Di-2-pyridyl Ketone Complexes of Copper(I): Efficient Photocatalysts for Norbornadiene–Quadricyclane Conversion

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Copper(I) complexes of di-2-pyridyl ketone (dpk), $[Cu(PPh_3)_2(dpk)]NO_3$, $[Cu_2I_2(PPh_3)_2(dpk)]$, and $[Cu_4I_4(dpk)_3]$, have been synthesized. The compounds were characterized by analytical and spectroscopic data. Their photocatalytic activity for the solar energy storage reaction norbornadiene (bicyclo[2.2.1]hepta-2,5-diene) to quadricyclane (tetracyclo$[3.2.0.0^{2,7}.0^{4,6}]$heptane) has been studied. The species $[Cu(dpk)_2]^+$, generated *in situ* from $[Cu(CH_3CN)_4]^+$ and dpk, was found to be a stable photocatalyst at $\lambda > 320$ nm.

The photoisomerization of norbornadiene (bicyclo[2.2.1]hepta-2,5-diene, nbd) to quadricyclane (tetracyclo$[3.2.0.0^{2,7}.0^{4,6}]$-heptane, q) has been of considerable interest in recent times as a solar energy storage process.[1–7] Since norbornadiene itself does not absorb at the wavelength of solar radiation, much effort has gone into finding a suitable catalyst that will absorb sunlight and sensitize the nbd to q transformation.[3–7] Among the transition-metal complexes, copper(I) compounds have been found to be the most promising catalysts for sensitization of nbd/q transformation.[3] We have studied di-2-pyridyl ketone (dpk) as a ligand for our copper(I) complexes, as the extended conjugation through the C=O group should provide a low-energy M→L charge-transfer absorption in the visible region. In this paper, we report the synthesis and characterization of new copper(I) complexes of di-2-pyridyl ketone and their photocatalytic activity for nbd/q transformation.

Experimental

All reactions were carried out with dry, oxygen-free solvents under a nitrogen atmosphere. Elemental analysis was performed on a Carlo Erba 1106 instrument and i.r. spectra recorded on a Perkin-Elmer 781 spectrophotometer. A Pye-Unicam SP 8-100 instrument was used to record u.v.–visible spectra of the compounds. The compounds $[Cu(CH_3CN)_4]ClO_4$, $[Cu(PPh_3)_2]NO_3$, and $[\{CuI(PPh_3)\}_4]$ were prepared by literature methods.[8] Di-2-pyridyl ketone was purchased from Aldrich and used without further purification.

Preparation of $[Cu(PPh_3)_2(dpk)]NO_3$.—The compound $[Cu(PPh_3)_2]NO_3$ (0.325 g, 0.5 mmol) was dissolved in CH_2Cl_2 (15 cm^3) and di-2-pyridyl ketone (0.092 g, 0.5 mmol) was added to the solution with stirring. The colour of the solution changed immediately to orange-red and stirring was continued for 15 min. The solvent was then removed under vacuum. The solid obtained was repeatedly washed with acetone and crystallized from CH_2Cl_2 by slow evaporation under N_2 (Found: C, 68.0; H, 4.6; N, 5.5. Calc. for $C_{47}H_{38}CuN_3O_4P_2$: C, 67.7; H, 4.6; N, 5.0%). $\lambda_{max.}(CH_2Cl_2)$: 424 nm (ε 480 dm^3 mol^{-1} cm^{-1}).

Preparation of $[Cu_2I_2(PPh_3)_2(dpk)]$.—The compounds $[\{CuI(PPh_3)\}_4]$ (0.181 g, 0.1 mmol) and di-2-pyridyl ketone (0.055 g, 0.3 mmol) were dissolved in degassed $CHCl_3$ (40 cm^3) and refluxed under N_2 with stirring for half an hour. A dark red solid was obtained on removing the solvent under vacuum. It was washed with acetone and crystallised from hexane by slow evaporation (Found C, 52.3; H, 3.7; N, 2.7. Calc. for $C_{47}H_{38}Cu_2I_2N_2OP_2$: C, 51.9; H, 3.5; N, 2.6%). $\lambda_{max.}(CH_2Cl_2)$: 480 (ε 680), 354 nm (ε 1 710 dm^3 mol^{-1} cm^{-1}).

