Figure 2. Temperature-variation profile of the proton NMR signals of cis-[Pt(DMSO)(C₃H₆)Cl₂] in CDCl₃. The downfield sets of resonances correspond to the DMSO protons; those to higher fields refer to the olefinic methyl protons.

Neither the cis-2-butene nor the trans-2-butene complex is fluxional below 50 °C. The trans-2-butene complex, in addition to the diastereotopically split methyl proton signals, shows two olefinic methyl proton doublets of equal intensity indicating that the vinylic methyl groups are experiencing different environments. Were the olefin rotating, the methyl proton chemical shifts would be averaged. The cis-2-butene ligand is not prochiral but can have two isomeric forms of the same kind as described for the propene system. Two sulfur methyl proton signals as well as two olefinic methyl proton doublets are observed. The corresponding signals are of unequal intensity and we ascribe them to the two isomers which, because these signals persist up to 50 °C, are not interconverting on an NMR time scale below this temperature.

3. Experimental Section

The variable-temperature spectra were carried out using a Varian HA 100 spectrometer. CDCl₃ was the solvent and TMS the reference.

cis-[Pt(DMSO)(C₂H₄)Cl₂]. Dimethyl sulfoxide (0.850 g) in 0.1 N HCl (50 ml) was added to a solution of K₂[PtCl₄] (4.150 g) in 0.1 N HCl (75 ml). The resulting solution was immediately placed under an atmosphere of ethylene and vigorously stirred. A pale gray solid began to deposit within 1 h, and after 2 days, the product was collected and was washed with water and then with ether (2.80 g). The solid was taken up in a small volume of boiling acetone and then was filtered under gravity to remove small amounts of platinum metal. The slow addition of hexane to the warm solution afforded white needles of the pure complex (2.5 g).

Anal. Calcd for [Pt(C₂H₆SO)(C₂H₄)Cl₂]: C, 12.9; H, 2.7; S, 8.6; Cl, 19.1. Found: C, 13.0; H, 2.7; S, 8.8; Cl, 18.9.

cis-[Pt(DMSO)(C₃H₆)Cl₂]. Propene was bubbled through a solution of cis-[Pt(DMSO)(C₂H₄)Cl₂] (0.40 g) in acetone (16 ml) for 1 h. The solution was reduced to dryness under vacuum, and the oily residue was dissolved in CH₂Cl₂ (1.5 ml) containing ether (1 ml); then 30–60 °C petroleum ether (15 ml) was added very slowly to precipitate very

pale yellow crystals. The collected product was washed with petroleum ether. The product (0.38 g) was recrystallized from CH₂Cl₂ (2 ml) containing ether (2 ml) by the slow addition of 30–60 °C petroleum ether (0.36 g).

Anal. Calcd for [Pt(C₂H₆SO)(C₃H₆)Cl₂]: C, 15.5; H, 3.1; S, 8.3; Cl, 18.4. Found: C, 15.9; H, 3.2; S, 8.1; Cl, 18.4.

cis-[Pt(DMSO)(*cis*-2-C₄H₈)Cl₂]. cis-2-Butene was bubbled through a solution of cis-[Pt(DMSO)(C₂H₄)Cl₂] (0.50 g) in acetone (11 ml) for 3 h. The solution was reduced to dryness and the crystalline residue was dissolved in CH₂Cl₂ (3 ml); then ether (2 ml) was added and precipitation was begun by the careful addition of 30–60 °C petroleum ether (10 ml). After cooling (4 °C; 15 h), the pale yellow needles were collected and were washed with petroleum ether. Recrystallization from CH₂Cl₂ (4 ml) containing ether (3 ml) by the careful addition of 30–60 °C petroleum ether (35 ml) afforded shiny, off-white flakes (0.22 g).

Anal. Calcd for [Pt(C₂H₆SO)(C₄H₈)Cl₂]: C, 18.0; H, 3.5; S, 8.0; Cl, 17.8. Found: C, 17.7; H, 3.6; S, 8.2; Cl, 18.1.

cis-[Pt(DMSO)(*trans*-2-C₄H₈)Cl₂]. This complex was prepared by the method described for the cis-2-butene complex. Following the removal of the solvent, the crystalline residue was precipitated from CH₂Cl₂ (1 ml) followed by the successive slow addition of ether (2 ml) and 30–60 °C petroleum ether (5 ml). The product was recrystallized from CH₂Cl₂ (2 ml) containing ether (2 ml) by the slow addition of 30–60 °C petroleum ether (10 ml) (0.32 g).

