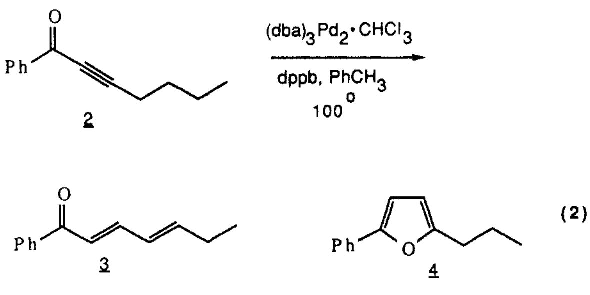
J. Am. Chem. Soc. **1988**, *110*, 2303-2305 2303

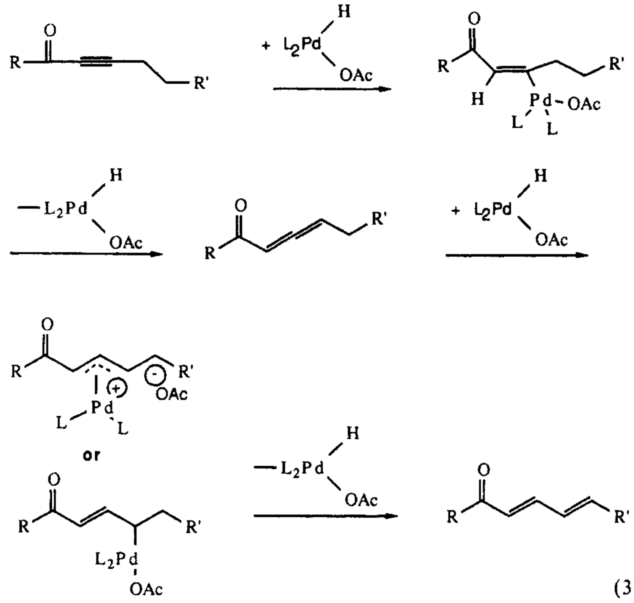


(2)

SmplSyn.01

system (Table I, entry 4) gave only the dienone in 82% yield.

The mechanism of this isomerization has not been established, but our qualitative observations suggest a reasonable possibility. Following the reaction by GC does not reveal the buildup of any intermediate. Upon the basis of the efficacy of the reaction when either palladium acetate or (dba)$_3$Pd$_2$ plus acetic acid is employed and the inefficiency when a Pd(0) species is generated by treating a Pd(2+) salt with an organoaluminum which may serve as an acid scavenger, we propose that the active catalyst is a hydridopalladium acetate.[15] By a series of hydropalladations–dehydropalladations as shown in eq 3, the isomerization proceeds presumably through an allene, either free or still complexed to palladium. Failure to detect the allene may be due to either its more rapid rate of hydropalladation to form the allylpalladium complex compared to the alkyne or because it is not freed from the palladium catalyst. The stability toward β-hydrogen insertion that is normally associated with such vinylpalladium complexes accounts for the previous failures to observe such reactions.[12] Readdition of the palladium hydride generates the allyl complex which may be either the σ-complex or a corresponding π-allyl-complex as depicted. Elimination of the elements of L$_2$Pd(H)OAc completes the sequence and reforms the catalyst. This last step is analogous to the final stage in the dehydrogenation of enones to dienones utilizing a stoichiometric amount of palladium(2+) salts.[19]



(3)

This isomerization suggests that a hydridopalladium acetate, a species not yet detected, may be a useful catalyst for a variety of organic reactions. We previously invoked its participation in a reductive enyne cyclization.[15] In unpublished work brought to our attention since the latter publication, Binger and Bentz[20] postulated its involvement in the isomerization of methylenecyclopropane. Other applications of this catalyst system are underway in our laboratories. The controlled isomerization of readily available alkynones to dienones should prove to be a simple and practical approach to these useful functional building blocks.

