J. Am. Chem. Soc. 1981, 103, 2431-2433 2431

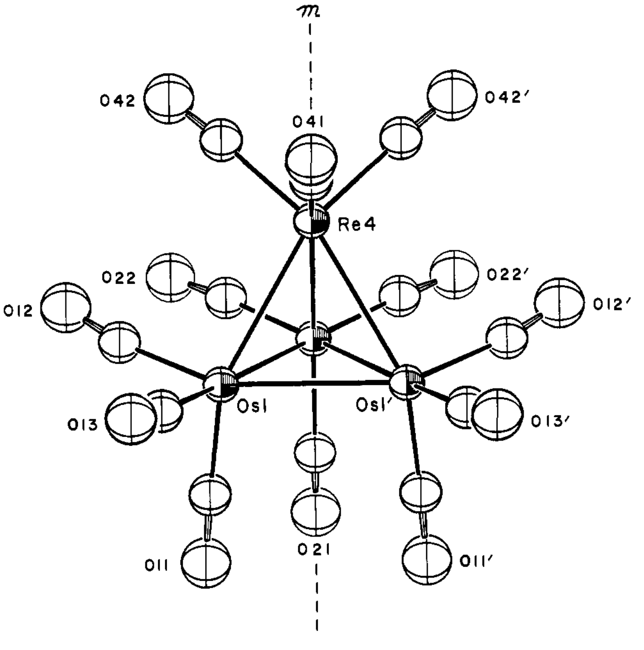
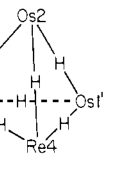


Figure 2. Molecular geometry of $(\mu\text{-H})_5Os_3Re(CO)_{12}$ (ORTEP-II diagram). Os(2) is not labeled. Relevant distances are as follows: Os(1)-Os(2) = Os(1′)-Os(2) = 2.838 (3) Å, Os(1)-Os(1′) = 2.964 (2) Å, Os(2)-Re(4) = 2.989 (4) Å, Os(1)-Re(4) = Os(1′)-Re(4) = 3.017 (3) Å. Distinction between osmium and rhenium atoms rests on the relative metal-metal bond distances. Note that, in general, M-M and M-H-M bond lengths in tetrahedral species tend to be about 0.1 Å *shorter* than in triangular species.

Os(2)-Os(1) is the *nonbridged* bond) and II (in which Os(2)-Os(1′) is the *nonbridged* bond).



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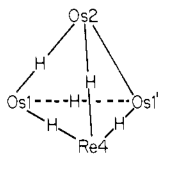

II

The compounds $(\mu\text{-H})Os_3Re(CO)_{15}(NCCH_3)$ and $(\mu\text{-H})_5Os_3Re(CO)_{12}$ have one and three rhenium-osmium bonds, respectively. A possible precursor to the latter is another compound with three Re-Os bonds, namely, $(H)Os_3Re(CO)_{15}$, which has been prepared in low yield [from $Re(CO)_5^-$ and $Os_3(CO)_{12}$][10] and structurally characterized.[11] However, we have not been able to demonstrate conversion of $(\mu\text{-H})Os_3Re(CO)_{15}(NCCH_3)$ to $(H)Os_3Re(CO)_{15}$. Another possible intermediate is a compound with two Re-Os bonds. In this case there may be a close analogy with the Os_3C portion of the $HOs_3(CO)_{10}CH_3/H_2Os_3(CO)_{10}(\mu\text{-}CH_2)/H_3Os_3(CO)_9(\mu_3\text{-}CH)$ system.[12] In particular this comparison suggests that the formation of new Re-Os bonds in the closure of $(\mu\text{-H})Os_3Re(CO)_{15}(NCCH_3)$ to $(\mu\text{-H})_5Os_3Re(CO)_{12}$ may occur via *intramolecular* "oxidative" addition of M-H bonds analogous to the formation of new C-Os bonds by cleavage of C-H bonds. Attempts to isolate and characterize intermediates in the bimetallic polyhedral closure reaction are continuing.

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η^5-Benzyl: Crystal Structure, Nucleophilic Properties, and Electron-Transfer Reactions of $CpFe(\eta^5\text{-}C_6Me_5CH_2)$, an Intermediate in C-H Activation by O_2 via $O_2^{-}\cdot$[1]

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The activation of C-H bonds, an important comtemporary problem, has been approached by organic chemists through H-radical abstraction (autoxidation)[2] and then by organometallic chemists through oxidative addition.[3] We have recently proposed[4] an alternative way of using organometallics to achieve this activation by using O_2 or air. If a neutral substrate MRH can transfer one electron to O_2 (a ready process considering the low redox potential $O_2/O_2^{-}\cdot$, −0.7 V vs. SCE), further deprotonation by $O_2^{-}\cdot$ is rendered possible through activation by the cationic organometallic moiety:

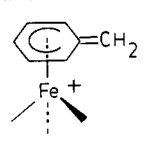
$$MRH + O_2 \rightarrow MRH^+ + O_2^{-}\cdot \xrightarrow{-HO_2} MR \qquad (1)$$

We have reported that the reaction of dioxygen with the 19-electron complex $CpFe^IC_6Me_6$ (**1**)[4] gives rise to H-atom abstraction (eq 2) while KO_2 deprotonates $CpFe^+C_6Me_6$ (**1**$^+$) to give

$$CpFe^IC_6Me_6 + {}^1/_4\,O_2 \xrightarrow[\text{pentane}]{25\ {}^\circ C} CpFe^{II}(\eta^5\text{-}C_6Me_5CH_2) + {}^1/_2\,H_2O \qquad (2)$$

the same complex, $CpFe(\eta^5\text{-}C_6Me_5CH_2)$ (**2**) in which the $C_6Me_5CH_2$ moiety is tentatively formulated as pentahapto coordinated (eq 2).

