5×10^7 dm^3 mol^{-1} s^{-1} in THF and since no reaction occurs in the absence of TEA. On the other hand, no luminescence quenching was observed with $P(OEt)_3$. The remarkable solvent dependence of quantum yield would arise, at least in part, from more efficient formation and a longer lifetime of free $\mathbf{1}^-$ in more polar acetonitrile compared with THF. In general, the one-electron reduction of $[Re(L)(CO)_3X]^{n+}$ (n = 0 or 1) results in the exchange of X with another ligand Y to give $[Re(L)(CO)_3Y]^{n+}$ (n = 0 or 1) as the final product after the loss of an electron from the substituted 19-electron species.[1,6,7] If the double substitution of the Br^- and CO ligands with $P(OR)_3$ proceeds by the initial loss of the Br^- ligand *via* $\mathbf{1}^-$, the mono-substituted 19-electron species $[Re(bpy)(CO)_3\{P(OR)_3\}]$ should undergo the substitution of the axial CO ligand with another $P(OR)_3$ before the loss of an electron. Alternatively, the double substitution would be the consequence arising from the initial substitution of a CO ligand with $P(OR)_3$ *via* $\mathbf{1}^-$.

Although details of the mechanism are still unclear, it should be noted that the evolution of CO in a CO_2-saturated DMF solution in the presence of $P(OEt)_3$ was as efficient as that in its absence at an early stage of the reaction but levelled off because of the efficient formation of **2** ineffective to the CO_2 photoreduction by TEA. The amount of CO evolved in the presence of $P(OEt)_3$ reached 140% based on the quantity of **1** used, twice as high as that in an Ar-purged solution, suggesting that CO_2 might react with $\mathbf{1}^-$ competitively with the $P(OEt)_3$ substitution or with an intermediate involved in the ligand substitution. On the other hand, $P(OEt)_3$ inhibits completely the photocatalytic evolution of H_2 in THF[2] and mostly the photoethylation of the bpy ligand by TEA.[8] Presumably, $P(OEt)_3$ would trap $\mathbf{1}^-$ before the generation of a hydride complex and much faster than a radical-coupling reaction of $\mathbf{1}^-$ with $Et_2N\dot{C}HMe$ generated by the loss of a proton from the cation radical of TEA.

The photochemical ligand substitution with $P(OR)_3$ provides a convenient method for the preparation of the bis(phosphito)Re^I complexes and a possible mechanistic probe for the redox photochemistry of **1** and related Re^I complexes.

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