Acknowledgment. We thank the National Science Foundation and the General Medical Sciences Institute of the National Institutes of Health for their generous support of our programs. A Deutsche Forschungsgemeinschaft fellowship to T.S. is acknowledged with thanks.

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[19] Donati, M.; Conti, F. *Tetrahedron Lett.* **1966**, 4953. Harrison, I. T.; Kimura, E.; Bohme, E.; Fried, J. H. *Tetrahedron Lett.* **1969**, *1589*. Dunne, K.; McQuillin, F. J. *J. Chem. Soc. C* **1970**, 2200. Collins, D. J.; Jackson, W. R.; Timms, R. N. *Tetrahedron Lett.* **1976**, 495. Jackson, W. R.; Strauss, J. V. *Aust. J. Chem.* **1978**, *31*, 1073.

[20] Binger, P., private communication of Diplomarbeit of Bentz, P., Max-Planck Institut fur Kohlenforschung, 1979.

Trihydrogen Complexes of Iridium

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Recent discoveries by Kubas and co-workers[1] demonstrating that dihydrogen complexes of transition metals are in some cases isolable species has prompted considerable activity in this area.[2] Several cases are now clearly established where metal polyhydride complexes have been shown to contain both dihydrogen and hydride ligands.[3,4] Such polyhydrides undergo facile exchange of hydride and dihydrogen ligands. In the case of the cationic Ir(III) complex [Ir(bq)(L)$_2$(H)(H$_2$)]$^+$ (bq = 7,8-benzoquinoline; L = PPh$_3$) it has been suggested that the H$_2$/H exchange process may occur via a coordinated H$_3$ unit.[4] Recent computational studies by Burdett and co-workers have pointed out that coordination of H$_3^+$ to suitable transition-metal fragments is feasible.[5] We now present evidence for coordination complexes of trihydrogen to Ir moieties of the type (η^5-C$_5$H$_5$)Ir(L).

Protonation of (η^5-C$_5$H$_5$)Ir(L)H$_2$[6] (L = PMe$_3$, PPh$_3$, AsPh$_3$) with HBF$_4$·Et$_2$O in Et$_2$O affords the salts [(η^5-C$_5$H$_5$)Ir(L)H$_3$]BF$_4$ in good yields (eq 1). Complexes **1**–**3** are colorless, moderately air-stable solids which are air sensitive in solution.[9]

$$(\eta^5\text{-}C_5H_5)Ir(L)H_2 + HBF_4\cdot Et_2O \rightarrow [(\eta^5\text{-}C_5H_5)Ir(L)H_3]BF_4 \qquad (1)$$

L = PMe$_3$ (**1**); PPh$_3$ (**2**); AsPh (**3**)

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[1] (a) Kubas, G. J.; Ryan, R. R.; Swanson, B. I.; Vergamini, P. J.; Wasserman, H. J. *J. Am. Chem. Soc.* **1984**, *106*, 451. (b) Kubas, G. J.; Ryan, R. R.; Wrobleski, D. A. *J. Am. Chem. Soc.* **1986**, *108*, 2294. (c) Kubas, G. J.; Ryan, R. R.; Wrobleski, D. A. *J. Am. Chem. Soc.* **1986**, *108*, 1339. (d) Kubas, G. J.; Unkefer, C. J.; Swanson, B. I.; Fukushima, E. *J. Am. Chem. Soc.* **1986**, *108*, 7000. (e) Kubas, G. J.; Ryan, R. R. *Polyhedron* **1986**, *5*, 473.

[2] (a) Upmacis, R.; Gadd, G. E.; Poliakoff, M.; Simpson, M. B.; Turner, J. J.; Wyman, R.; Simpson, A. F. *J. Chem. Soc., Chem. Commun.* **1985**, 27. (b) Conroy-Lewis, F. M.; Simpson, S. J. *J. Chem. Soc., Chem. Commun.* **1986**, 506. (c) Chinn, M. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1987**, *109*, 5865. (d) Bianchini, C.; Mealli, C.; Peruzzini, M.; Zanobini, F. *J. Am. Chem. Soc.* **1987**, *109*, 5548. (e) Conroy-Lewis, F. M.; Simpson, S. J. *J. Chem. Soc., Chem. Commun.* **1987**, 1675.

