Designing Copper(I) Photosensitizers for the Norbornadiene−Quadricyclane Transformation Using Visible Light: An Improved Solar Energy Storage System

Federico Franceschi,[†] Massimo Guardigli,[†] Euro Solari,[†] Carlo Floriani,*[,†] Angiola Chiesi-Villa,[‡] and Corrado Rizzoli[‡]

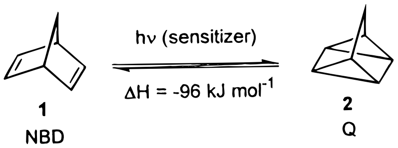
Institut de Chimie Minérale et Analytique, BCH, Université de Lausanne, CH-1015 Lausanne, Switzerland, and Dipartimento di Chimica, Università di Parma, I-43100 Parma, Italy

Received May 22, 1997[⊗]

Four copper(I) complexes have been designed as photosensitizers for assisting the norbornadiene (NBD) → quadricyclene (Q) isomerization with the purpose of carrying out the reaction using visible light and achieving a high NBD/photocatalyst turnover. All complexes contain π-delocalized bidentate $N\frown O$ monoanionic ligands. Their syntheses have been performed either by the metathesis reaction from CuCl or by reaction of the monoprotic ligands with Cu_5Mes_5 (Mes ≡ 2,4,6-$Me_3C_6H_2$) in the presence of norbornadiene. The dinuclear complexes $[Cu_2L_2(\mu\text{-NBD})]$, **3**, $[Cu_2L'_2(\mu\text{-NBD})]$, **4**, $[Cu_2L''_2(\mu\text{-NBD})]$, **5**, and $[Cu_2L'''_2(\mu\text{-NBD})]$, **6** [where L = 2-methyl-8-oxoquinolinato, L′ = 2-methyl-5,7-dichloro-8-oxoquinolinato, L″ = 4-oxoacridinato, and L‴ = 2-(2-oxo-3,5-di-*tert*-butyl phenyl)benzotriazole], have been isolated and characterized in the solid state, including the X-ray analysis on **3** and **6**. All compounds show absorption in the visible spectrum, due to the presence of metal-to-ligand charge-transfer (MLCT) bands. Most were active in assisting the NBD → Q conversion, although the best results were obtained in the case of **3**, for which we give a detailed report. Complex **3** is the precursor, in the presence of NBD, of the photoactive monomeric species [CuL(NBD)], **9**, where a single C═C binds copper(I), of which complex **7**, [CuL(NBN)] [NBN ≡ norbornene], can be regarded as a model compound. The NBD photoisomerization assisted by **3** (see **9**) has been carried out in methanol by visible light irradiation ($\lambda = 405$ nm) with a photoisomerization quantum yield of 0.029. Turnover numbers (moles of Q produced/mole of photocatalyst) of *ca.* 5000 were obtained in this solvent. An increase of the temperature gave rise to a significative quantum yield enhancement. The other compounds were less efficient than **3** in assisting the NBD → Q photoisomerization under visible light irradiation, most probably due to the low energy of their MLCT excited states.

Introduction

Scheme 1



A very chemical approach to the problem of solar energy storage involves the photochemical conversion of an unstrained to a strained molecule,[1] which can in turn release thermal energy in the reverse catalyzed process. This approach is exemplified by the norbornadiene (NBD, **1**)/quadricyclene (Q, **2**) system[2] (Scheme 1) whereby the conversion between the two species is accompanied by the formation and cleavage of two C−C bonds.

The availability of **1** and the large enthalpy variation ($\Delta H_{2\rightarrow1} = -96$ kJ mol^{-1})[3] of the reaction make this process particularly attractive. However, NBD does not absorb above 300 nm;[4] thus a suitable sensitizer is required in order to obtain the NBD → Q isomerization under visible light irradiation. Indeed, the **1** → **2** photoconversion is assisted, other than by organic sensitizers,[5] by a variety of transition metal complexes,[6−9] although the most successful and widely employed have been copper(I)−halo[7e,f] and copper(I)−phosphane[7a−c,8b,c,f,g] derivatives. This

---

* To whom correspondence should be addressed.

[†] University of Lausanne.

[‡] University of Parma.

[⊗] Abstract published in *Advance ACS Abstracts,* August 15, 1997.

(1) (a) Kutal, C. *Sci. Pap. Inst. Phys. Chem. Res. (Jpn.)* **1984**, *78*, 186. (b) Yoshida, Y.; Miki, S.; Hijiya, T.; Asaka, Y. *Bull. Soc. Chim. Belg.* **1982**, *91*, 469. (c) Jones, G.; Chiang, S. H.; Xuan, P. T. *J. Photochem.* **1979**, *10*, 1. (d) Laird, T. *Chem. Ind. (London)* **1978**, *6*, 186. (e) Jones, G.; Reinhard, T. E.; Bergmark, W. R. *Sol. Energy* **1978**, *20*, 241.

(2) For a recent review dealing with several aspects concerning the use of NBD in solar energy storage, see: Bren', V. A.; Dubunosov, A. A.; Minkin, V. I.; Chernoivanov, V. A. *Russ. Chem. Rev.* **1991**, *60*, 451.

(3) This is an average value. For the single experimental determinations, see: (a) Harel, Y.; Adamson, A. W.; Kutal, C. *J. Phys. Chem.* **1987**, *91*, 901. (b) Maruyama, K.; Tamiaki, H.; Kawabata, S. *J. Chem. Soc., Perkin Trans. 2* **1986**, 543. (c) Ragharachari, K.; Haddon, R. C.; Roth, H. D. *J. Am. Chem. Soc.* **1983**, *105*, 3110. (d) Rogers, D. W.; Choi, L. S.; Girellini, R. S.; Holmes, T. J.; Allinger, N. L. *J. Phys. Chem.* **1980**, *84*, 1810. (e) Steele, W. V. *J. Chem. Thermodyn.* **1978**, *10*, 919. (f) Wiberg, K. B.; Connon, H. A. *J. Am. Chem. Soc.* **1976**, *98*, 5411. (g) Kabakoff, D. S.; Bünzli, J.-C. G.; Oth, J. M. F.; Hammond, W. B.; Berson, J. B. *J. Am. Chem. Soc.* **1975**, *97*, 1510. (h) Hall, H. K., Jr.; Smith, C. D.; Baldt, J. H. *J. Am. Chem. Soc.* **1973**, *95*, 3197. (i) Turner, R. B.; Goebel, P.; Mallon, B. J.; von Doering, W. E.; Coburn, J. F.; Pomeranz, M. *J. Am. Chem. Soc.* **1968**, *90*, 4315.

(4) Dilling, W. L. *Chem. Rev.* **1966**, *66*, 373 and references therein.

(5) (a) Nishimura, Y.; Oishi, S.; Sakuragi, H.; Tokumaru, K. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 2937. (b) Taoda, H.; Hayakawa, K.; Kawase, K. *J. Chem. Eng. Jpn.* **1987**, *20*, 335. (c) Arai, T.; Wakabayashi, T.; Sakuragi, H.; Tokumaru, T. *Chem. Lett.* **1985**, 279. (d) Barwise, A. J. G.; Gorman, A. A.; Leyland, R. L.; Smith, P. G.; Rodgers, M. A. J. *J. Am. Chem. Soc.* **1978**, *100*, 1814. (e) Hammond, G. S.; Wyatt, P.; DeBoer, C. D.; Turro, N. J. *J. Am. Chem. Soc.* **1964**, *86*, 2532. (f) Hammond, G. S.; Fischer, A.; Turro, N. J. *J. Am. Chem. Soc.* **1961**, *83*, 4674.

(6) Kutal, C. *Adv. Chem. Ser.* **1978**, *168*, 158.

(7) (a) Onishi, M.; Hiraki, K. *Inorg. Chim. Acta* **1992**, *202*, 27. (b) Onishi, M.; Hiraki, K.; Itoh, H.; Eguchi, H.; Abe, S.; Kawato, T. *Inorg. Chim. Acta* **1988**, *145*, 105. (c) Borsub, N.; Chang, S.-C.; Kutal, C. *Inorg. Chem.* **1982**, *21*, 538. (d) Sterling, R. F.; Kutal, C. *Inorg. Chem.* **1980**, *19*, 1502. (e) Schwendiman, D. P.; Kutal, C. *J. Am. Chem. Soc.* **1977**, *99*, 5677. (f) Schwendiman, D. P.; Kutal, C. *Inorg. Chem.* **1977**, *16*, 719.

work has been mainly pursued by C. Kutal. However, a number of relevant questions have yet to be answered.

(1) The appropriate coordination environment of copper(I) binding NBD has so far been disregarded. In fact, the search for an ancillary ligand which can act as an efficient photosensitizer when bound to copper(I) has been neglected. In this context, the isolation of a copper(I)−NBD complex in $[CuCl(NBD)]_4$[10] is not particularly relevant because of the absence of any potential photosensitizer in the coordination environment of copper(I) and the lack of information on the copper(I)−NBD fragment present in solution.