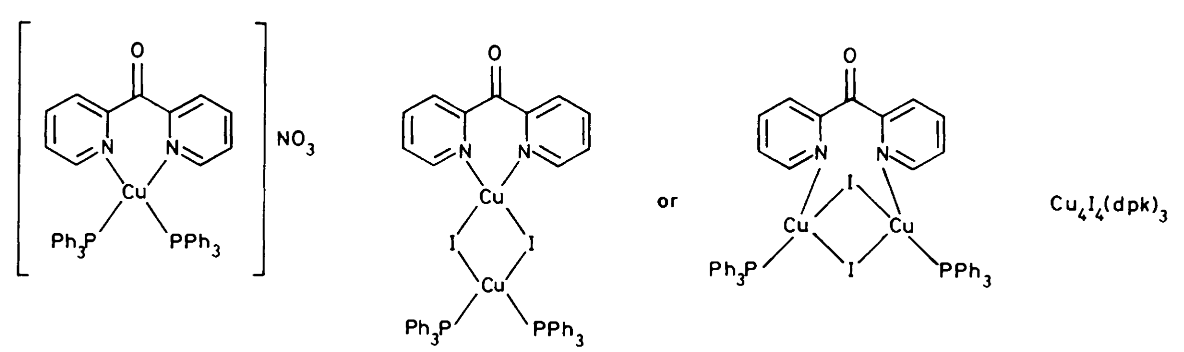
Preparation of $[Cu_4I_4(dpk)_3]$.—Di-2-pyridyl ketone (0.276 g, 1.5 mmol) was dissolved in acetone (25 cm^3) and CuI (0.190 g, 1 mmol) was added slowly, with stirring, to the solution. The colour of the solution changed to red and a dark red solid precipitated. Stirring was continued for 5 min and then the red solid was filtered off. It was washed repeatedly with acetone and then crystallized from CH_2Cl_2 as dark red crystals (Found: C, 30.2; H, 1.9; N, 6.4. Calc. for $C_{33}H_{24}Cu_4I_4N_6O_3$: C, 30.1; H, 1.8; N, 6.4%). $\lambda_{max.}(CH_2Cl_2)$: 365 nm (ε 1 470 dm^3 mol^{-1} cm^{-1}).

Photochemical Reaction and Analysis.—All solutions were prepared under N_2 and the solvent was carefully deoxygenated by a nitrogen stream before use. In a typical run, copper(I) catalyst (2×10^{-3} mol dm^{-3}) and 0.4 mol dm^{-3} nbd were dissolved in CH_2Cl_2 and irradiated in a Hannovia Photochemical reactor using a 200-W high-pressure mercury lamp surrounded by a Pyrex absorption sleeve. The sleeve, obtained from Ace glass, had 50% transmittance at 320 nm. The quadricyclane formed was analysed by g.l.c. on a Shimadzu GC-9A gas chromatograph using a 7 ft × 5 mm SE-30 column and a flame ionization detector.

Quantum Yields.—Quantum yield determinations were carried out using an optical bench equipped with a water-cooled lamp housing (Photochemical Research Associates, model ALH 215), a 100-W high-pressure mercury arc lamp (Osram HBo 100 W/2), and a monochromator (Photochemical Research Associates, model B 102). Dichloromethane solutions containing 2×10^{-3} mol dm^{-3} copper(I) catalyst and 0.4 mol dm^{-3} nbd were photolysed under N_2 with 313-nm light in a special 1-cm u.v.–visible spectrophotometer cell obtained from Hellma for anaerobic work. In all cases the solutions absorbed 99% of the light. Light intensities were measured by ferrioxalate actinometry.[9] The quantum yields reported here were determined by averaging three quantum yields calculated between 1 and 2% q formation, for the nbd concentration specified.

Results and Discussion

The copper(I) complexes of di-2-pyridyl ketone (dpk), **(1)**—**(3)** are shown in Figure 1. Complex **(1)** was synthesized by treating $[Cu(PPh_3)_2]NO_3$ with dpk in CH_2Cl_2 under N_2 (see Experimental section). Conductivity studies in dmf (dimethylformamide) indicate the compound to be a 1:1 electrolyte. The compound has a strong absorption band at 424 nm (Figure 2)



(1) **(2a)** **(2b)** **(3)**

Figure 1. The Cu^I-dpk complexes

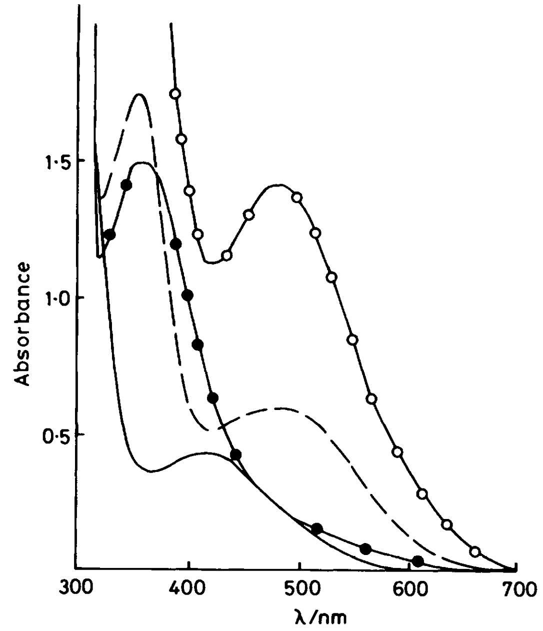


Figure 2. Electronic absorption spectra of 1×10^{-3} mol dm^{-3} solutions in CH_2Cl_2: $[Cu(PPh_3)_2(dpk)]NO_3$ (——); $[Cu_2I_2(PPh_3)_2(dpk)]$ (- - -); $[Cu_4I_4(dpk)_3]$ (●); $[Cu(CH_3CN)_4]^+$–dpk (1:4) (○)