[3] (a) Morris, R. H.; Sawyer, J. F.; Shiralian, M.; Zubkowski, J. D. *J. Am. Chem. Soc.* **1985**, *107*, 5581. (b) Morris, R. H.; Bautista, M.; Earl, K. A.; Sella, A. *J. Am. Chem. Soc.* **1987**, *109*, 3780. (c) Sweany, R. L. *J. Am. Chem. Soc.* **1985**, *107*, 2374.

[4] Crabtree, R. H.; Lavin, M. J. *J. Chem. Soc., Chem. Commun.* **1985**, 1661. Crabtree, R. H.; Lavin, M. J.; Bonneviot, L. *J. Am. Chem. Soc.* **1986**, *108*, 4032.

[5] Burdett, J. K.; Phillips, J. R.; Pourian, M. R.; Poliakoff, M.; Turner, J. J.; Upmacis, R. *Inorg. Chem.* **1987**, *26*, 3054.

[6] The dihydride precursors were prepared by reaction of the diiodides (η^5-C$_5$H$_5$)Ir(L)I$_2$ with zinc/acetic acid in methanol.[7] The diiodides were prepared by treatment of (η^5-C$_5$H$_5$)Ir(ethylene)$_2$[8] with I$_2$ followed by reaction with 1 equiv of the appropriate ligand.

[7] Moss, J. R.; Graham, W. A. G. *Inorg. Chem.* **1977**, *16*, 75.

[8] Lawson, R. J. Ph.D. Dissertation, University of Illinois, 1978.

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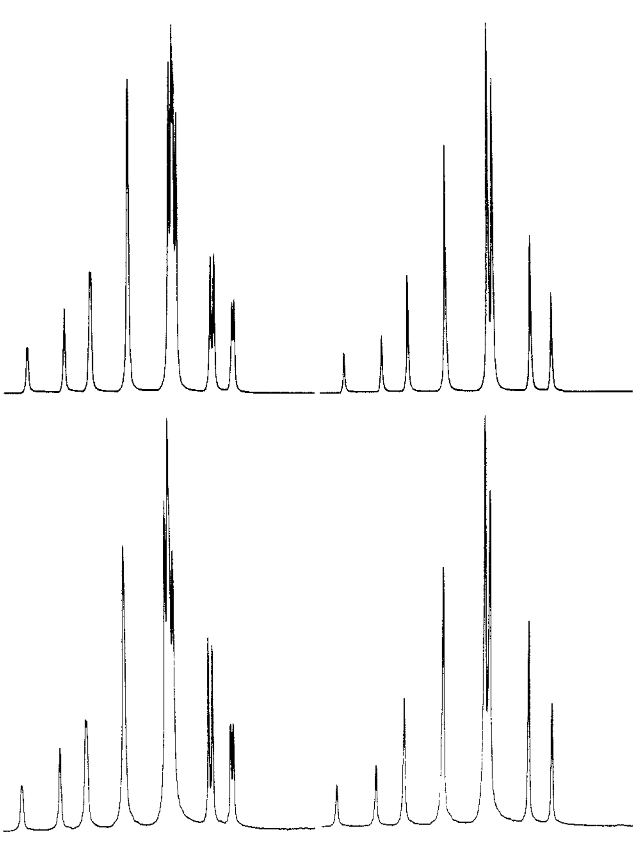


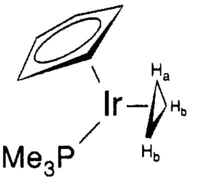
Figure 1. Experimental (bottom) and computer-simulated (top) ^1H NMR spectra of **2**, with and without ^{31}P decoupling (CD_2Cl_2, 176 K, 500 MHz). Coupling constants are J_{H-H} = 260 Hz, J_{H_A-P} = ±8.3 Hz, and J_{H_B-P} = ∓16 Hz.

