

Figure 2. ORTEP⁷ drawings for $\text{Cu}_2(\text{NBA})_2(\mu\text{-Dabco})$, with thermal ellipsoids at the 33% probability level. (a) Top view, showing tilting of one naphthalene plane. (b) Side view, including atom labeling scheme. Primed and unprimed atoms are related by the crystallographic mirror plane, which passes through C16, C17, C22, and C23.

Solutions of $\text{Cu}_2(\text{NBA})_2$ change from olive green to turquoise on addition of Lewis bases B, as expected for the reaction $\text{Cu}_2(\text{NBA})_2 + \text{B} \rightleftharpoons \text{Cu}_2(\text{NBA})_2\text{B}$. (The electronic spectra of $\text{Cu}_2(\text{NBA})_2$ and $\text{Cu}_2(\text{NBA})_2\text{B}$ are similar to those previously reported⁵ for $\text{Cu}_2(m\text{-XBA})_2$ and $\text{Cu}_2(m\text{-XBA})_2(\text{py})_2$.) Equilibrium constants (Table I) for binding of pyridine (3) and quinuclidine (5) to $\text{Cu}_2(\text{NBA})_2$ are comparable to those in the literature for binding to $\text{Cu}(\text{acac})_2$.¹¹ These bases cannot assume an internal bridging position in **2**. On the other hand, the larger binding constants for pyrazine (4) and Dabco (6), respectively, are consistent with internal coordination. We have conclusively demonstrated this coordination mode in the case of Dabco by performing a crystal-structure analysis of $\text{Cu}_2(\text{NBA})_2(\mu\text{-Dabco})$ (see Figure 2).^{8b}

In the $\text{Cu}_2(\text{NBA})_2(\mu\text{-Dabco})$ structure ($\text{Cu} \cdots \text{Cu}$ 7.403 (4) Å), the coordination environment about Cu is square pyramidal, with the copper atoms displaced ca. 0.14 Å out of the β -diketone plane toward the Dabco N atoms (see Figure 2). This geometry is similar to those in complexes such as $(\text{quinoline})\text{Cu}(\text{acac})_2$ ¹² and $[(\text{hfac})_2\text{Cu}]_2(\mu\text{-L})$ (L = pyrazine and Dabco).¹³

Experimental and theoretical treatments of $\text{Cu}_2(\text{NBA})_2(\mu\text{-Dabco})$ indicate that rotation of bound Dabco is rapid at room temperature. Molecular-mechanics calculations,¹⁴ for example, yield a rotation barrier of ca. 20 kJ mol⁻¹. Also, thermodynamic data for binding of Dabco to $\text{Cu}_2(\text{NBA})_2$ ($\Delta H = -30$ kJ mol⁻¹ and $\Delta S = -50$ J mol⁻¹ K⁻¹; 0–30 °C., in CHCl_3) are similar to those expected if the guest molecule retains one rotational degree of freedom.¹⁵

These experiments constitute the first investigation of selective intramolecular coordination of bifunctional Lewis bases to a relatively rigid transition-metal host. We are currently studying

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(12) Ooi, S.; Fernando, Q. *Chem. Commun.* **1967**, 532–533. These pyramidal environments compare with the "Cu(acac)₂" moieties in $\text{Cu}_2(\text{NBA})_2 \cdot 2\text{CHCl}_3$, which are planar within ca. 0.02 Å.

(13) HfacH = 1,1,1,5,5,5-hexafluoro-2,4-pentanedione. Durley, R. C. E.; Hughes, D. L.; Truter, M. R. *Acta Crystallogr., Sect. B* **1980**, *36*, 2991–2997. Belford, R. C. E.; Fenton, D. E.; Truter, M. R. *J. Chem. Soc., Dalton Trans.* **1974**, 17–24.

