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Preliminary communication

Photochemical generation of pyridine- and polypyridine-Co(I) complexes by visible light irradiation of $[Co(bpy)_3](BPh_4)_2$ and $[Co(py)_6](BPh_4)_2$

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Abstract

The $Co(bpy)_3^{2+}$ and $Co(py)_6^{2+}$ complex cations form ion pairs with BPh_4^- counter-anions in pyridine solution. Excitation of the charge-transfer absorption band of the ion pair produces the corresponding Co(I) complexes, BPh_4^- being the electron source.

Deep blue Co(I) polypyridine and pyridine complexes are of interest in a number of contexts. $Co(bpy)_3^+$ (**1**) can reduce H_2O [1] and CO_2 [2,3] and can be produced by reduction of $Co(bpy)_3^{2+}$ with $NaBH_4$ [4], or by electrochemical [5], pulse-radiolytic [6], and photochemical [1,2] methods. The last method is of particular interest and requires use of $Ru(bpy)_3^{2+}$ as a photosensitizer and a tertiary amine as a sacrificial electron donor. $Co(py)_6^+$ (**2**) also reduces H_2O and CO_2 in pyridine solution [7], and is active in promoting catalytic cyclotrimerization [8] and hydro-oligomerization [9] of alkynes. Until now the only viable method for generating **2** involved dissolving $(\eta^6\text{-}BPh_4)Co(py)_2$ in neat pyridine [7], but the synthesis of this parent compound is rather complex. We report here a direct photochemical method for the generation of both **1** and **2** that makes them readily accessible reagents.

Serendipitously, we observed that pyridine solutions containing $[Co(bpy)_3](BPh_4)_2$ or $[Co(py)_6](BPh_4)_2$ (**3**) turn blue on sunlight exposure, indicating that photochemical Co(II) reduction takes place in the absence of added sensitizer. The formation of **1** and **2** was monitored spectrophotometrically by use of their characteristic absorptions at 630 and at 780 nm [7], respectively; TLC analysis (SiO_2, n-hexane) of the solution indicated the presence of diphenyl as oxidized counterpart. We conclude that in both cases the photoredox process can be formulated as shown for **3** in eq. 1

$$\underset{(3)}{[Co(py)_6](BPh_4)_2} \xrightarrow{h\nu,\ py} \underset{(2)}{[Co(py)_6](BPh_4)} + \tfrac{1}{2}\ Ph_2 + py \cdot BPh_3 \qquad (1)$$

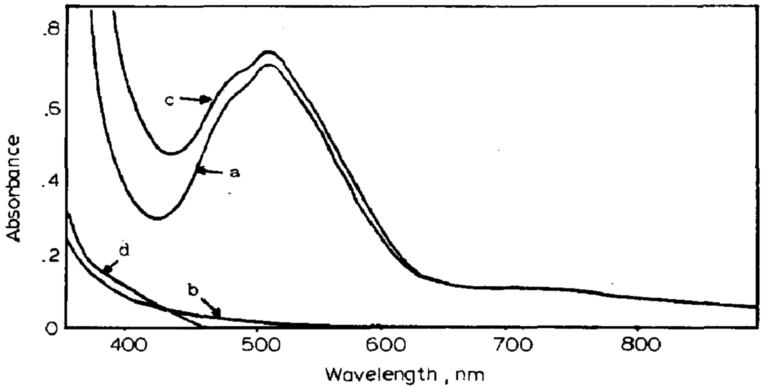

Fig. 1. Spectra of pyridine solutions of $Co(py)_6(BPh_4)_2$ in the absence and in the presence of excess $NaBPh_4$: a, $[Co(py)_6(BPh_4)_2] = 2.4 \times 10^{-2}$ *M*; b, $[NaBPh_4] = 2.4 \times 10^{-1}$ *M*; c, $[Co(py)_6(BPh_4)_2] = 2.4 \times 10^{-2}$ *M*, $[NaBPh_4] = 2.4 \times 10^{-1}$ *M*; d, line given by subtraction of spectra b and a from c.

Subsequent experiments were carried out on 0.03 *M* pyridine solutions of **3** with a 150 W slide projector equipped with interference filters for wavelength selection as light source. Although **3** has an absorption maximum at 510 nm (Fig. 1a), we found that light centered at about 500 nm was inactive, the photoredox process requiring irradiation at about 400 nm. In this region a charge-transfer ion pair can be observed (Fig. 1d) when a tenfold excess of $NaBPh_4$ is present. From these observations we infer that the photoredox electron transfer is a consequence of a charge-transfer excitation of the $Co(py)_6{}^{2+}$,$BPh_4{}^-$ ion pair. There are other examples in which the $BPh_4{}^-$ anion is irreversibly oxidized when excited in a charge-transfer ion pair [10,11,12].

Temperature markedly affects process (1). For generation of **2** on irradiation at 400 nm the quantum yields were 0.051, 0.077, and 0.29 at 5, 25, and 50 °C, respectively. For the formation of **1**, the quantum yields were 0.016 at 25 °C and 0.037 at 50 °C.

Photogeneration of **2** can thus be very easily brought about. Owing to the interesting chemistry shown by **2**, we examined some of its known stoichiometric reactions and catalytic processes by exposing pyridine solutions of **3** to sunlight.

1. A 0.04 *M* pyridine solution (100 ml) of **3** under an atmosphere of CO was exposed to sunlight for 2 weeks in a 1000 ml flask. The colour changed from pink to reddish-brown. IR analysis of the solution showed an absorption band (1890 cm^{-1}) in the CO stretching region attributable to $Co(CO)_4{}^-$. The photochemical synthesis of a metal carbonyl from a coordination compound is rather uncommon [13]. In our case the formation of $Co(CO)_4{}^-$ anion probably occurs by disproportionation of **2** induced by CO, as described in ref. 7.

2. Hex-1-yne (1 ml) was added to 10 ml of a 0.03 *M* pyridine solution of **3** under an inert atmosphere in a Pyrex Schlenk tube, which was exposed to sunlight for 5 hours. GLC analysis revealed that there had been quantitative conversion of the starting alkyne into 1,3,5- and 1,2,4- tributylbenzene (1 : 2 molar ratio). As far as we know this is the first example of a photoinduced cyclotrimerization of alkynes.

3. Diphenylacetylene (0.5 g) was added to 25 ml of a 0.01 *M* pyridine solution of **3** stirred under H_2 in a Pyrex Schlenk tube, which was exposed to sunlight for 3 days. GLC analysis showed that 80% of the alkyne had reacted. (*E*,*Z*)-1,2,3,4-tetra-

phenyl-butadiene [14] in 50% yields was identified in the reaction mixture by ^1H NMR. Such a hydro-dimerization of diphenylacetylene differs from that carried out thermally in the presence of preformed **2** [9], which gave (*E*,*E*)-1,2,3,4-tetraphenylbutadiene in quantitative yield. Presumably, even in the photochemical reaction the primary product is the (*E*,*E*)-isomer, which undergoes further photochemical reaction. Irradiation with sunlight of a pyridine solution of (*E*,*E*)-1,2,3,4-tetraphenylbutadiene does in fact give a mixture of organic products containing the (*E*,*Z*)-isomer.

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