Anal. Calcd for [Pt(C₂H₆SO)(C₄H₈)Cl₂]: C, 18.0; H, 3.5; S, 8.0; Cl, 17.8. Found: C, 18.2; H, 3.4; S, 8.2; Cl, 17.9.

cis-[Pt(DMSO)(1-C₄H₈)Cl₂]. This complex was prepared by the method described for the cis-2-butene compound.

Anal. Calcd for [Pt(C₂H₆SO)(C₄H₈)Cl₂]: C, 18.0; H, 3.5; S, 8.0; Cl, 17.8. Found: C, 18.2; H, 3.5; S, 7.9; Cl, 17.8.

Registry No. cis-[Pt(DMSO)(ethylene)Cl₂], 31902-28-0; cis-[Pt(DMSO)(propene)Cl₂], 39832-16-1; cis-[Pt(DMSO)(1-butene)Cl₂], 39722-88-8; cis-[Pt(DMSO)(cis-2-butene)Cl₂], 61128-89-0; cis-[Pt(DMSO)(trans-2-butene)Cl₂], 61176-42-9; K₂[PtCl₄], 10025-99-7.

References and Notes

(1) Y. N. Kukushkin, *Inorg. Chim. Acta*, **9**, 117 (1974), and references therein.
(2) F. A. Cotton, R. Francis, and W. D. Horrocks, *J. Phys. Chem.*, **64**, 1534 (1960).
(3) J. H. Price, A. N. Williamson, R. F. Schramm, and B. B. Wayland, *Inorg. Chem.*, **11**, 1280 (1972).
(4) J. S. Anderson, *J. Chem. Soc.*, 1042 (1936).
(5) W. F. Currier and J. H. Webber, *Inorg. Chem.*, **6**, 1539 (1967); J. Selbin, W. E. Bull, and L. H. Holmes, *J. Inorg. Nucl. Chem.*, **16**, 219 (1961); W. Kitching, C. J. Moore, and D. Doddrell, *Inorg. Chem.*, **9**, 541 (1970).
(6) N. C. Payne, private communication.
(7) R. Cramer, *J. Am. Chem. Soc.*, **86**, 217 (1964); R. Cramer, *Inorg. Chem.*, **4**, 445 (1965).
(8) J. Ashley-Smith, Z. Douek, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc., Dalton Trans.*, 128 (1974), and references therein.

Contribution from the Department of Chemistry, University of Georgia, Athens, Georgia 30602

Transition Metal Photoassisted Valence Isomerization of Norbornadiene. An Attractive Energy-Storage Reaction

Dwight P. Schwendiman and Charles Kutal*

Olefins undergo a variety of facile thermal and photochemical reactions in the presence of transition metal complexes. Examples of such metal-assisted processes include cis–trans isomerization, hydrogen shifts, hydrogenation, and dimerization.[1] During an investigation into the role of transition metal compounds in the photoassisted reactions of strained olefins, we have observed that norbornadiene (NBD) undergoes efficient valence isomerization to quadricyclene (Q) in the presence of catalytic amounts of cuprous chloride (reaction 1).[2] The surprising absence of significant competing

$$\text{NBD} \xrightarrow[h\nu]{\text{CuCl}} \text{Q} \tag{1}$$
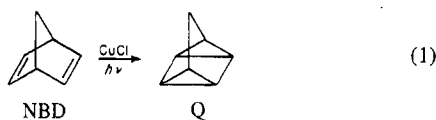
side reactions suggests the existence of a specific cuprous chloride–norbornadiene interaction which predisposes the olefin toward isomerization. The mechanistic implications of this premise prompted us to undertake a detailed spectral and photochemical study of the system, the results of which are reported here. We find evidence that the preassembly of norbornadiene and CuCl in a stoichiometric complex is a key feature of the mechanism and, furthermore, that the specificity of product formation is understandable in terms of the bonding properties of CuCl.

Experimental Details

Commercially available norbornadiene (Aldrich) was distilled from metallic potassium under a nitrogen atmosphere. The electronic spectrum of a 1.0 M solution of the freshly distilled diene exhibited no absorption above 295 nm. CuCl was prepared by a literature procedure[3] and stored in a desiccator under nitrogen. All solvents were dried by standard techniques and kept under nitrogen.

In a typical photolysis experiment a nitrogen-purged solution of 1.0 M norbornadiene and ~5 × 10⁻³ M cuprous chloride in chloroform was irradiated at 313 nm in 1-cm quartz cells using a medium-pressure mercury merry-go-round apparatus and suitable blocking filters. Light intensity was determined by ferrioxalate actinometry.[4] The resulting norbornadiene–quadricyclene mixture was analyzed by gas chromatography using a Varian 2700 gas chromatograph equipped with a flame ionization detector and containing a 6 ft × 1/8 in. 1.5% OV-101 on Chromosorb W (80–100 mesh) stainless steel column. The operating temperatures of the instrument were as follows: injector, 135–140 °C; column, 75–80 °C; detector, 250 °C. Flow rates of nitrogen carrier gas between 10 and 15 ml were employed.