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(15) The theoretical value of ΔS (–73 J mol⁻¹ K⁻¹) was calculated according to: Fowler, R.; Guggenheim, E. A. *Statistical Thermodynamics*; Cambridge University Press: Cambridge, 1949; pp 106–111. Geometric data for Dabco are from: Nimmo, J. K.; Lucas, B. W. *Acta Crystallogr., Sect. B* **1976**, *32*, 348–353.

the dynamics of these complexation reactions by NMR in analogous diamagnetic species and examining the effects of insertion of guest molecules on the electronic, magnetic, and redox properties of these complexes.

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Supplementary Material Available: Illustration of close intermolecular contacts in $\text{Cu}_2(\text{NBA})_2 \cdot 2\text{CHCl}_3$, packing diagrams, and tables of bond distances and angles, fractional coordinates, and thermal parameters for $\text{Cu}_2(\text{NBA})_2 \cdot 2\text{CHCl}_3$ and $\text{Cu}_2(\text{NBA})_2(\mu\text{-Dabco}) \cdot 2\text{CH}_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ (16 pages); tables of observed and calculated structure factors for $\text{Cu}_2(\text{NBA})_2 \cdot 2\text{CHCl}_3$ and $\text{Cu}_2(\text{NBA})_2(\mu\text{-Dabco}) \cdot 2\text{CH}_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ (37 pages). Ordering information is given on any current masthead page.

Photoinitiated Quadricyclane–Quadricyclane Rearrangements

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The norbornadiene–quadricyclane couple has emerged as the most intensively studied valence isomerization² because of its latent promise for solar energy storage.³ The strain energy of quadricyclane (96 kcal mol⁻¹)⁴ exceeds by 13 kcal mol⁻¹ the sum of the strain of its constituent rings. As a consequence, this highly energetic molecule enters readily into thermal⁵ and photochemical cycloadditions,⁶ is especially prone to metalation,^{7a} transition-metal-promoted isomerization,^{7b} and attack by electrophiles,⁸ and engages in photosensitized cycloreversion.⁹ Our recent devel-

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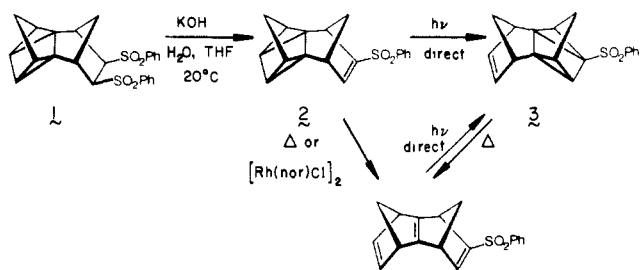
(5) (a) Smith, C. D. *J. Am. Chem. Soc.* **1966**, *88*, 4273. (b) Rieber, N.; Alberts, J.; Lipsky, J. A.; Lemal, D. M. *Ibid.* **1969**, *91*, 5668. (c) Tabushi, I.; Yamamura, K.; Yoshida, Z. *Ibid.* **1972**, *94*, 787. (d) Jenner, G.; Papadopoulos, M. *Tetrahedron Lett.* **1985**, 725. (e) LeBlanc, B. F.; Sheridan, R. S. *J. Am. Chem. Soc.* **1985**, *107*, 4554.

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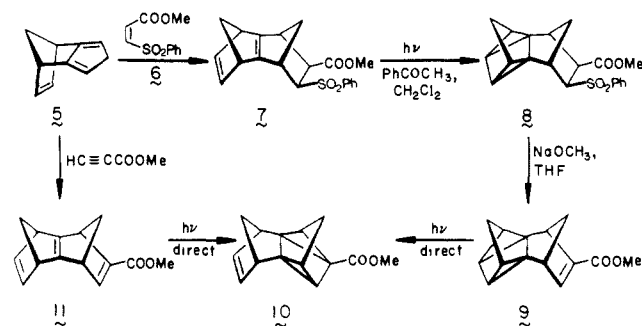
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Scheme I