(2) To date the light source employed in the **1** → **2** metal-assisted photoconversion is not quite in the visible region, and no data are available using light with $\lambda > 400$ nm. To overcome this problem, substituted NBDs which absorb in the visible region have been employed.[8d,11] However, these also have major disadvantages, such as the limited availability of starting materials and, in many cases, the significant lowering of the isomerization enthalpy change.

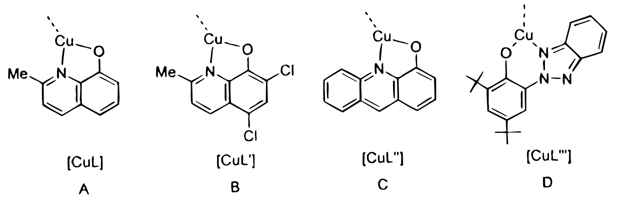
(3) The copper(I)-assisted **1** → **2** photoconversion is usually characterized by limited turnover numbers. Although the data in the literature are vague, the highest value is around 400.[7e]

(4) The search for a catalyst for the reverse **2** → **1** thermal reaction has been overlooked.

In an attempt to address these issues we have investigated a series of copper(I)−organic fragments which successfully bind NBD. Four of the more significant contain the 2-methyl-8-oxoquinolinato (A), the 2-methyl-5,7-dichloro-8-oxoquinolinato (B), the 4-oxoacridinato (C), and the 2-(2-oxo-3,5-di-*tert*-butyl phenyl)benzotriazole (D) bidentate monoanions, shown in Scheme 2.

The copper(I) fragments A−D have characteristic absorptions in the visible region due to charge-transfer transitions involving copper(I) and the ligand. These species are therefore potential sensitizers in the visible region, allowing the **1** → **2** photoisomerization to occur literally in sunlight. Indeed, using the copper(I) fragment A as sensitizer we obtain NBD → Q isomerization with the highest turnover numbers ever observed for a copper(I)-assisted reaction.

Scheme 2



Experimental Section

General Procedure. All reactions were carried out under an atmosphere of purified nitrogen. Solvents were dried and distilled before use by standard methods. Infrared spectra were recorded with a Perkin-Elmer FT 1600 spectrophotometer. UV−vis spectra were recorded with a Hewlett-Packard 8452A diode array spectrophotometer. NMR spectra were recorded on a 200-AC or a 400-DPX Bruker instrument. GC analyses were carried out using a HP 5890 Series II system equipped with a flame ionization detector and a methyl siloxane capillary column; GC−MS analyses were carried out on a HP 5890A GC system using a Petrocol DH capillary column coupled with a HP 5970 mass selective detector. CuCl[12] and Cu_5Mes_5[13] were prepared according to the reported procedure. Other reagents, unless otherwise noted, were commercially available.

Photolysis Experiments. Photolysis experiments were performed with a 500-W super-high-pressure mercury arc lamp. Interference filters (bandwidth 10 nm) were used to isolate the desired Hg emission line, and a cooled distilled water filter was employed to aid heat removal. The photolysis cell consisted of a 10 mm square spectrophotometric cell modified for anaerobic work. A thermostatable cell holder was used in order to reproducibly locate the cell in the light beam. The temperature of the irradiated solutions was kept at 25 ± 1 °C, unless otherwise noted. Incident light intensity, determined by ferrioxalate actinometry,[14] was in the range 1.2×10^{17} to 2.4×10^{16} quanta s^{-1} depending on the Hg emission line.

The samples were prepared in a nitrogen atmosphere glovebox. The solutions were irradiated while being thoroughly stirred with a miniature magnetic stirring bar. Small aliquots of the irradiated solutions were analyzed for NBD and Q content using GC and GC−MS techniques. The systems were calibrated with standard NBD/Q solutions, showing in both cases a 1:1 correspondence between the NBD integrated area and the Q integrated area. In order to check the mass balance of the reaction *n*-octane was added, in some cases, as an internal standard. The quantum yields reported here were determined between 1 and 2% Q conversion for the NBD concentration employed (1.0 M, unless otherwise noted). The concentration of the sensitizer was sufficiently high to ensure $>99\%$ absorption of the incident light.

Photolysis experiments were also performed with a solar spectrum simulator equipped with a 1500-W xenon lamp, using Pyrex Schlenk flasks. The temperature of the sample compartment was about 45 °C.

Reverse Isomerization. The catalysts for the reverse Q → NBD isomerization were tested in Pyrex Schlenk flasks at room temperature. Sample preparation and analysis for NBD and Q content at different times were performed as described above. Experimental conditions were as follows: Pd on carbon, 100 mg in 30 mL of 0.7 M Q in benzene; molecular sieves (Union Carbide, Type 4 Å), 7.6 g in 30 mL of Q 0.6 M in benzene.

Synthesis of LNa. NaH (6.0 g, 250 mmol) was slowly added to a THF (550 mL) solution of LH (23.0 g, 144 mmol). The yellow-green suspension was stirred for 30 min and then refluxed for 2 h. The excess NaH was removed by filtration to give an orange-green solution, which was then evaporated to dryness. The yellow residue was treated with *n*-hexane (250 mL) and the pale yellow solid filtered off and dried *in vacuo* (23.8 g, 97.5%). Anal. Calcd for $C_{10}H_8NONa$ (181.17): C, 66.30; H, 4.45; N, 7.73. Found: C, 66.58; H, 4.33; N, 7.80. ^{1}H NMR

---

(8) (a) Basu, A.; Saple, A. R.; Sapre, N. Y. *J. Chem. Soc., Dalton Trans.* **1987**, 1797. (b) Fife, D. J.; Moore, W. M.; Morse, K. W. *J. Am. Chem. Soc.* **1985**, *107*, 7077. (c) Orchard, S. W.; Kutal, C. *Inorg. Chim. Acta* **1982**, *64*, 95. (d) Maruyama, K.; Terada, K.; Yamamoto, Y. *J. Org. Chem.* **1981**, *46*, 5294. (e) Maruyama, K.; Terada, K.; Naruta, Y.; Yamamoto, Y. *Chem. Lett.* **1980**, 1259. (f) Grutsch, P. A.; Kutal, C. *J. Am. Chem. Soc.* **1979**, *101*, 4228. (g) Grutsch, P. A.; Kutal, C. *J. Am. Chem. Soc.* **1977**, *99*, 6460.

(9) (a) Grutsch, P. A.; Kutal, C. *J. Am. Chem. Soc.* **1986**, *108*, 3108. (b) Ikezawa, H.; Kutal, C.; Yasufuku, K.; Yamazaki, H. *J. Am. Chem. Soc.* **1986**, *108*, 1589. (c) Grutsch, P. A.; Kutal, C. *J. Chem. Soc., Chem. Commun.* **1982**, 893. (d) Juris, A.; Sandrini, D.; Rancati, E. *Chim. Ind. (Milan)* **1980**, *62*, 837.

(10) Baezinger, N. C.; Haight, H. L.; Doyle, J. R. *Inorg. Chem.* **1964**, *3*, 1535.

(11) (a) Maafi, M.; Lion, C.; Aaron, J.-J. *New J. Chem.* **1996**, *20*, 559. (b) Maafi, M.; Aaron, J.-J.; Lion, C. *Chem. Lett.* **1994**, 1865. (c) Wu, Q. H.; Zhang, B. W.; Ming, Y. F.; Cao, Y. *J. Photochem. Photobiol. A: Chem.* **1991**, *61*, 53. (d) Yamashita, Y.; Hanaoka, T.; Takeda, Y.; Mukai, T.; Miyashi, T. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 2451. (e) Yamashita, Y.; Hanaoka, T.; Takeda, Y.; Mukai, T. *Chem. Lett.* **1986**, 1279. (f) Maruyama. K.; Tamiaki, H.; Yanai, T. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 781. (g) Maruyama, K.; Tamiaki, H.; Kawabata, S. *J. Org. Chem.* **1985**, *50*, 4742. (h) Yoshida, Z. *J. Photochem.* **1985**, *29*, 27. (i) Hirao, K.; Ando, A.; Hamada, T.; Yonemitsu, O. *J. Chem. Soc., Chem. Commun.* **1984**, 300. (j) Toda, T.; Hasegawa, E.; Mukai, T.; Tsuruda, H.; Hagiwara, T.; Yoshida, T. *Chem. Lett.* **1982**, 1551. (k) Maruyama, K.; Tamiaki, H. *Chem. Lett.* **1982**, 1699. (l) Maruyama, K.; Terada, K.; Yamamoto, *Y. Chem. Lett.* **1981**, 839. (m) Kaupp, G.; Prinzbach, H. *Helv. Chim. Acta* **1969**, *52*, 956. (n) Edman, J. R.; Simmons, H. E. *J. Org. Chem.* **1968**, *33*, 3808. (o) Edman, J. R. *J. Org. Chem.* **1967**, *32*, 2920. (p) Cristol, S. J.; Snell, R. L. *J. Am. Chem. Soc.* **1958**, *80*, 1950.