Proton NMR observations at ambient temperature show appropriate cyclopentadienyl and ligand resonances. In each case, only one signal is detected in the hydride region.[10] For complex **2**, the low-temperature spectrum (183 K, CD_2Cl_2, 500 MHz) reveals an AB_2X spin system (X = ^{31}P). With ^{31}P decoupling, the spectrum is simplified to a second-order AB_2 system (see Figure 1). In spite of the chemical shift differences between H_A and H_B (1.0 ppm), a second-order spectrum was obtained even at 500 MHz, due to the extremely large proton–proton coupling. Similarly, the low-temperature spectrum of **3** is an AB_2 spin system. Simulation of the spectra[11] obtained at both 250 and 500 MHz gave values for J_{H-H} of 100, 287, and 410 Hz for compounds **1**, **2**, and **3**, respectively (178 K). These large coupling constants are quite anomalous when compared to related trihydride complexes such as $(\eta^5\text{-}C_5Me_5)Os(CO)H_3$ (J_{H-H} = 8.9 Hz).[12] A closely related cationic iridium complex $[(\eta^5\text{-}C_5Me_5)Ir(PMe_3)H_3]BF_4$ (**4**) has been reported with J_{H-H} = 56.3 Hz.[13]

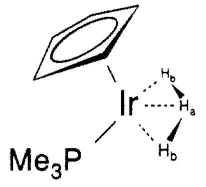
By analogy to dihydrogen complexes where partial deuteriation leading to HD complexes is diagnostic ($^1J_{H-D}$ values of 22–34 Hz have been observed, corresponding to large proton–proton couplings[1,2b–e,3a]), we have taken advantage of facile H/D exchange between the trihydride cations and D_2O to prepare mixtures of isotopic composition D_xH_{3-x} (x = 1–3). Low-temperature ^1H NMR spectra of partially deuteriated **1** exhibit no resolvable H–D couplings.[14] Similarly, the ^2H NMR spectrum of partially deuteriated **1** at 183 K consists of two resonances at −12.4 and −13.9 ppm, showing no resolvable D–H coupling. In this case, line widths are 15 Hz. A relaxation rate determination for **1**-d_3 reveals that the ^2H T_1 is 25 ms. Rapid relaxation of the quadrupolar (I = 1) deuterium nuclei in these complexes leads to loss of coupling information.

Significant upfield isotope effects are observed in the low-temperature ^1H NMR spectrum of partially deuteriated **1**. The isotope shifts of the H_A resonance induced by successive replacement of H_B with D are 72–76 ppb per D substitution.[15] The effect on the H_B resonance of substitution at H_A with D is only 34 ppb. Substitution of one of the equivalent B sites with D has no effect on the position of the H_B resonance.

The large proton–proton couplings in **1–3** and large isotope shifts observed in **1** indicate substantial bonding interactions between the "hydride" ligands. Two possible structures for **1** are a symmetric or closed form **1a** and an open structure **1b**. The asymmetry of the isotope effects noted above is strong evidence for the open structure **1b**. This is consistent with theoretical predictions that the open structure is more stable.[5] Our observations are inconsistent with formulation of these complexes as dihydrogen–hydride species.[17]



1a



1b

Attempts to confirm the structure of **1** by X-ray diffraction methods have been inconclusive thus far. A well-refined structure was obtained, but the hydride ligands could not be reliably located.[18] The infrared spectrum of **1**-H_3 (CH_2Cl_2 solution) reveals an absorption of medium intensity at 2170 cm^{-1} which is replaced by a band at 1459 cm^{-1} in **1**-D_3. Similar bands were obtained for **2** and **3**. No absorptions assignable to H–H modes could be conclusively identified.[19]

The remarkably large[20] H–H coupling constants observed in **1–3** are apparently inversely related to the electron density at the metal center. Thus the best donor ligand (PMe_3) leads to the lowest J value. This trend is continued in the previously reported complex **4**, which differs from **1** in that the cyclopentadienyl ligand has been replaced by pentamethylcyclopentadienyl.[13] These results indicate that **4** and **1–3** represent a continuum of structures ranging from a formally Ir(V) trihydride to a trihydrogen complex. These trihydrogen complexes may be regarded as $Ir(I)H_3^+$ com-

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[9] Satisfactory analytical data (C, H) have been obtained for **1–3**.