Scheme II

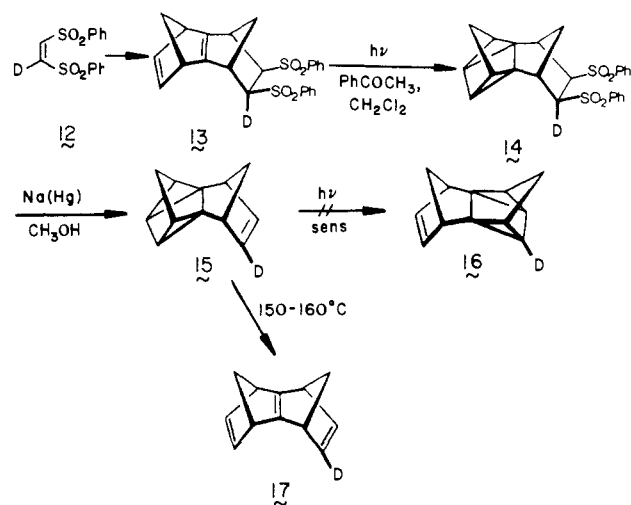


opment of a synthetic approach to *syn*-sesquinorbornatrienes¹⁰ has now made it possible to advance the first experimental demonstration of a heretofore unprecedented structural isomerization of this ring system, which for convenience has been dubbed as the quadricyclane–quadricyclane (Q–Q) rearrangement.

The first set of reactions studied began with the previously reported 1. The desired β -elimination of phenylsulfonic acid was most efficiently achieved (80%) by exposure of 1 to the overnight action of KOH in aqueous tetrahydrofuran at room temperature (Scheme I). Irradiation of degassed CH_2Cl_2 solutions of the highly crystalline (mp 173 °C, air-stable 2 contained in sealed Pyrex tubes with a 450-W Hanovia lamp for 3 h afforded the quadricyclane 3 (mp 161 °C)¹¹ in quantitative yield. The progress of this photoisomerization could readily be monitored by NMR (in CD_2Cl_2) by noting the disappearance of the characteristic vinyl sulfone doublet ($J = 3.3$ Hz) of 2 at δ 7.09 and its supplantation by an AB system at δ 6.18 and 6.12 ($J = 5.6, 2.9$ Hz) due to 3. Heating either 2 or 3 in bromobenzene- d_5 at 140–150 °C under anaerobic conditions for 1 week resulted in ca. 50% conversion to the oxygen-sensitive triene 4.¹¹ The same transformation could be effected quantitatively and more mildly by reacting 2 with a catalytic quantity of $[\text{Rh}(\text{nor})\text{Cl}]_2$ in CDCl_3 at 50 °C for 3.5 h. Upon direct irradiation as described above, 4 underwent reconversion to 3 at a rate qualitatively equivalent to that exhibited by 2 (assessed by competition experiment).

The carbomethoxy analogue 9 has also been obtained successfully (Scheme II). Heating 5 in the neat with 6¹² at 55–60 °C overnight under argon gave in quantitative yield the below-plane anti-Alder adduct 7 (mp 143 °C). The required quadricyclane 9 (mp 42 °C) proved accessible by acetophenone-sensitized irradiation of 7 (71%) and β -elimination of the phenylsulfonyl group in 8 (mp 164 °C) with sodium methoxide in dry tetrahydrofuran (4 h, 20 °C, 61%).¹¹ The photoisomerization of 9 also

Scheme III



proceeded with exceptional efficiency (450-W Hanovia lamp, Pyrex, 1.5 h) to give 10 (mp 50–52 °C) as the sole product. The response of triene ester 11¹³ to direct irradiation proved to be entirely comparable to that of 9 and gave only 10. Unfortunately, the extreme air sensitivity of 4 and 11 has so far precluded the measurement of quantum yields for their photoisomerization.