(12) Brauer, G. *Handbook of Preparative Inorganic Chemistry*, 2nd ed.; Academic: New York, 1965; Vol. 2, pp 1005−1007.

(13) Meyer, E. M.; Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Organometallics* **1989**, *8*, 1067.

(14) Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London, A* **1956**, *235*, 518.

(400 MHz, CD_3OD, 298 K): δ 7.92 (d, $J = 8.3$ Hz, 1H); 7.18 (t, $J = 7.9$ Hz, 1H); 7.16 (d, $J = 8.3$ Hz, 1H); 6.83 (d, $J = 7.9$ Hz, 2H); 2.65 (s, 3H, CH_3). IR (Nujol, ν_{max}/cm^{-1}): 1608 (w), 1585 (m), 1550 (s), 1503 (s), 1452 (s), 1364 (s), 1342 (s), 1201 (s), 1098 (s), 1061 (w), 862 (m), 827 (s), 795 (m), 744 (s), 730 (s), 578 (w), 552 (w), 520 (w), 498 (w), 442 (m), 406 (w).

Synthesis of 3. Method A. To a methanol (200 mL) suspension of CuCl (6.92 g, 63.9 mmol) was added freshly distilled NBD (5.89 g, 63.9 mmol), and to this mixture was added dropwise a methanol (200 mL) solution of LNa (10.55 g, 63.9 mmol). The resulting red solution turned yellow within a few minutes and was stirred for 30 min. The solution was reduced to half of its initial volume, resulting in the precipitation of a yellow solid. The product was filtered off, dried *in vacuo*, and then suspended in hexane (150 mL). The suspension was stirred for 5 min before being collected and dried *in vacuo* (14.22 g, 83%).

Synthesis of 3. Method B. To a solution of LH (1.49 g, 9.35 mmol) and freshly distilled NBD (0.54 g, 5.90 mmol) in THF (100 mL) was added Cu_5Mes_5 (1.71 g, 1.87 mmol). The resulting deep yellow solution gave a yellow microcrystalline solid on standing, which was then filtered off and dried *in vacuo* (2.13 g, 85%). Crystals suitable for X-ray analysis were grown in concentrated methanol solution containing an equimolar amount of NBD. Anal. Calcd for $C_{27}H_{24}N_2O_2Cu_2$ (535.59): C, 60.55; H, 4.52; N, 5.23. Found: C, 60.91; H, 4.73; N, 5.18. ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K) δ: 8.13 (d, $J = 8$ Hz, 1H, Ar); 7.32 (m, 2H, Ar); 6.88 (m, 2H, Ar); 5.67 (broad s, 2H, CH═CH); 4.00 (s, 1H, CH); 2.88 (s, 3H, CH_3); 2.04 (s, 1H, CH_2). ^{1}H NMR (200 MHz, CD_3OD, 298 K): δ 8.26 (d, $J = 8.6$ Hz, 1H, Ar); 7.48 (d, $J = 8.6$ Hz, 1H, Ar); 7.36 (t, $J = 7.7$ Hz, 1H, Ar); 7.04 (d, $J = 7.7$ Hz, 1H, Ar); 6.94 (d, $J = 7.7$ Hz, 1H, Ar); 5.93 (broad s, 2H, CH═CH); 3.99 (s, 1H, CH); 2.93 (s, 3H, CH_3); 2.03 (s, 1H, CH_2). ^{13}C NMR (100.6 MHz, CD_2Cl_2, 298 K): δ 156.4; 141.8; 139.5; 129.2; 128.5; 122.6; 115.4; 114.2; 111.8; 97.8; 64.1; 51.3; 26.8. IR (Nujol, ν_{max}/cm^{-1}): 1560 (s), 1506 (m), 1430 (s), 1335 (s), 1304 (m), 1281 (m), 1230 (w), 1113 (m), 1082 (w), 1054 (w), 1034 (w), 984 (w), 916 (w), 870 (w), 835 (s), 787 (w), 748 (m), 726 (s), 613 (m), 515 (m), 475 (w), 425 (w). UV−vis (methanol, λ_{max}/nm (ϵ_{max}/M^{-1} cm^{-1})): 262 (73 900); 378 (5920).

Synthesis of 4. To a solution of L′H (2.15 g, 9.41 mmol) and freshly distilled NBD (4.34 g, 47.1 mmol) in THF (100 mL) was added Cu_5Mes_5 (1.72 g, 1.88 mmol) to give an amber solution. Addition of hexane (200 mL) and standing at 5 °C for 2 h resulted in the precipitation of a yellow solid. The product was filtered off and dried *in vacuo* (2.57 g, 70%). Anal. Calcd for $C_{27}H_{20}N_2O_2Cl_4Cu_2$ (641.37): C, 50.56; H, 3.14; N, 4.37. Found: C, 50.37; H, 3.45; N, 3.96. ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K) δ: 8.45 (d, $J = 8.6$ Hz, 1H, Ar); 7.51 (s, 1H, Ar); 7.46 (d, $J = 8.6$ Hz, 1H, Ar); 6.66 (broad s, 2H, CH═CH); 3.64 (s, 1H, CH); 2.90 (s, 3H, CH_3); 1.98 (s, 1H, CH_2). IR (Nujol, ν_{max}/cm^{-1}): 1550 (s), 1494 (s), 1306 (w), 1278 (w), 1245 (w), 1222 (w), 1194 (w), 1150 (w), 1117 (w), 1083 (w), 1050 (w), 1022 (w), 961 (m), 933 (w), 883 (w), 861 (m), 822 (m), 783 (m), 744 (s), 683 (s), 660 (w), 532 (m), 469 (w). UV−vis (THF, λ_{max}/nm (ϵ_{max}/M^{-1} cm^{-1})): 278 (53 900); 424 (7780). The very low solubility of the complex in the absence of free NBD prevented us from obtaining reliable quantitative spectra in methanol, which was the solvent used for the photoisomerization. In this solvent, however, the absorption spectrum showed maxima at 272 and 396 nm.

Synthesis of 5. To a solution of Cu_5Mes_5 (0.94 g, 1.03 mmol) and freshly distilled NBD (0.94 g, 13.3 mmol) in THF (100 mL) was added L″H (1 g, 5.12 mmol) to give a wine red solution, which was stirred for 5 min. A deep red solid separated, which was filtered off and dried *in vacuo* (1.5 g, 96.5%). Anal. Calcd for $C_{33}H_{24}N_2O_2Cu_2$ (607.66): C, 65.23; H, 3.98; N, 4.61. Found: C, 65.38; H, 4.10; N, 4.32. ^{1}H NMR (200 MHz, CD_2Cl_2, 298 K) δ: 8.84 (s, 1H, Ar); 8.37 (d, $J = 8.8$ Hz, 1H, Ar); 8.04 (d, $J = 8.3$ Hz, 1H, Ar); 7.87 (t, $J = 8.8$ Hz, 1H, Ar); 7.58 (t, $J = 8.3$ Hz, 1H, Ar); 7.42 (t, $J = 8.8$ Hz, 1H, Ar); 7.12 (d, $J = 8.3$ Hz, 1H, Ar); 6.93 (d, $J = 8.8$ Hz, 1H, Ar); 5.88 (broad s, 2H, CH═CH); 4.22 (s, 1H, CH); 2.10 (s, 1H, CH_2). IR (Nujol, ν_{max}/cm^{-1}): 1622 (w), 1594 (w), 1567 (w), 1511 (s), 1422 (w), 1394 (s), 1328 (s), 1280 (s), 1228 (w), 1128 (w), 1081 (m), 1067 (m), 1050 (m), 917 (w), 764 (m), 750 (s), 722 (s), 589 (w). UV−vis (methanol, λ_{max}/nm (ϵ_{max}/M^{-1} cm^{-1})): 240 (60 700); 282 (66 100); 474 (5230).

Table 1. Experimental Data for the X-ray Diffraction Studies on Crystalline Complexes **3** and **6**

complex	**3**	**6**
formula	$C_{27}H_{24}Cu_2N_2O_2 \cdot 3CH_4O$	$C_{47}H_{56}Cu_2N_6O_2$
a, Å	9.902(2)	14.829(2)
b, Å	16.770(3)	7.489(1)
c, Å	9.649(2)	20.442(2)
α, deg	92.63(2)	90
β, deg	118.48(2)	93.49(1)
γ, deg	90.39(2)	90
V, Å^3	1406.1(6)	2266.0(5)
Z	2	2
formula weight	631.7	864.1
space group	$P\bar{1}$ (No. 2)	*P*2/*c* (No. 13)
t, °C	−130	22
λ, Å	1.541 78	0.710 69
ρ_{calc}, g cm^{-3}	1.492	1.266
μ, cm^{-1}	21.65	9.81
transm coeff	0.845−1.000	0.941−1.000
R^a	0.053	0.046
w$R_2{}^a$	0.156	0.100

^{a} $R = \sum|\Delta F|/\sum|F_o|$ calculated on the unique observed data [$I > 2\sigma(I)$]. w$R_2 = [\sum|\Delta F^2|^2/\sum w|F_o{}^2|^2]^{1/2}$ calculated on the unique data having $I > 0$.