[10] ^1H NMR data (CD_2Cl_2, 298 K) **1**, δ −13.2 ppm, doublet, J_{P-H} = 10 Hz; **2**, δ −12.4 ppm, doublet, J_{P-H} = 8 Hz; **3**, δ −12.7 ppm, singlet.

[11] Simulation of spectra was carried out by using the Bruker simulation program PANIC: **1**, δ_A = −12.4 ppm, δ_B = −13.9 ppm, J_{H_A-P} = ±8 Hz, J_{H_B-P} = ∓19 Hz; **2**, δ_A = −11.8 ppm, δ_B = −12.8 ppm, J_{H_A-P} = ±8.3 Hz, J_{H_B-P} = ∓16 Hz; **3**, δ_A = −12.0 ppm, δ_B = −13.1 ppm. See Supplementary Material for details.

[12] Graham, W. A. G.; Hoyano, J. K. *J. Am. Chem. Soc.* **1982**, *104*, 3722.

[13] Bergman, R. G.; Gilbert, T. M. *J. Am. Chem. Soc.* **1985**, *107*, 3506.

[14] At 183 K, ^1H NMR hydride resonances for **1** and **2** have line widths of 2–3 Hz. A T_1 determination (180-τ-90 method) for **1**-H_3 gave a value of 300 ms: (178 K, 500 MHz) T_1 values for **2** and **3** are 200 ms (193 K, 500 MHz) and 210 ms (178 K, 490 MHz), respectively.

[15] The isotope shifts reported here are somewhat larger than those previously reported for dihydrogen complexes (37 ppb[2b]; 30 ppb[2c]) and for free dihydrogen (36 ppb[16]). For comparison the upfield isotope shift in the classical species $[(\eta^5\text{-}C_5H_5)Ru(dmpe)(H)(D)]BF_4$ is only 8 ppb: (Heinekey D. M.; Chinn, M. S., unpublished results).

[16] Evans, D. F. *Chem. Ind.* **1961**, 1960.

[17] In previously reported H_2/H complexes, coupling between coordinated dihydrogen and the adjacent hydride ligand has been not been detectable.[3a,b,4] Reported couplings between coordinated dihydrogen and ^{31}P nuclei in adjacent ligands are invariably small (2–5.8 Hz).[2c,e,3b]

[18] Pale yellow crystals of **1** were obtained by slow cooling of a CH_2Cl_2 solution. The compound crystallizes in the orthorhombic space group $P2_12_12_1$ with a = 8.858 (3) Å, b = 10.358 (2) Å, c = 14.326 (4) Å, V = 131.32 Å^3 and d_{calcd} = 2.14 g cm^{-3} for Z = 4. One molecule of composition $C_8H_{17}PIrBF_4$ forms the asymmetric unit. Patterson synthesis followed by iterative least-squares refinement and ultimately full-matrix refinement of the non-hydrogen atoms resulted in convergence to an unweighted residual of 0.032 and a weighted residual of 0.039. See Supplementary Material for details of the structure determination.

[19] In dihydrogen complexes, H–H modes have rarely been conclusively identified. Cf. ref **1a** and **2a**.

[20] The H–H coupling constant in **3** actually exceeds the value of ca. 280 Hz expected for dihydrogen itself (calculated from J_{H-D} = 43.2 Hz[21] or J_{H-T} = 299.3 Hz[22]).

plexes or as H_3^- complexes of Ir(III). In this situation the designation of the formal oxidation state is dependent on the extent of back donation from the metal to the ligand.