The extent of reaction was determined by comparing the gas chromatographic peak areas (determined by planimetry) of the irradiated sample with those of an unirradiated standard. Since the detector responses were determined experimentally to be virtually identical for norbornadiene and quadricyclene, the ratio of peak areas is a direct measure of isomeric composition.

Electronic absorption spectra were determined using a Cary 15 spectrophotometer.

Results and Discussion

The key photochemical results can be summarized as follows: (1) The CuCl photoassisted conversion proceeds with high quantum efficiency, the quantum yield at 313 nm having a value of 0.3–0.4 in chloroform and 0.2–0.3 in ethanol. Irradiation in the absence of CuCl affords no quadricyclene; likewise the thermal reaction is negligibly slow. (2) The process is catalytic in CuCl. Thus >200 mol of quadricyclene is formed per mole of CuCl. (3) The conversion can be driven to >90% completion, since the thermal reversion of quadricyclene to norbornadiene is not catalyzed by CuCl. (4) The conversion appears to proceed cleanly.[5] A sample in which 58% of the norbornadiene had been converted to quadricyclene contained <1% side products. (5) The photoreaction exhibits a marked solvent dependence. While isomerization proceeds efficiently in chloroform and ethanol, no detectable conversion occurs in acetonitrile.

The involvement of a metal–olefin complex in the photoassisted conversion is suggested by spectral data. Thus a 2 × 10⁻³ M CuCl–0.1 M norbornadiene solution in chloroform or ethanol displays an intense band ($\lambda_{max}^{CHCl_3}$ 253 nm, ϵ 7.9 × 10³; λ_{max}^{EtOH} 248 nm, ϵ 6.3 × 10³) whose tail absorbs 99% of the incident light at 313 nm (Figure 1). We assign this band, which is absent in the spectra of the parent compounds, as a charge-transfer (involving the metal and olefin) transition within a ClCu–NBD π complex. The 1:1 stoichiometry for this species in solution[6] was inferred from a Hildebrand–Benesi treatment[7] of the spectral data obtained from a series of ethanol solutions containing a constant amount of CuCl and
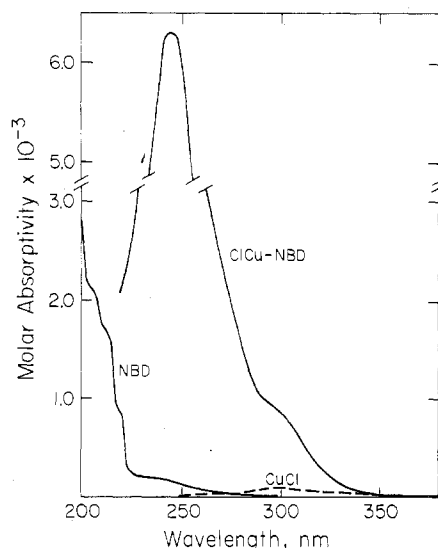

Figure 1. Spectral evidence for π-complex formation (spectra taken in ethanol).
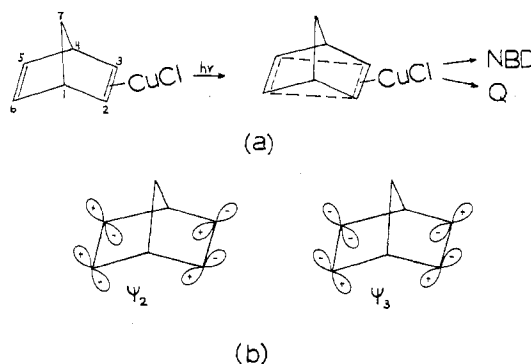

Figure 2. (a) Proposed mechanism of the CuCl photoassisted isomerization of norbornadiene to quadricyclene. (b) Representation of the highest filled (ψ_2) and lowest unfilled (ψ_3) π molecular orbitals on norbornadiene.

varying concentrations (0.1–1.28 M) of norbornadiene. The usual plot of [CuCl]/A_λ (A_λ is the absorbance at a fixed wavelength) vs. 1/[NBD] yields a horizontal straight line, indicating that complex formation (eq 2) is complete in the

$$\text{CuCl} + \text{NBD} \rightleftharpoons \text{ClCu–NBD} \tag{2}$$

concentration range studied. Since both CuCl and norbornadiene are essentially transparent at 313 nm in ethanol or chloroform, we consider the photoassisted conversion observed at this wavelength to be characteristic of the stoichiometric ClCu–NBD π complex. This conclusion is compelled especially strongly by our finding that no detectable complex formation occurs in acetonitrile, a solvent in which photoreactivity is conspicuously absent.[8]