Our interest in the possibility of Q–Q rearrangement in the parent hydrocarbon prompted the preparation of 15. Metallation¹⁴ of (*Z*)-1,2-bis(phenylthio)ethylene¹⁵ followed by quenching with CH_3OD at –100 °C and H_2O_2 oxidation gave 12. This dienophile was subsequently transformed via 14 to the labeled quadricyclane (Scheme III). Because the $>\text{CD}=\text{CH}<$ bond in 15 cannot be excited by direct irradiation, recourse was made to sensitization. No detectable change was noted with acetone, acetophenone, or benzophenone. This result was not unexpected since Turro had earlier demonstrated that quadricyclane in its triplet state most rapidly decays to unrearranged ground state.^{2a,16} Heating 15 to 150–160 °C in bromobenzene- d_5 furnished 17 whose irradiation in the presence of benzophenone afforded a mixture of 16 and its vinyl deuterium isomer.

Thus, the Q–Q rearrangement operates readily in the absence of sensitizer only when the remaining double bond carries an electronegative group.¹⁷ The resulting population by 2 and 9 of the S_1 energy surface allows for interconversion with their isomeric quadricyclanes 3 and 10. Why are the latter compounds the respective apparent energy minima? At least two interesting possibilities merit consideration. Roth and Jones have shown by CIDNP methods that the cation radical derived from quadricyclane can be readily generated by photochemical electron transfer to acceptors such as 1-cyanonaphthalene.¹⁸ This discrete species undergoes irreversible conversion to the norbornadiene cation radical in competition with back electron transfer. In the present examples, electron transfer from the quadricyclane moiety in 2 and 9 to the proximal electron-deficient double bond could induce considerable weakening of the basal (as drawn) cyclopropyl σ bonds, with eventual rebonding to deliver the observed products. The reverse process is inoperative because the presence of an electron-withdrawing group on the quadricyclanyl substructure of 3 and 10 inhibits electron donation to the isolated π bond.¹⁹ The

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second option has its origins in the conformation-reactivity relationships of triplet olefins.¹⁹

The preceding considerations assume, of course, that the reaction chronology bypasses the intervention of *syn*-sesquiorbornatrienes. This question remains under active investigation.

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Reaction of sp² C-H Bonds in Unactivated Alkenes with Bis(diphosphine) Complexes of Iron

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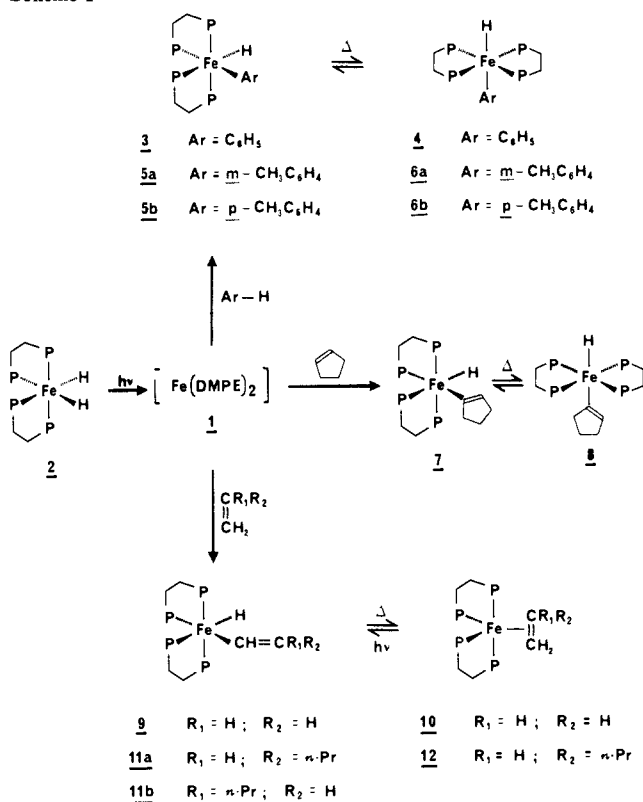
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Over the last 10 years, there has been much interest in the chemistry of coordinatively unsaturated transition-metal complexes, particularly in the activation of alkyl C-H bonds by complexes of Ir,¹ Rh,^{1b,2} Re,³ and W.⁴ Some early fundamental work^{5a-c} in the area of C-H bond activation involved Fe(DMPE)₂ (**1**) [DMPE = 1,2-bis(dimethylphosphino)ethane], a reactive intermediate generated by reductive elimination of naphthalene from *cis*-FeH(Np)(DMPE)₂ [Np = 2-naphthyl]; however, this system was limited in that only substrates with a reactivity greater than (or comparable to) that of the naphthalene byproduct could be examined. In addition, this route to **1** necessarily required reaction temperatures close to room temperature, where any thermally labile products may not have been sufficiently stable to be observed or characterized.