The observed coupling constants in **1**–**3** are highly temperature dependent. In complex **3**, J_{H-H} = 376 Hz at 176 K, increasing steadily to J_{H-H} = 570 Hz at 189 K. Similar trends are seen in **1** and **2** (see Supplementary Material). The origin of this pronounced temperature dependence remains obscure. Very recently, Chaudret and co-workers[23] have reported similar observations of large, temperature dependent H–H couplings in closely related *neutral* ruthenium complexes. Further studies to elucidate the structures of **1**–**3** and related complexes are in progress.

Acknowledgment. We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for their support of this research. We acknowledge receipt of a Cottrell grant-in-aid from the Research Corporation. A generous loan of iridium trichloride from Johnson-Matthey, Inc. is appreciated.

Registry No. 1, 113161-52-7; **2**, 113161-54-9; **3**, 113180-40-8; (η^5-C_5H_5)Ir(PMe_3)H_2, 113161-55-0; (η^5-C_5H_5)Ir(PPh_3)H_2, 113161-56-1; (η^5-C_5H_5)Ir($AsPh_3$)H_2, 113161-57-2.

Supplementary Material Available: X-ray structure data for **1**, including details of data collection and refinement, experimental (^{1}H and ^{1}H {^{31}P}) NMR spectra and computer-simulated spectra for **1** and **2** at various temperatures, and a table of J_{H-H} as a function of temperature for **1**–**3** (10 pages); table of observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

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[21] Nageswara Rao, B. D.; Anders, L. R. *Phys. Rev.* **1965**, *140*, A112.

[22] Neronov, Yu. I.; Barzakh, A. E. *Zh. Eksp. Teor. Fiz.* **1977**, *72*, 1659.

[23] Arliguie, T.; Chaudret, B.; Devillers, J.; Poilblanc, R. *C. R. Acad. Sci. Paris* **1987**, *305* (series II), 1523.

Stereochemistry and Mechanism of [4 + 2] Photocycloaddition of Pummerer's Ketone to Furan

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Received November 12, 1987

On the basis of the stereochemistry of photoaddition of MeOD to Pummerer's ketone (PK) **1**, Hart and co-workers[1] suggested that "an excited state or intermediate in which the C=C bond is twisted more than 90°" might be the chemically reactive intermediate. The reaction course was suggested to be syn addition to the "trans" double bond, by analogy to the reaction course followed on photoaddition of MeOD to derivatives of cycloheptenone and cyclooctenone.[2] We have recently presented kinetic data which suggest that [2 + 2] photocycloaddition of alkenes to nonconstrained cyclohexenones may proceed via *trans*-cyclohexenones.[3] Photoaddition of reactive 1,3-dienes to cycloheptenones and cyclooctenones[4] as well as 1-acetylcycloalkenes (n = 6–8)[5] gives trans fused [4 + 2] cycloadducts, which has generally been ascribed to capture by the diene of a ground-state *trans*-enone. This conclusion has been confirmed in eight-ring systems by formation of the same adduct(s) on excitation of the enone at low temperature followed by dark reaction with added diene.[5] Because of our interest in *trans*-cyclohexenones as possible reaction intermediates in the photochemistry of *cis*-cyclohexenones,[3] we have investigated the photoaddition of PK to furan.

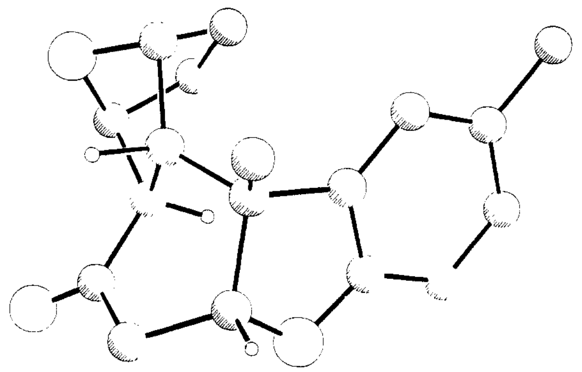


Figure 1. X-ray crystal structure of the cycloadduct **2**.