Synthesis of 6. To a solution of L‴H (4.30 g, 13.3 mmol) and freshly distilled NBD (1.23 g, 13.3 mmol) in THF (125 mL) was added Cu_5Mes_5 (2.43 g, 2.66 mmol) to give a deep yellow solution, which was then reduced to half of its initial volume. Addition of *n*-hexane (50 mL) resulted in the precipitation of a yellow solid. The product was filtered off and dried *in vacuo* (3.45 g, 60%). Crystals suitable for X-ray analysis were grown in concentrated methanol/toluene solution. Anal. Calcd for $C_{47}H_{56}N_6O_2Cu_2$ (864.09): C, 65.33; H, 6.53; N, 9.73. Found: C, 65.49; H, 6.67; N, 9.79. ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ 8.03 (d, $J = 2.4$ Hz, 1H, Ar); 7.99 (m, 2H, Ar); 7.59 (m, 2H, Ar); 7.38 (d, $J = 2.4$ Hz, 1H, Ar); 5.54 (broad s, 2H, CH═CH); 4.10 (s, 1H, CH); 2.05 (s, 1H, CH_2); 1.54 (s, 9H, CH_3); 1.34 (s, 9H, CH_3). ^{13}C NMR (100.6 MHz, CD_2Cl_2, 298 K): δ 158.1; 142.7; 135.5; 128.0; 127.3; 125.7; 125.6; 118.5; 117.9; 116.5; 100.0; 51.3; 36.3; 34.4; 31.7; 29.7. IR (Nujol, ν_{max}/cm^{-1}): 1620 (w), 1606 (w), 1547 (m), 1526 (w), 1479 (s), 1444 (s), 1404 (m), 1359 (m), 1346 (m), 1322 (s), 1256 (s), 1227 (m), 1198 (w), 1132 (m), 1108 (w), 1052 (w), 923 (w), 873 (m), 834 (m), 769 (m), 732 (s), 632 (m). UV−vis (methanol, λ_{max}/nm (ϵ_{max}/M^{-1} cm^{-1})): 304 (4530); 414 (1330).

Synthesis of 7. To a suspension of LH (1.92 g, 12.1 mmol) and freshly distilled norbornene (NBN) (2.32 g, 24.2 mmol) in *n*-hexane (100 mL) was added Cu_5Mes_5 (2.22 g, 2.43 mmol). Stirring for 10 min gave a yellow suspension. The product was collected and dried *in vacuo* (2.8 g, 72%). Anal. Calcd for $C_{17}H_{18}NOCu$ (315.88): C, 64.64; H, 5.74; N, 4.43. Found: C, 64.38; H, 5.69; N, 4.89. ^{1}H NMR (200 MHz, CD_3OD, 298 K): δ 8.39 (d, $J = 8.3$ Hz, 1H, Ar); 7.60 (d, $J = 8.3$ Hz, 1H, Ar); 7.54 (t, $J = 7.8$ Hz, 1H, Ar); 7.22 (d, $J = 7.8$ Hz, 1H, Ar); 7.14 (d, $J = 7.8$ Hz, 1H, Ar); 5.16 (s, 2H, CH═CH); 3.51 (m, 2H, CH); 3.05 (s, 3H, CH_3); 1.85 (m, 2H, CH_2CH_2); 1.55 (dt, $J_{1-2} = 9.7$ Hz, $J_{1-3} = 1.7$ Hz, 1H, CH_2); 1.32 (m, 2H, CH_2CH_2); 1.25 (dt, $J_{1-2} = 9.7$ Hz, $J_{1-3} = 1.7$ Hz, 1H, CH_2). IR (Nujol, ν_{max}/cm^{-1}): 1560 (s), 1505 (s), 1426 (s), 1337 (s), 1318 (w), 1299 (m), 1283 (s), 1162 (w), 1114 (m), 1105 (m), 1066 (w), 1054 (w), 1031 (w), 964 (w), 942 (w), 930 (w), 898 (w), 872 (w), 828 (s), 792 (w), 754 (s), 742 (s), 735 (m), 605 (m), 506 (m), 455 (m). UV−vis (methanol, λ_{max}/nm (ϵ_{max}/M^{-1} cm^{-1})): 264 (34 400); 378 (2860).

X-ray Crystallography for Complexes 3 and 6. Suitable crystals were mounted in glass capillaries and sealed under nitrogen. The reduced cells were obtained with the use of TRACER.[15] Crystal data and details associated with data collection are given in Tables 1 and S1. Data were collected on a single-crystal diffractometer (Rigaku AFC6S at 143 K for **3**, Siemens AED at 295 K for **6**). For intensities

---

(15) Lawton, S. L.; Jacobson, R. A. "*TRACER*", *a cell reduction program*, Ames Laboratory; Iowa State University of Science and Technology: Ames, IA, 1965.

and background the individual reflection profiles were analyzed.[16] The structure amplitudes were obtained after the usual Lorentz and polarization corrections,[17] and the absolute scale was established by the Wilson method.[18] The crystal quality was tested by ψ scans showing that crystal absorption effects could not be neglected. Data were then corrected for absorption using a semiempirical method[19] for **3** and the program ABSORB[20] for **6**. Anomalous scattering corrections were included in all structure factor calculations.[21b] Scattering factors for neutral atoms were taken from ref 21a for non-hydrogen atoms and from ref 22 for H.

Structure solutions were based on the observed reflections $[I > 2\sigma(I)]$. The refinements were carried out using the unique reflections with $I > 0$. The structures were solved by the heavy-atom method starting from a three-dimensional Patterson map.[23] During the least-squares analysis the function minimized was $\sum w(\Delta F^2)^2$.[24] In the last stage of refinement the weighting scheme $w = 1/[\sigma^2(F_o^2)+(aP)^2]$ (with $P = (F_o^2 + 2F_c^2)/3$ was applied with a resulting in the values of 0.1098 and 0.0415 for **3** and **6**, respectively.

Refinement of both complexes was carried out first isotropically, then anisotropically for all the non-H atoms, except for the methyl carbon atoms of a *tert*-butyl group in **6** (C12, C13, and C14), which were found to be statistically distributed over two positions (A and B) isotropically refined with site occupation factors of 0.6 and 0.4, respectively. During the refinement the C−C bond distances within the disordered *tert*-butyl group were constrained to be 1.54(1) Å.

The hydrogen atoms, except those associated with the disordered *tert*-butyl group in **6**, which were ignored, were located from difference maps and introduced prior to the final refinements as fixed-atom contributions with isotropic U's fixed at 0.05 and 0.10 Å^2 for **3** and for **6**, respectively. As often observed for data collected at low temperature, in complex **3** the final difference map showed four residual peaks ranging from 1.07 to 1.20 e Å^{-3} located along the Cu−O and Cu−C bonds. The final difference map in **6** showed no unusual features.

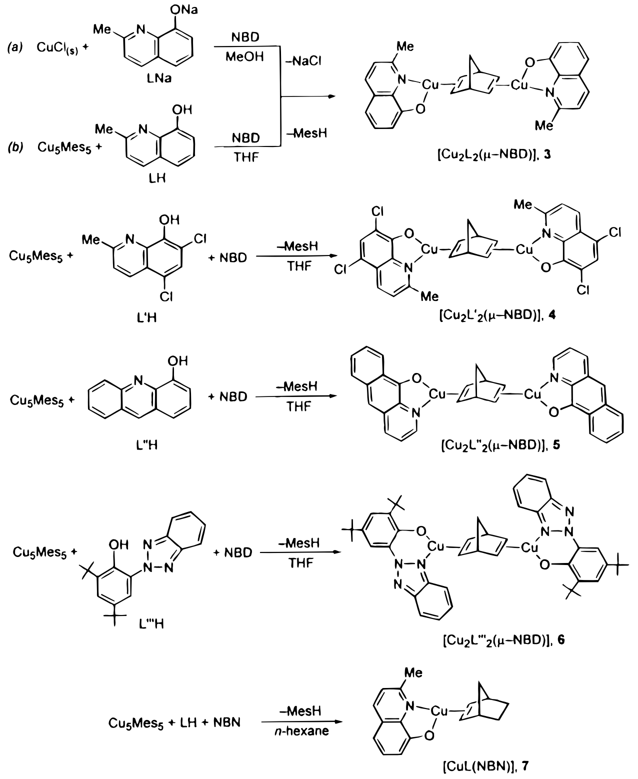
Final atomic coordinates are listed in Tables S2 and S3 for non-H atoms and in Tables S4 and S5 for hydrogens. Thermal parameters are given in Tables S6 and S7, and bond distances and angles in Tables S8 and S9.[25]

Results

1. Synthesis. The synthesis of the model compound **3** has been carried out using either the conventional metathesis reaction (pathway a) or the organometallic methodology (pathway *b*) shown in Scheme 3. Compounds **4**−**7** were synthesized only using the organometallic methodology.