An attractive formulation of the mechanism of photoassisted conversion is presented in Figure 2. Irradiation at 313 nm populates a charge transfer excited state of the ClCu–NBD π complex. Although we are uncertain at present as to the direction of charge transfer—metal to olefin or olefin to metal—the practical consequences in terms of the bonding changes within the olefin are similar in either case. Thus the transfer of a 3d electron from Cu(I) to the lowest unoccupied π molecular orbital,[9] ψ_3, on norbornadiene weakens the bonding between C_2–C_3 and C_5–C_6 while enhancing that between C_2–C_6 and C_3–C_5. Electron transfer in the opposite sense, from the highest occupied π molecular orbital, ψ_2, on norbornadiene to the metal, produces a *qualitatively* similar effect on the bonding. The electronically excited complex may then partition between relaxation pathways that lead to

norbornadiene and quadricyclene.

The absence of norbornadiene dimers among the photoproducts of reaction 1 is noteworthy, since there is ample precedent for facile thermal[10,11] and photochemical[12] cycloadditions of norbornadiene in the presence of transition metal compounds. The role generally ascribed to the metal in such intermolecular addition processes is that of a template binding two (or more) proximal norbornadiene molecules, which subsequently react to form the dimer. Thus the availability of at least two coordination sites on the metal appears to be a key prerequisite for dimerization. Our data suggest that CuCl possesses little residual bonding affinity beyond that employed in forming the ClCu–NBD complex. The reluctance of this latter species to expand its coordination number,[13] either by simple addition of a second norbornadiene molecule or by oxidative addition, precludes the occurence of dimerization. Consequently, valence isomerization (Figure 2) emerges as the predominant chemical pathway for utilizing the excitation energy of the absorbed photon. Indeed it is our feeling that CuCl may be prototypal of a class of transition metal compounds which can specifically effect this transformation.[14]

Finally, we wish to note that a solar energy storage system based upon the norbornadiene–quadricyclene interconversion possesses several attractive features: (i) Norbornadiene is prepared from relatively inexpensive starting materials (acetylene and cyclopentadiene). (ii) The specific energy storage capacity, $\sim$230–260 cal/g of quadricyclene produced,[15] is 3–4 times greater than that of water-based sensible heat systems. (iii) Sunlight is stored as chemical rather than thermal energy, thus preluding the need for extensive insulation of the storage medium. (iv) Energy may be stored indefinitely, since reversion of quadricyclene to norbornadiene is negligibly slow at room temperature. Addition of appropriate transition metal catalysts,[16] however, effects rapid reversion with release of the excess energy.

The above characteristics make a norbornadiene-based system particularly promising for applications utilizing low-grade ($\sim$100 °C) heat such as the heating and cooling of buildings and hot water preparation.[17] Further work aimed at developing a viable energy storage system based upon reaction 1 is underway, including the search for transition metal–norbornadiene complexes which absorb more strongly in the wavelength region of available solar energy.

Registry No. CuCl, 7758-89-6; norbornadiene, 121-46-0; quadricyclene, 278-06-8.