Table. Photochemical isomerization of nbd to q in the presence of copper(I) catalysts

Catalyst	% q after 12 h[a]	Turnover number[b]	Quantum yield[c]
$[Cu(PPh_3)_2(dpk)]NO_3$	7.2	14	0.17
$[Cu_2I_2(PPh_3)_2(dpk)]$	15.9	32	0.25
$[Cu(PPh_3)(bipy)Cl]$	0.45	1	0.063[d]
$[Cu_4I_4(dpk)_3]$[e]	17.0	34[e]	0.36
$[Cu(CH_3CN)_4]^+$ + dpk (1:2)	2.4	5	
(1:4)	8.5	17.0	0.22

[a] All irradiations were performed for 12 h using a high-pressure mercury lamp with a Pyrex filter (λ > 320 nm) in CH_2Cl_2 solvent; [nbd] = 0.4, [catalyst] = 2×10^{-3} mol dm^{-3}. [b] Moles of q after 12 h/moles of catalyst. [c] Determined at 313 nm using an optical bench. [d] Taken from ref. 7. [e] Most of the compound remained insoluble in CH_2Cl_2. Since we used the supernatant liquid, the actual copper(I) concentration is much lower than 0.002 mol dm^{-3}. The turnover number here represents the lower limit.

which can be assigned to a Cu→dpk π* c.t.t.l. (charge-transfer-to-ligand) transition. The insignificant shift of the carbonyl-stretching frequency ν_{CO} (1 680 cm^{-1}) in the i.r. spectrum of the compound from that of free di-2-pyridyl ketone (1 690 cm^{-1}) points to *N,N*-co-ordination of the ligand.[10] On the basis of i.r., u.v.–visible, conductivity, and analytical data, the compound is formulated as $[Cu(PPh_3)_2(dpk)]NO_3$ having the structure shown in Figure 1.

Refluxing $[\{CuI(PPh_3)\}_4]$ with dpk in $CHCl_3$ produced compound (**2**) in good yield. Conductivity studies in dmf showed the compound to be a non-electrolyte and its i.r. spectrum had ν_{CO} at 1 678 cm^{-1}, indicating *N,N*-co-ordination. The compound, on the basis of its analytical and conductivity data, is formulated as $[Cu_2I_2(PPh_3)_2(dpk)]$. Two alternative structures, (**2a**) and (**2b**) as shown in Figure 1, are possible. The u.v.–visible spectrum of the compound has strong absorption bands at 480 and 354 nm (Figure 2). Copper(I)–pyridine compounds typically have a Cu→py (py = pyridine) charge-transfer transition at 310 nm.[4] Consequently the low-energy band at 480 nm is indicative of di-2-pyridyl ketone acting as a chelating $\widehat{N\,N}$ donor to one copper(I) centre, rather than as a bridging ligand with pyridine-like co-ordination to two such centres. Although on the basis of the u.v.–visible spectrum structure (**2a**) seems more likely, a clear choice is not possible. Attempts are underway to grow single crystals of this compound for structural determination.

Reaction of CuI with dpk produced compound (**3**) as a dark red solid which is a non-electrolyte in dmf. It has an absorption band at 365 nm (Figure 2) and its i.r. spectrum has ν_{CO} at 1 670 cm^{-1}. On the basis of analytical data, the compound is best formulated as $[Cu_4I_4(dpk)_3]$. It has very low solubility in most organic solvents which is in agreement with a tetrameric structure. However, a definitive structural assignment will be possible only after *X*-ray structure determination, which is being attempted.

Catalytic Studies.—Norbornadiene (0.4 mol dm^{-3}) and the copper(I) catalysts (2×10^{-3} mol dm^{-3}) in CH_2Cl_2 solvent were irradiated with Pyrex-filtered light from a 200-W high-pressure mercury lamp and the results are given in the Table. The Pyrex filter had 50% transmittance at 320 nm ensuring that the reaction was carried out with visible light. The absorption spectra of (**1**)—(**3**) in the visible region remained unaltered on addition of excess of nbd, indicating that ground-state complex formation does not take place. Consequently, the sensitization mechanism with these catalysts must be through bimolecular energy transfer from the excited copper(I) complexes to the ground state of nbd. Such a sensitization mode is well documented in the literature.[3] U.v.–visible spectral changes in the photocatalytic reactions with **(1)**—**(3)** indicated partial decomposition of the catalysts at the end of the photolysis in each case.