They have been isolated in good yields as crystalline solids. The procedures reported in the Experimental Section prevent the disproportionation of copper(I) to copper(II) and copper metal, which usually occurs when hard donor atoms are used in combination with copper(I).[26] Solutions of complexes **3**−**7** in a variety of solvents have a limited stability toward the disproportionation reaction, although this can be prevented in the presence of excess NBD. The occurrence of such a reaction is a clear indication of the lability of the copper(I)−alkene complex, thus the copper(I) fragments A−D disproportionate when not stabilized by the olefinic ligand (see Discussion). The nature of the complexes has been analyzed by solution NMR spectroscopy and, in the cases of **3** and **6**, by X-ray analysis.

Scheme 3[a]



[a] Mes ≡ 2,4,6-Me$_3$C$_6$H$_2$; NBD ≡ norbornadiene; NBN ≡ norbornene.

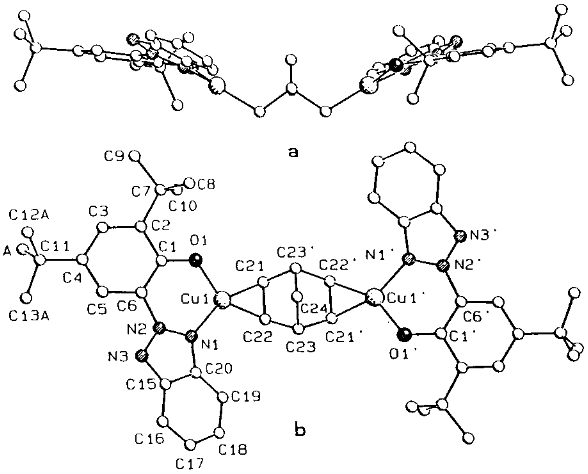


Figure 1. A SCHAKAL drawing of complex **3**: (a) side view, (b) top view.

In both compounds (see Figure 1, complex **3**, and Figure 2, complex **6**) the N1, O1, C21, C22 coordination environment of copper(I) is planar, Cu1 and Cu2 being displaced by 0.012(1) Å in **3** and Cu1 by 0.007(1) Å from the coordination plane. The Cu−O and Cu−N bond distances vary considerably in **3** and **6**, according to the different nature of the bidentate ligand, although for both they are much shorter than in the case of the tetrameric [LCu(CO)]$_4$ carbonyl derivative (Cu−O$_{av}$, 2.04; Cu−N$_{av}$, 2.06 Å),[27] where the metal achieves tetracoordination and

---

(16) Lehmann, M .S.; Larsen, F. K. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1974**, *A30*, 580.

(17) Data reduction, structure solution, and refinement were carried out on a Quansan personal computer equipped with an INTEL Pentium processor.

(18) Wilson, A. J. C. *Nature (London)* **1942**, *150*, 151.

(19) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1968**, *A24*, 351.

(20) Ugozzoli, F. *Comput. Chem.* **1987**, *11*, 109.

(21) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV; (a) p 99, (b) p 149.

(22) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(23) Sheldrick, G. M. *SHELX76, Program for crystal structure determination*; University of Cambridge: Cambridge, England, 1976.

(24) Sheldrick, G. M. *SHELXL92, Program for crystal structure refinement*, University of Göttingen: Göttingen, Germany, 1992.

(25) See the paragraph at the end of the paper regarding the Supporting Information.

(26) Hathaway, B. J. In *Comprehensive Coordination Chemistry*; Wilkinson, G.; Gillard, R. D., Mc Cleverty, J. A., Eds.; Pergamon: Oxford, England, 1987; Vol. 5, Chapter 53.

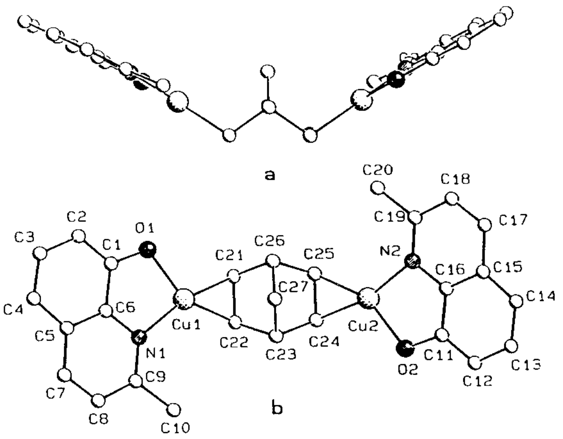
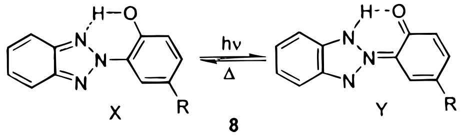


Figure 2. A SCHAKAL view of complex **6**: (a) side view, (b) top view. The prime refers to a transformation of −*x*, *y*, 0.5 − *z*. Disorder has been omitted for clarity.

Scheme 4[a]



[a] R = Me.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Complex **3**

Cu1−O1	1.933(4)	O1−C1	1.327(5)
Cu1−N1	1.992(3)	O2−C11	1.328(5)
Cu1−C21	1.988(3)	N1−C6	1.373(6)
Cu1−C22	2.011(4)	N1−C9	1.323(6)
Cu2−O2	1.949(4)	N2−C16	1.379(6)
Cu2−N2	1.992(3)	N2−C19	1.326(6)
Cu2−C24	1.997(4)	C21−C22	1.389(6)
Cu2−C25	2.019(4)	C24−C25	1.403(6)
C21−Cu1−C22	40.6(2)	Cu1−N1−C9	132.4(3)
N1−Cu1−C22	124.5(2)	Cu1−N1−C6	108.3(3)
N1−Cu1−C21	165.1(2)	C6−N1−C9	119.2(3)
O1−Cu1−C22	149.7(2)	Cu2−N2−C19	131.8(4)
O1−Cu1−C21	109.1(2)	Cu2−N2−C16	108.1(2)
O1−Cu1−N1	85.8(2)	C16−N2−C19	119.9(4)
C24−Cu2−C25	40.9(2)	Cu1−C21−C26	114.7(2)
N2−Cu2−C25	123.6(2)	Cu1−C21−C22	70.6(2)
N2−Cu2−C24	164.4(2)	Cu1−C22−C21	68.8(2)
O2−Cu2−C25	150.6(2)	Cu1−C22−C23	116.0(2)
O2−Cu2−C24	109.8(2)	Cu2−C24−C23	113.2(3)
O2−Cu2−N2	85.8(2)	Cu2−C24−C25	70.4(2)
Cu1−O1−C1	111.4(2)	Cu2−C25−C24	68.7(2)
Cu2−O2−C11	110.8(3)	Cu2−C25−C26	115.4(3)

Table 3. Selected Bond Distances (Å) and Angles (deg)[a] for Complex **6**

Cu1−O1	1.870(3)	N1−C20	1.353(8)
Cu1−N1	1.935(4)	N2−N3	1.329(6)
Cu1−C21	1.959(5)	N2−C6	1.444(7)
Cu1−C22	1.976(5)	N3−C15	1.345(7)
O1−C1	1.306(6)	C21−C22	1.353(8)
N1−N2	1.334(6)		
C21−Cu1−C22	40.2(2)	N2−N1−C20	104.0(4)
N1−Cu1−C22	116.3(2)	N1−N2−C6	124.3(4)
N1−Cu1−C21	156.2(2)	N1−N2−N3	115.3(4)
O1−Cu1−C22	150.2(2)	N3−N2−C6	120.2(4)
O1−Cu1−C21	110.1(2)	N2−N3−C15	102.7(4)
O1−Cu1−N1	93.5(2)	Cu1−C21−C23′	116.9(4)
Cu1−O1−C1	125.0(3)	Cu1−C21−C22	70.6(3)
Cu1−N1−C20	132.1(4)	Cu1−C22−C21	69.2(3)
Cu1−N1−N2	123.5(3)	Cu1−C22−C23	117.6(4)

[a] Prime denotes a transformation of −*x*, *y*, 0.5 − *z*.

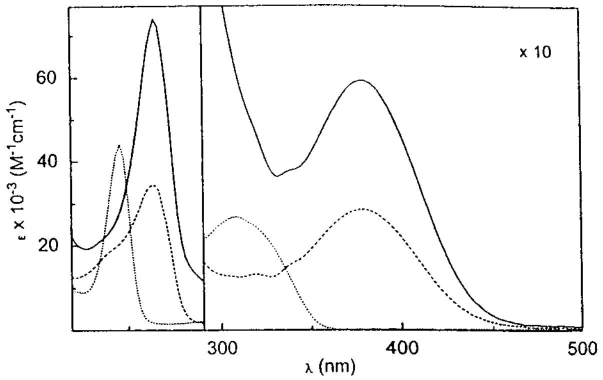


Figure 3. Absorption spectra of the complexes **3** (—) and **7** (- - -) and of the ligand LH (···) in methanol solution.