References and Notes

(1) M. Wrighton, *Chem. Rev.*, **74**, 401 (1974).
(2) Brief, qualitative mention of this process has appeared previously; however no mechanisitc studies were performed: D. J. Trecker, R. S. Foote, J. P. Henry, and J. E. McKeon, *J. Am. Chem. Soc.*, **88**, 3021 (1966). We have found that CuBr and CuI are also effective in promoting quadricyclene production.
(3) G. Brauer, "Handbook of Preparative Inorganic Chemistry", R. F. Riley, Translation Ed., 2d ed, Academic Press, New York, N.Y., 1963, p 1005.
(4) C. G. Hatchard and C. A. Parker, *Proc. R. Soc. London, Ser. A*, **235**, 518 (1956).
(5) We sporadically encountered samples in which some apparent decomposition of the C$_7$ hydrocarbons had occurred. We attribute this problem to the presence of impurities (particularly oxygen) which promote undesirable thermal reaction.
(6) The solid-state structure of the complex exists as tetrameric (ClCuNBD)$_4$ units in which each copper atom is bonded in an exo configuration to one norbornadiene molecule: N. C. Baenziger, H. L. Haight, and J. R. Doyle, *Inorg. Chem.*, **3**, 1535 (1964).
(7) L. J. Andrews and R. M. Keefer, "Molecular Complexes in Organic Chemistry", Holden-Day, San Francisco, Calif., 1964.
(8) The absence of complex formation in acetonitrile is presumably due to the strong solvation of CuCl, thus preventing the copper from coordinating to norbornadiene: I. M. Kolthoff and J. F. Coetzee, *J. Am. Chem. Soc.*, **79**, 1852 (1957).
(9) We employ a delocalized LCAO–MO scheme to describe the π bonding in norbornadiene, since there is considerable evidence for homoconjugation of the double bonds in the molecule: F. A. Van Catledge, *J. Am. Chem. Soc.*, **93**, 4365 (1971), and references cited therein. While certain complicating features (such as σ–π mixing) are neglected in this approach, we feel that it adequately identifies the major changes in electron density responsible for the observed photobehavior of norbornadiene.
(10) G. N. Schrauzer, *Adv. Catal.*, **18**, 373 (1968).
(11) A. R. Fraser, P. H. Bird, S. A. Bezman, J. R. Shapley, R. White, and J. A. Osborn, *J. Am. Chem. Soc.*, **95**, 597 (1973).
(12) B. Hill, K. Math, D. Pillsbury, G. Voecks, and W. Jennings, *Mol. Photochem.*, **5**, 195 (1973).
(13) R. G. Salomon and J. K. Kochi, *J. Am. Chem. Soc.*, **95**, 1890 (1973).
(14) For example, preliminary studies in our laboratory indicate that certain copper(I) phosphine complexes promote the photochemical valence isomerization of norbornadiene.
(15) D. S. Kabakoff, J.-C. Bunzli, J. P. M. Oth, W. B. Hammond, and J. A. Berson, *J. Am. Chem. Soc.*, **97**, 1510 (1975), and references cited therein.
(16) K. C. Bishop, *Chem. Rev.*, **76**, 461 (1976).
(17) S. G. Talbert, D. H. Frieling, J. A. Eibling, and R. A. Nathan, *Sol. Energy*, **17**, 367 (1975).

Contribution from the Department of Chemistry,
University of Wisconsin, Madison, Wisconsin 53706

Crystal Structure of Niobium Tetrachloride

D. R. Taylor, J. C. Calabrese, and E. M. Larsen*

We wish to report the first accurate detailed determination of the structure of NbCl$_4$. Niobium tetrachloride has been reported as being both monoclinic[1,2] and orthorhombic,[3] while its structure has been described[4] as similar to that of α-NbI$_4$.[5] McCarley[3] found NbCl$_4$ was not isomorphic with α-NbI$_4$ but he was unable to obtain a suitable single crystal due to twinning and disorder problems. Other workers[1,6] have had similar difficulties with niobium halides.

Suitable crystals of niobium tetrachloride were synthesized by the reaction of niobium pentachloride (5 g) with niobium metal (0.5 g) in a sealed and evacuated Pyrex ampule (15 cm long and 20 mm in diameter). The ampule was positioned in a tube furnace so that the pentachloride, when liquid, covered the metal. The reactants were maintained at a uniform temperature of 300 °C throughout the week long reaction. At the completion of the reaction, the walls of the ampule were covered with dark brown niobium tetrachloride in quantitative yield. This method of preparation differs from that previously reported[3,7] in which the metal and pentachloride were separated and a temperature gradient of 250 to 400 °C was used. The air-sensitive product was handled in an inert atmosphere throughout all manipulations.

The crystal chosen, a needle with well-defined faces, was wedged in a Lindemann glass capillary under dry N$_2$ and placed on a Syntex P$\bar{1}$ autodiffractometer equipped with a graphite monochromated Mo Kα radiation source. The Syntex procedure, which included partial rotation photographs along each of the reciprocal axes, revealed a monoclinic lattice with cell dimensions a = 8.140 (5), b = 6.823 (4), c = 8.852 (6), β = 91.92 (5), V = 491.4 (5).[8] Data were collected for $^1/_4$ of the sphere from 3° $\leq$ 2θ $\leq$ 50° using a scan time to background time ratio of 0.67. Stability of the intensities was indicated throughout the data collection from two standard reflections monitored after every 50 observations. The data

Table I. Positional Parameters for NbCl$_4$

Nb(1)	0	0.221 98 (8)	0
Cl(1)	0.028 13 (12)	0	0.213 20 (11)
Cl(2)	−0.278 92 (11)	0.243 71 (16)	0.023 02 (10)
Cl(3)	0.024 48 (12)	0.5	0.187 34 (11)