For the sake of comparison, photolysis under identical conditions was also carried out with $[Cu(PPh_3)(bipy)Cl]$ (bipy = 2,2′-bipyridyl), which has been reported earlier to be an effective photocatalyst under visible light for nbd/q transformation.[7] As seen from the results in the Table, di-2-pyridyl ketone complexes of Cu^I proved to be much more efficient catalysts for this process. The quantum yields for nbd/q isomerization were determined separately at 313 nm for all the complexes in CH_2Cl_2 and are given in the Table.

In some experiments, the photocatalyst was generated *in situ* from $[Cu(CH_3CN)_4]^+$ and dpk. Addition of dpk to a CH_2Cl_2 solution of $[Cu(CH_3CN)_4]^+$ immediately gave a dark red colour suggesting complexation of dpk to Cu^I. The u.v.–visible spectrum of the solution has an intense absorption maximum at 494 nm (ε 1 400 $dm^3 mol^{-1} cm^{-1}$) which can be assigned to a Cu⟶dpk π^* c.t.t.l. transition. The similarity of the absorption spectrum with that reported for $[CuL_2]^+$ (L = 2,2′-bipyridyl, 1,10-phenanthroline, and their derivatives) complexes[11] suggests the compound to be $[Cu(dpk)_2]^+$. The results obtained on photolysis of nbd in the presence of $[Cu(CH_3CN)_4]^+$ and dpk are given in the Table. They show that the catalytic activity depends on the dpk:$[Cu(CH_3CN)_4]^+$ molar ratio and is highest for dpk:$[Cu(CH_3CN)_4]^+$ = 4:1. The absorption spectrum of the dpk–$[Cu(CH_3CN)_4]^+$ solution (dpk:Cu = 4:1) was unaltered on addition of nbd indicating no complex formation and remained unchanged at the end of the photolysis period. This clearly shows that the catalyst in this case was considerably more photostable than the other Cu^I–dpk complexes.

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References

1 D. J. Fite, W. M. Moore, and K. W. Morse, *J. Am. Chem. Soc.*, 1985, **107**, 7077.

2 R. R. Hautala, J. Little, and E. Sweet, *Sol. Energy*, 1977, **19**, 503; G. Jones, T. E. Reinhardt, and W. R. Bergmark, *ibid.*, 1978, **20**, 241; G. Jones, S. Chiang, and P. T. Xnan, *Photochemistry*, 1978, **10**, 1.

3 C. Kutal, D. P. Schwendiman, and P. Grutsch, *Sol. Energy*, 1977, **19**, 651; D. P. Schwendiman and C. Kutal, *J. Am. Chem. Soc.*, 1977, **99**, 5677; *Inorg. Chem.*, 1977, **16**, 719; P. A. Grutsch and C. Kutal, *Adv. Chem. Ser.*, 1978, **168**, 158; *J. Am. Chem. Soc.*, 1979, **101**, 4228; C. Kutal and P. A. Grutsch, *Adv. Chem. Ser.*, 1979, **173**, 325; C. Kutal in, 'Solar Energy Chemical Conversion and Storage,' eds. R. R. Hautala, R. B. King, and C. Kutal, Humena Press, Clifton, 1979; R. F. Sterling and C. Kutal, *Inorg. Chem.*, 1980, **19**, 1502; S. W. Orchard and C. Kutal, *Inorg. Chim. Acta*, 1982, **64**, 195.

4 N. Borsub, S. Chang, and C. Kutal, *Inorg. Chem.*, 1982, **21**, 538.

5 K. Maruyama, K. Terada, and Y. Yamamoto, *J. Org. Chem.*, 1981, **46**, 5294.

6 S. Salzaki, K. Ohkubo, F. Fujiiwara, and A. Ohyoshi, *J. Mol. Catal.*, 1982, **16**, 181.

7 K. Maruyama, K. Terada, Y. Naruta, and Y. Yamamoto, *Chem. Lett.*, 1980, 1259.

8 P. Hemmerich and C. Sigwart, *Experientia*, 1963, **19**, 488; *Inorg. Synth.*, 1979, **19**, 93; *Inorg. Chem.*, 1972, **11**, 1818.

9 C. G. Hotchard and C. A. Parker, *Proc. R. Soc. London, Ser. A*, 1956, **235**, 518.

10 R. R. Osborne and R. W. McWhinnie, *J. Chem. Soc. A*, 1967, 2075.

11 S. Sakai, I. Okitaka, and K. Ohkubo, *Inorg. Chem.*, 1984, **23**, 198.

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