An alternative, more versatile route to **1** is by photolysis of the dihydride FeH₂(DMPE)₂ (**2**). We have examined the reactions of **1**, generated photochemically at low temperature, with hydrocarbons, and report here the formation of products arising from Fe insertion into sp² C-H bonds of *unactivated* alkenes.

Irradiation⁷ of a dilute solution of **2** in benzene at room temperature led to elimination of dihydrogen and formation of a mixture of *cis*-FeH(C₆H₅)(DMPE)₂ (**3**) and *trans*-FeH(C₆H₅)(DMPE)₂ (**4**)⁸ (Scheme I). Irradiation of a solution of **2** in toluene at -80 °C similarly led to elimination of dihydrogen and initially afforded a mixture of the *cis*-tolyl hydrides **5a** and **5b**.⁹ On warming to 0 °C, **5a** and **5b** isomerized to give an

Scheme I



equilibrium mixture containing **5a** and **5b** as well as the *trans* isomers **6a** and **6b**. The complexes **3-6** have been reported previously as products formed on elimination of naphthalene from FeH(Np)(DMPE)₂ in benzene or toluene.^{5c} It has been reported recently that photolysis of **2** in toluene at room temperature affords the DMPE-bridged dimer Fe₂(DMPE)₅.¹⁰ In our experience, this product is only obtained in the presence of excess DMPE.

Photolysis of **2** in solutions containing alkenes led primarily to the formation of products arising from insertion of **1** into an sp² C-H bond. On irradiation of **2** at -80 °C in a solution of cyclopentene (5% in cyclopentane) a single *cis* product formed quantitatively. This compound was assigned the structure **7**, and on warming to 0 °C it isomerized to give an equilibrium mixture of *cis*- and *trans*-cyclopentenyl hydrides **7** and **8** in a 1:3 ratio. When the reaction mixture was quenched with 2 equiv of deuteriotrifluoroacetic acid in THF at -78 °C, cyclopentene was liberated with deuterium incorporated only at the vinylic positions.

Photolysis of **2** in a solution of ethylene (4% in pentane or cyclopentane) at -80 °C afforded a 10:1 mixture of the *cis*-vinyl hydride **9** and the known π-complex **10**.^{5a} When warmed to room temperature, the C-H insertion product **9** isomerized to the π-complex. Similarly, photolysis of **2** in a solution of 1-pentene (5% in pentane) at -80 °C led to two major products in approximately equal amounts, and we assign these as the *Z* and *E* isomers **11a** and **11b**, which would arise by insertion of **1** into the terminal sp² bonds of 1-pentene.¹¹ Small amounts of the π-complex **12** were always present (ca. 5-10%) in the reaction mixture, and when the sample was warmed to room temperature, both **11a** and **11b** isomerized to **12**. This sequence is analogous to that reported¹² for the reaction of ethylene with the coordinatively unsaturated iridium species (η⁵-Me₅C₅)Ir(PMe₃), where the concurrent formation of a π-complex and a C-H insertion product has been demonstrated.

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(8) Attempts to isolate the complexes arising from direct C-H bond cleavage failed, apparently due to facile elimination of arene or alkene.

(9) The initial formation of exclusively *cis* addition products is consistent with an oxidative addition which proceeds via a three-center transition state see ref 5b.