Table 4. Absorption Data in Methanol Solution

compd	λ_{max}/nm (ϵ_{max}/M^{-1} cm^{-1})		
LH	246 (44100)	308 (2730)	
3	262 (73900)		378 (5920)
7	264 (34400)		378 (2860)
L‴H	302 (2900)	340 (2870)	
6	304 (4530)	350 (2050 sh)	414 (1330)

the oxygen of the ligand bridges two copper(I) ions. The structural parameters of the benzotriazole ligand[28] are in agreement with the bonding sequence shown in Scheme 3 for **6**, and in the X tautomer shown in Scheme 4 (see Table S9). A significant difference between the two complexes remains in the Cu−alkene distances, being much shorter in **6** than in **3** (see Tables 2 and 3) (Cu−C, 1.988(3)−2.019(4) Å in **3**; 1.959(5)−1.976(5) Å in **6**), the distance between Cu1 and Cu2 from the midpoint of the alkene functionality being 1.876(4) and 1.882(4) Å in **3**, and 1.847(5) Å in **6**. Such a structural parameter is in agreement with the higher lability of the metal−alkene interaction in **3**, thus allowing **3** to behave as a better catalyst. The copper(I)−alkene distance[29] usually found in the literature varies from 2.08 Å in $[Cu(dien)(NBN)]^+$ [30] to 1.97 Å in $[CuCl(NBD)]_4$.[10] Differently from what was observed in $[Cu(dien)(NBN)]^+$, we did not find for either complex **3** or **6** any Cu···H interaction with the bridging methylene of NBD.

The dimeric nature in the solid state of **3** and **6** can be misleading in the sense that they are not the reactive species (see Discussion) and the dimeric nature is merely a result of the lower solubility of the dimeric *vs* the corresponding monomeric form. In order to mimic the existence of this monomeric form (*vide infra*) we have also synthesized and characterized the [CuL(NBN)] complex, **7** (NBN ≡ norbornene).

2. Photochemistry. The absorption spectrum of **3** in methanol shows an intense band (λ_{max} = 262 nm, ϵ_{max} = 73 900 M^{-1} cm^{-1}) in the UV and a weaker band (λ_{max} = 378 nm, ϵ_{max} = 5920 M^{-1} cm^{-1}) near the visible (Figure 3 and Table 4). The tail of the latter band belongs in the visible and is responsible for the yellow color of compound **3**. The more intense band is due to transitions in the L ligand (as indicated by the comparison with the absorption spectrum of the free

---

(27) Pasquali, M.; Fiaschi, P.; Floriani, C.; Zanazzi, P. F. *J. Chem. Soc., Chem. Commun.* **1983**, 613.

(28) Carofiglio, T.; Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Polyhedron* **1996**, *15*, 4435.

(29) Van Koten, G.; James, S. L.; Jastrzebski, J. T. B. H. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A.;,Wilkinson, G., Eds.; Pergamon: Oxford, England, 1995; Vol. 3, Chapter 2.

(30) Pasquali, M.; Floriani, C.; Gaetani-Manfredotti, A.; Chiesi-Villa, A. *J. Am. Chem. Soc.* **1978**, *100*, 4918.

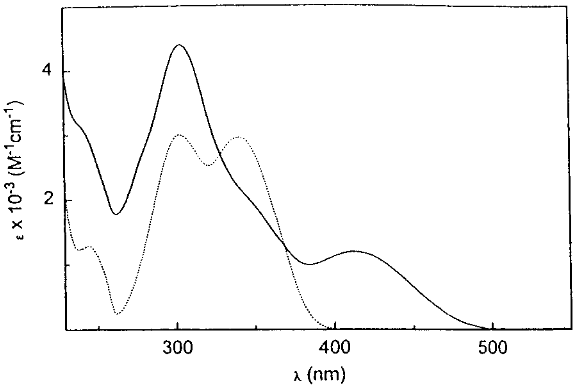


Figure 4. Absorption spectra of the complex **6** (—) and of the ligand L‴H (···) in methanol solution.

ligand, also shown in Figure 3), while the other band is attributed to a MLCT transition involving copper(I) and the same ligand. Such a band is similar to the MLCT absorption bands usually shown by copper(I) complexes containing N$^\frown$N bidentate heterocyclic ligands and π-acceptor ligands.[31] A further support for this assignment is provided by the observation that switching the solvent from methanol to less polar solvents causes the band to shift to longer wavelengths (for example, in THF the band occurs at 408 nm).

In an attempt to shift the MLCT band to lower energies, we have tried both a ligand containing electron-withdrawing substituents (2-methyl-5,7-dichloro-8-hydroxyquinoline, L′H) and a structurally similar ligand with a more extended π-system (4-hydroxyacridine, L″H). As expected, significant red shifts of the MLCT band are observed (in methanol solution λ_{max} = 396 nm and 474 nm for **4** and **5**, respectively), although these complexes were inefficient in assisting the NBD → Q photoisomerization.

The absorption spectrum of **6** in methanol shows bands in the UV (λ_{max} = 304 nm, ϵ_{max} = 4530 M^{-1} cm^{-1} and a shoulder at about 350 nm) and a weaker band in the visible (λ_{max} = 414 nm, ϵ_{max} = 1330 M^{-1} cm^{-1}) (Figure 4 and Table 4). By comparison with the absorption spectrum of the free ligand (Figure 4) the first two bands are easily assigned to ligand transitions while the other is again attributed to a MLCT transition. The latter absorption band shows the expected red shift in weakly polar solvents (λ_{max} = 434 nm in THF).

Compound **7** (relatively unstable even in dilute solution) has an absorption spectrum very similar to that of **3** and shows the same ligand-centered and MLCT transitions (Figure 3). The molar extinction coefficients are, however, lower than those of **3**, in agreement with the presence of only one [CuL] moiety in the complex (Table 4).

Sensitized NBD → Q isomerization takes place upon irradiation of methanol solutions of **3** containing NBD. A quantum yield of 0.029 is obtained for this reaction upon excitation at 405 nm. The quantum yield depends on the irradiation wavelength; it is practically constant on excitation of the MLCT absorption band (*i.e.*, excitation at 365 or 405 nm), while a higher value (0.17) is obtained on irradiation at 313 nm. The high value found at this wavelength could be ascribed, at least in part, to excitation in the Cu(I)−NBD charge-transfer absorption bands. Such bands are known to give rise to absorption at this wavelength in the CuCl−NBD complex and to determine photoinduced NBD → Q isomerization with high quantum yields.[7f] However, the presence of these bands cannot be proved because they, if any, are overlapped by the intense absorption band due to the L ligand (for the CuCl−NBD complex in ethanol the Cu(I)−NBD charge-transfer band has λ_{max} = 248 nm and ϵ_{max} = 6300 M^{-1} cm^{-1}).[7f]

As mentioned above, **4** and **5** are inefficient in sensitizing the **1** → **2** isomerization. In methanol solution the photoisomerization quantum yield measured using **4** as sensitizer is *ca.* 0.001, while **5** does not give rise to any detectable production of Q.

As far as **6** is concerned, sensitized NBD → Q isomerization does not take place on irradiation of the MLCT absorption band. It is observed, however, by irradiating at 313 nm with a quantum yield of 0.035. As in the case of **3**, NBD → Q isomerization at this excitation wavelength may be ascribed to direct excitation in Cu(I)−NBD charge-transfer absorption bands.

Photoinduced NBD → Q isomerization is obtained also using **7** as sensitizer. The complex does not show decomposition in the presence of an excess of NBD, and the photoisomerization quantum yield upon excitation at 405 nm is identical to that obtained with **3**.

Considering that the main objective in the development of new sensitizers for the NBD → Q photoisomerization is the use of sunlight to perform the reaction, we have concentrated on the measurements concerning **3** and upon irradiation with visible light at 405 nm. In order to investigate in more detail the factors that influence the photoisomerization process, we have studied the effect on the quantum yield of (i) the solvent, (ii) the NBD concentration, and (iii) the temperature.

(i) Effect of the Solvent. First, it is interesting to note that the red shift of the MLCT absorption band of **3** observed in weakly polar solvents, like THF, determines a better overlap between the absorption spectrum of the complex and the sunlight spectrum, and therefore the use of these solvents instead of methanol could allow a more efficient absorption of sunlight. Unfortunately, the quantum yield in THF (0.011) is considerably lower than that in methanol. However, similar NBD → Q conversion rates are obtained when photolysis experiments are performed in methanol and THF solution using the solar spectrum simulator. This indicates that the better spectral overlap in THF can, at least in part, compensate for the lower quantum yield in this solvent. Analogous experiments have shown that the quantum yields in CH_2Cl_2 or benzene (in which the absorption spectra are similar to that in THF) are comparable to that in THF.