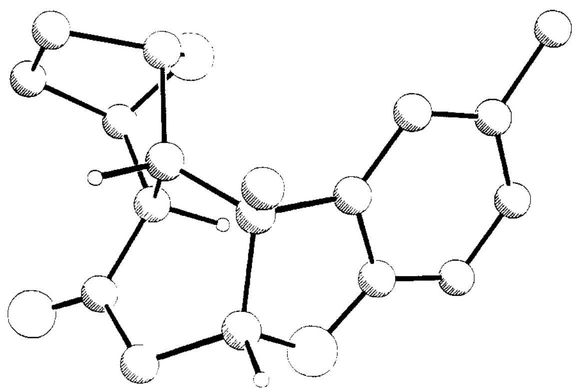
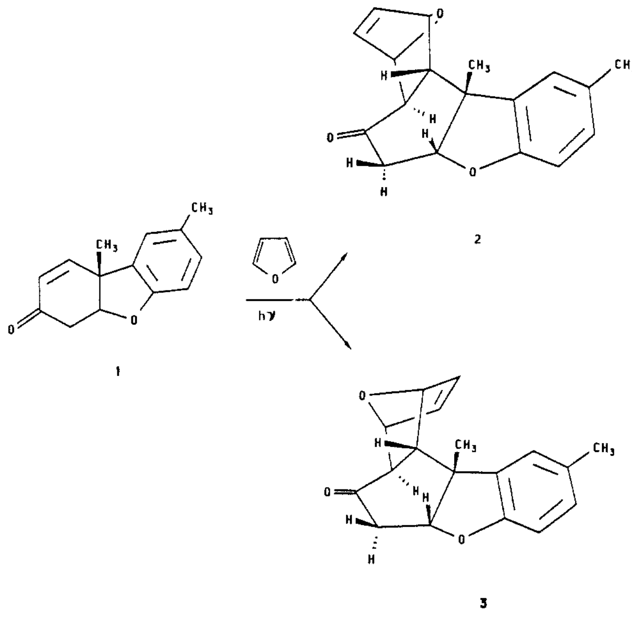


Figure 2. X-ray crystal structure of the cycloadduct **3**.

Scheme I



Irradiation of a 0.005 M solution of PK in neat furan at room temperature through Pyrex led to isolation of two PK–furan adducts, **2** (mp 219–220 °C) and **3** (mp 208–209 °C) (Scheme I). The assignment of trans stereochemistry to the ring junction protons was made from completely decoupled 300 MHz ^{1}H NMR spectra (see Supplementary Material) and was confirmed by X-ray crystallography (see Figures 1 and 2 for the crystal structures of **2** and **3**). Both **2** and **3** crystallized in the centrosymmetric, monoclinic space group $P2_1/c$, with unit cells parameters as

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[1] Dunkelblum, E.; Hart, H.; Jeffares, M. *J. Org. Chem.* **1978**, *43*, 3409.

[2] Dunkelblum, E.; Hart, H. *J. Am. Chem. Soc.* **1977**, *99*, 644. Hart, H.; Dunkelblum, E. *J. Am. Chem. Soc.* **1978**, *100*, 5141.

[3] Schuster, D. I.; Brown, P. B.; Capponi, L. J.; Rhodes, C. A.; Scaiano, J. C.; Weir, D. *J. Am. Chem. Soc.* **1987**, *109*, 2533.

[4] Corey, E. J.; Tada, M.; LeMahieu, R.; Libit, L. *J. Am. Chem. Soc.* **1965**, *87*, 2051. Eaton, P. E.; Lin, K. *J. Am. Chem. Soc.* **1965**, *87*, 2052. Eaton, P. E.; Lin, K. *J. Am. Chem. Soc.* **1964**, *86*, 2087.

[5] Eaton, P. E. *Acc. Chem. Res.* **1968**, *1*, 50.

0002-7863/88/1510-2305$01.50/0