(ii) Effect of the NBD Concentration. The isomerization quantum yield in methanol does not show a significative dependence on the NBD concentration in the range 0.1−4.0 M NBD, but lower quantum yields are obtained in more concentrated solutions and the isomerization quantum yield in neat NBD is only 0.005 (Figure 5). A somewhat lower quantum yield is also obtained in dilute NBD solutions ([NBD] < 0.1 M).

(iii) Effect of the Temperature. The quantum yield in methanol undergoes a significant increase (more than a factor of 2) on raising the temperature from 20 to 60 °C, close to the boiling point of the solvent (Figure 6). A similar behavior was also found in THF.

Appreciable photodegradation of the sensitizer does not take place under the routine conditions for quantum yield measurements (few hours of irradiation). In order to check both the selectivity of the reaction and the photostability of the catalyst, high-conversion experiments, which required up to 100 h irradiation, have been performed in methanol using the solar

---

(31) (a) Munakata, M.; Kitagawa, S. In *Copper Coordination Chemistry: Biochemical & Inorganic Perspectives*; Karlin, K. D., Zubieta, J., Eds.; Adenine: New York, 1983; pp 473−495 and references therein. (b) McMillin, D. R.; Gamache, R. E., Jr.; Kirschoff, J. R.; Del Paggio, A. *Ibid.*; pp 223−235 and references therein.

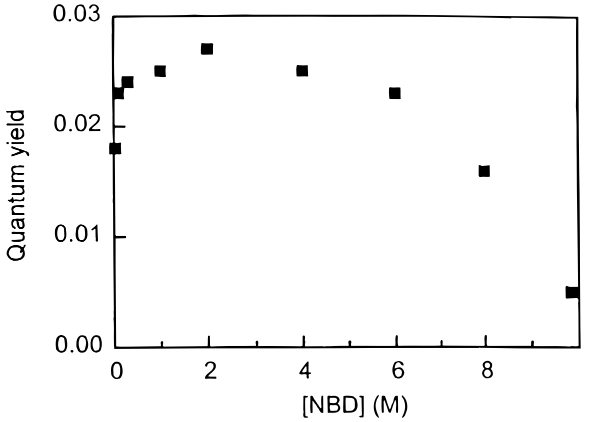


Figure 5. Quantum yield dependence on the NBD concentration for the NBD → Q isomerization sensitized by **3** in methanol and upon irradiation at 405 nm. The value at [NBD] ≈ 10 M is obtained in neat norbornadiene.

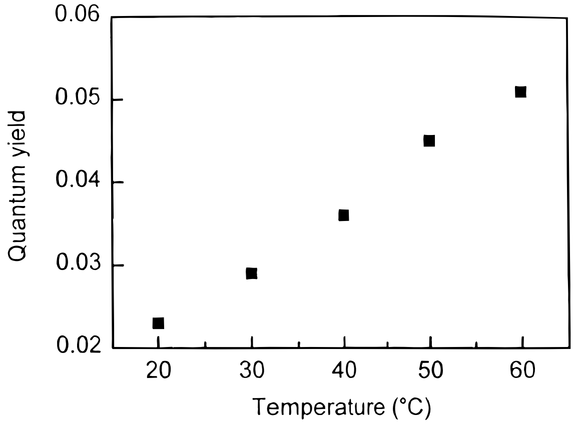


Figure 6. Quantum yield dependence on the temperature for the NBD → Q isomerization sensitized by **3** in methanol, upon irradiation at 405 nm. The NBD concentration is 1.0 M.

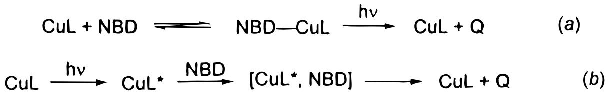
spectrum simulator. Turnover numbers (moles of Q produced/mole of **3**) of about 5000 and NBD → Q conversions of more than 95% are obtained. Almost all (>98%) of the starting NBD is found as Q or NBD at the end of the reaction, and GC analysis does not show any evident side product. Again, the irradiated solutions do not show relevant photodegradation of the sensitizer. However, small quantities of white precipitate are usually present at the ends of the reactions.

3. The Thermal Q → NBD Conversion. As for the few cases reported in the literature, we used heterogeneous catalysts, namely, Pd/C (10% content of Pd) and molecular sieves (MS), for the Q → NBD assisted transformations. The Q lifetime in our experimental conditions is 40 min for MS and 40 h for Pd/C in benzene, while methanol cannot be used for MS. There is, however, a major difference between the two catalysts. Pd/C catalyzes the Q → NBD transformation without the formation of significant amounts of byproducts, while in the case of MS a not insignificant amount of Q has been transformed into a NBD polymer. In both cases the catalyst is not very active resulting in low turnover numbers, as reported in the literature.[32]

Discussion

The choice of our model compounds **3** and **6** deserves some comments at this stage. The aim of using π-delocalized ligands focused on obtaining MLCT absorption in (or near) the visible region in the corresponding complexes, thus affecting the sensitization ability of the copper(I) fragments in the NBD → Q photoconversion process. In the case of L''' the choice was even more subtle.

Scheme 5



Ultraviolet absorbers which have the basic 2-(2-hydroxyphenyl)benzotriazole structure, as shown for **8**, are a very important class of photostabilizers.

Their photolability was explained as being due to an excited state intramolecular proton transfer through the intramolecular hydrogen bond (X ↔ Y)[33-35] although such an explanation was questioned.[36] Since the intramolecular hydrogen bond seems fundamental to this explanation,[33-35] we decided to replace it with a transition metal, which would chelate the oxygen and nitrogen, and then investigate its effect on the photochemical and photophysical properties. The metal is expected to mediate the influence of the solvent on the photochemical and photophysical properties of the photostabilizers[33-35] and also to stabilize, preferentially, one of the two (X or Y) forms of **8**. In addition, by utilizing ligands such as **8** we hoped to achieve the photochemical activation of substrates bound to the metal.

In both cases L[37] and L''' have important additional properties. Their monoanionic nature gives rise to neutral copper(I) complexes, which are inert toward the loss of the bidentate ligand, unlike previous reports for neutral bidentate ligands in copper(I) cationic complexes.[26] The inertness of the ancillary ligand is an important prerequisite in designing any kind of catalyst. The use of a bidentate ligand with a narrow $N\frown O$ bite angle [N−Cu−O = 85.6(3)°, **3**; 93.7(2)°, **6**] results in a copper(I) fragment geometry which suffers from coordinative unsaturation because it cannot rearrange to a linear bonding mode. On the other hand, copper(I) in this coordination geometry will bind a single C=C bond, avoiding undesirable bis(alkene) complexes. Such bis(alkene) complexes may be eventually responsible for some cycloaddition reactions occurring to the detriment of the NBD → Q transformation.[7e]

Copper(I) compounds can sensitize the photoisomerization reaction of norbornadiene to quadricyclene via two distinct mechanisms. The first (Scheme 5a) features the formation of a ground-state copper(I)−NBD complex that, upon absorption of a photon, generates the Q molecule and releases the sensitizer.[7] An alternative pathway (Scheme 5b) involves sensitization due to the bimolecular interaction of a photoexcited Cu(I) compound with ground-state NBD.[8]

Structural and electronic factors (availability of vacant coordination sites, ability of the Cu(I) compound to give

---

(32) Card, R. J.; Neckers, D. C. *J. Org. Chem.* **1978**, *43*, 2958.

(33) Heller, H. J.; Blattman, H. R. *Pure Appl. Chem.* **1972**, *30*, 145; **1986**, *36*, 141. Heller, H. J. *Eur. Polym. J. Suppl.* **1969**, 105.

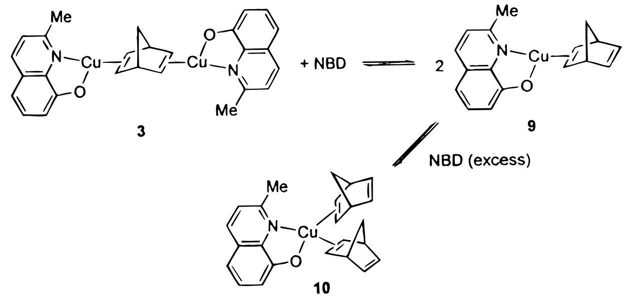
(34) (a) Klöpfer, W. In *Advances in Photochemistry*; Pitts, J. N., Hammond, S. S., Gallnick, K., Eds.; Wiley: New York, 1977; Vol. 10, p 311 and references therein. (b) Williams, D. L.; Heller, A. *J. Phys. Chem.* **1970**, *74*, 4473.

(35) (a) Wösner, G.; Goeller, G.; Rieker, J.; Hoier, H.; Sterowski, J. J.; Daltrozzo, E.; Neurieter, M.; Kramer, E. A. *J. Phys. Chem.* **1985**, *89*, 3629; (b) **1984**, *88*, 5544.

(36) (a) Catalan, J.; Fabero, F.; Guijarro, M. S.; Claramunt, R. M.; Santa Maria, M. D.; de la Conception Foces-Foces, M.; Cano, F. H.; Elguero, J.; Sastre, R. *J. Am. Chem. Soc.* **1990**, *112*, 747 and references therein. (b) Rabek, J. K. In *Mechanisms of Photophysical Processes and Photochemical Reactions in Polymers*; Wiley: New York, 1987. (c) Goeller, G.; Rieker, J.; Maier, A.; Sterowski, J. J.; Daltrozzo, E.; Neurieter, M.; Port, H.; Wiechmann, M.; Kramer, E. A. *J. Phys. Chem.* **1988**, *92*, 1452.

(37) Some preliminary information on the binding ability of the [CuL] fragment, able to coordinate carbon monoxide and to collapse into a tetranuclear structure, have been published: ref 27.

Scheme 6



electron- and/or energy-transfer interactions with the diene in the excited state) determine the preferred pathway.

The use of copper(I) complexes with heterocyclic bidentate amines as sensitizers for the NBD → Q photoisomerization was originally proposed by Kutal.[6] Such complexes have absorption bands in (or near) the visible due to the presence of low-energy MLCT transitions,[31] and it has been thought that, in the presence of a coordinated NBD molecule, excitation in the MLCT absorption could lead to NBD → Q isomerization. This process could be due to an intramolecular energy transfer from the MLCT state to a reactive state (most likely a NBD-localized triplet excited state) or be related to partial delocalization of the increased positive charge of the copper ion on the alkene. Examples of this type of copper(I) complex as sensitizers are present in the literature,[8d,e] but the authors did not find any evidence of ground-state association between the complex and NBD, and hence a bimolecular sensitization process was proposed.

In our case the peculiar characteristics of the $N\frown O$ bidentate ligands allowed, other than the presence in the copper(I) complex of a MLCT absorption in the visible, the synthesis and characterization of the copper(I) complex−NBD adducts. Therefore, the NBD → Q photoisomerization sensitized by these complexes, in particular by **3**, should follow the ground-state complex mechanism depicted in Scheme 5a.

However, an important question to ask before discussing the metal-assisted **1** → **2** photoisomerization process concerns the actual species in solution which undergoes the photoexcitation. Although we isolated dimeric compounds in the solid state, a number of facts seem to support the existence, in solution, of a prevailing monomeric complex **9** according to the equilibrium in Scheme 6, and mainly in the presence of free NBD, as is the case when we run the photochemical reaction.

A slow disproportionation of **3** to copper(II) and copper metal has been observed in solution although it can be suppressed in the presence of excess NBD. The ^{1}H NMR spectrum of **3** in the presence of free NBD shows a fast exchange between bound and free alkene. The resolution of NBD signals in two separate sets of resonances corresponding to free and complexed NBD has been observed only below 200 K. The copper(I)−alkene bond lability is further supported by the fact that **7** acts as a photocatalyst for the NBD → Q conversion.

The effect of NBD on the equilibrium depicted in Scheme 6 is proved by the increased solubility of **3** in methanol in the presence of an excess of NBD. In a typical experiment, a *ca.* 6-fold increase of solubility is obtained using a methanol solution 0.1 M in NBD (which corresponds to an NBD:**3** ratio of 4:1). This result shows that **9** is present in the solution of **3** even in the presence of relatively small amounts of NBD. The presence of excess norbornene (which forms the 1:1 complex **7**) has the same effect on the solubility of **3**.

Additional support for **9**, formed from **3** in the presence of excess NBD, comes from photolysis experiments performed on **3** in the absence of free NBD. As demanded by the mechanism described in Scheme 5a, irradiation of **3** alone in methanol gives rise to production of Q. Concurrently, some disproportionation of the released [CuL] to copper metal and copper(II) is observed. The measured quantum yield for Q production (*ca.* 0.006) is, however, much lower than those measured in the presence of NBD. This can be rationalized assuming that the monomeric species **9** is responsible for the NBD → Q transformation in the presence of NBD and that this species has a photoisomerization quantum yield higher than **3**. An alternative explanation, namely, the complete inactivity of **3** toward the NBD → Q photoisomerization and the presence of significative amounts of **9** even in solutions of **3** without free NBD, cannot, however, be excluded.

In spite of these supports on the existence of **9**, we were unable to isolate it in the solid state. UV−vis experiments show only small differences between the absorption spectra above 300 nm of **3** in methanol and in NBD 0.1 M, even if the latter is quite close to that of **7**.

Let us turn our attention to the dependence of the isomerization quantum yield on the concentration of NBD. As is shown in Figure 5, the best performance of the catalyst occurs up to 4 M NBD in methanol, in the region where the monomeric species **9** is presumably almost the unique species present. At much higher concentrations, we observed a significant drop of the quantum yield, which is most probably due to the formation, under such conditions, of the bis(alkene) complex **10** (see Scheme 6), and in turn would cause deactivation of the [CuL] photosensitizer (see below). The **9** → **10** conversion, however, seems incomplete even in neat NBD. On the other hand, the low quantum yields obtained in diluted NBD solutions could be ascribed to an incomplete conversion of the dimer in the monomeric species.

Concerning the solvent dependence of the quantum yield, it is interesting to note that in Kutal's work on the CuCl-assisted NBD → Q photoisomerization, quantum yields were independent of the solvent, except when the solvent (*e.g.*, acetonitrile) coordinates the copper(I) ion and hinders the formation of the CuCl−NBD adduct. In our work, we found that, when **3** is used as sensitizer, the photoisomerization quantum yield in methanol is significantly higher than those obtained in the other solvents. The fact that the MLCT absorption band of **3** is at the highest energy in methanol and that in this solvent compounds **4** and **5** (which are less efficient or not at all efficient in sensitizing the isomerization) show MLCT absorption bands at lower energies suggests that the dependence of the photoisomerization quantum yield on the solvent derives from energetic reasons. Thus, even a relatively small decrease in the energy of the MLCT excited state leads to a lower efficiency in sensitizing the photoisomerization. In this way the behavior of **4** and **5** (and perhaps even **6**) as sensitizers can be explained. The inefficiency of compound **10** in sensitizing the isomerization may have a similar explanation, considering that in neat NBD the absorption spectrum shows a MLCT band at *ca.* 420 nm. Inactivity of **10** due to the occurrence of a dimerization reaction instead of the NBD → Q isomerization (which seemed possible assuming a bis(alkene) nature for this compound) can be excluded because we have not found any dimeric product even in neat NBD. Finally, it was noticed that the temperature dependence of the quantum yield observed using **3** as precursor catalyst suggests some kind of thermal activation in the sensitized photoisomerization process.

The measurement at high values of NBD → Q conversion shows a remarkable selectivity, with no relevant side products indicated either by the mass balance of the reaction or by GC analysis of the products. The small quantities of white precipitate observed in some reactions consist presumably of a norbornadiene polymer (NBD is known to self-polymerize to an insoluble white powder within a few hours at room temperature).[38]

Finally, we should emphasize that, even if the values for the NBD → Q photoisomerization quantum yield obtained using **3** as precursor catalyst are not very high compared to those reported in many previous works, there are no cases in which the quantum yield for photoisomerization of unsubstituted NBD has been measured upon irradiation with visible light ($\lambda > 400$ nm). Moreover, it is worthwhile noting the remarkable photostability of the catalyst, evidenced by the high turnover numbers (about 5000) and overall NBD → Q conversions (over 95%) obtained.

Conclusions

The photoassisted NBD → Q conversion has been achieved with interesting quantum yields and very high conversions and turnover numbers by designing appropriate copper(I) photosensitizers. For the first time, using π-delocalized $N\frown O$ bidentate monoanionic ligands, we have generated copper(I) fragments with the appropriate geometrical and electronic properties for binding a single alkene functionality. Their kinetic inertness toward the loss of the bidentate ligand and the lability toward the olefin exchange make them ideal model compounds for assisting the NBD → Q photoisomerization. The use of π-delocalized ligands has allowed the move from the UV to the visible region in the NBD → Q transformation.

Acknowledgment. We thank the Action COST D3 (European Program for Scientific Research) for financial support and Dr. Philippe Blech for some exploratory work in the field.

Supporting Information Available: ORTEP drawings (Figures S1 and S2) and tables giving crystal data and details of the structure determination, fractional atomic coordinates, anisotropic and isotropic thermal parameters, bond lengths, and bond angles for **3** and **6** (14 pages). Ordering information is given on any current masthead page.

IC9706156

---

[38] Rapean, J. C.; Shaw, P. V. U.S. Patent 3 860 497, 1975; *Chem. Abstr.* **1975**, *82*, P139523i.