However, others[5] have depicted the same systems as zwitterionic, e.g., $CpFe^+(\eta^6\text{-}C_6H_nMe_{6-n}CH_2)^-$. Indeed the crystal structure of $CpFe^+(\text{fluorenyl}^-)$ clearly suggests that it is a zwitterion[6] in which the arene ligand is η^6 coordinated. It is now necessary to address the question of the nature of the ligand in unstabilized deprotonated arene complexes. Much interest in the benzyl ligand has arisen since the $\eta^1 \rightleftharpoons \eta^3$ interconversion was shown to be responsible for the catalytic activity of complexes bearing it.[7] The possibility of pentahapto coordination of the benzyl cation (A) was first stressed by Hoffmann[8] in 1977 who also noted the lack of experimental evidence supporting this proposal and compared the structure with the η^4-trimethylenemethane as shown in (B).



(A)

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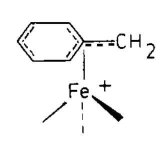

(B)

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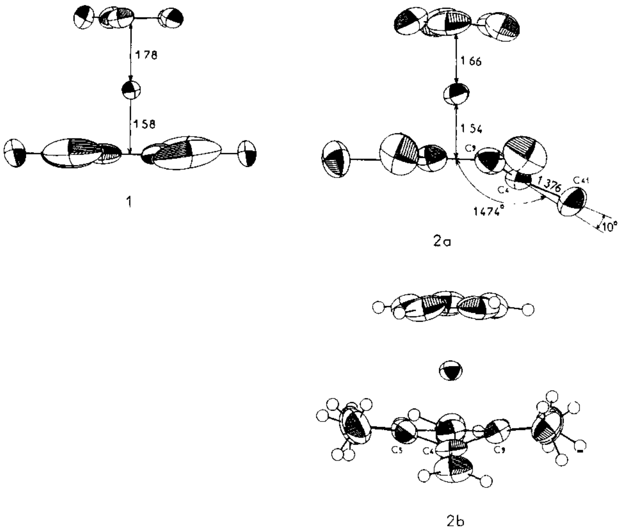

Figure 1. Compared projections of the molecular structures of **1** and **2**. Note (2b) that both the hydrogen atoms of the cyclopentadienyl and the methyl groups are pulled in toward the center of the complex. Selected distance and angle: Fe–C4, 2.487 (7) Å; C3–C4–C5, 111.7 (5)°.

We report here the (i) accurate structural modification (from X-ray diffraction) resulting from the H-atom abstraction of **1** by O_2, showing inter alia that the new ligand is best viewed as η^5-benzyl with a slightly bent and twisted exocyclic double bond which can be hydrogenated and (ii) chemistry of the ligand subsequent to C–H activation, e.g., bond formation with a variety of elements by nucleophilic substitution or addition and electron-transfer reactions. On a 60-mmol scale, eq 2 gives 96% of crude **2** and a precipitate of only 3% of crude $\mathbf{1}^+OH^-$. **2** is extremely pentane soluble and is thus not a zwitterion. Recrystallization from 50 mL of pentane at −21 °C gives 10.2 g of red-black crystals found suitable for the X-ray study.[9] Crystal structures before and after H-atom abstraction (**2** vs. **1**) are compared in figure 1. In **2**, the ferrocene-like[11] Cp–Fe distance is 0.12 (1) Å shorter than in **1**.[10] The arene–iron distance, however, is only shorter by 0.04 (1) Å in **2**. This indicates that there is more spin density on the Cp than on C_6Me_6 in **1**. The ring carbon attached to the methylene unit is clearly uncoordinated in **2**; thus the ligand is bound η^5, not η^6. However, the folding dihedral angle in the pentamethylbenzyl ligand is only 32.6°, below the range of dihedral angles in the cyclohexadienyl ligands (39–50)[8] but still three times larger than in $CpFe^+$(fluorenyl$^-$)(11°).[6] The exocyclic carbon C_{41} is not exactly in the $C_3C_4C_5$ plane but slightly bent upward by 10°. Precise location of the methylene hydrogen atoms on the difference Fourier synthesis provides evidence (Figure 1) that the exocyclic CH_2 is also twisted by 11° due to the steric demand of the ortho methyl groups. The juxtacyclic bond C_4–C_{41}, 1.376 (9) Å, is exactly as expected for a C═C bond. This high double bond character is also demonstrated by the ready hydrogenation of **2** by using a THF solution of Pd on charcoal at 20 °C to give $CpFe(\eta^5\text{-}C_6Me_6H)$ (**3**)[12] as orange crystals after recrystallization from pentane, the reduction being stereospecifically exo.[13]

Nucleophilic substitution by **2** occurs in a variety of organic (20 °C) and organometallic halides[14,15] (−20 °C) to give high yields of yellow $CpFe^+$ arene salts recrystallized in ethanol as hexafluorophosphates (eq 3).

$$CpFe(\eta^5\text{-}C_6Me_5CH_2) + RX \xrightarrow{THF} \underset{\mathbf{4\text{–}9}}{CpFe^+(\eta^6\text{-}C_6Me_5CH_2R)\ X^-} \quad (3)$$

RX (yields): PhCOCl (**4**, 90%); $SiMe_3Cl$ (**5**, 87%); PPh_2Cl (**6**, 68%); $CpFe(CO)_2Cl$ (**7**, 56%); $CpMo(CO)_3I$ (**8**, 59%); $Mn(CO)_5Br$ (**9**, 75%)

This very general reaction affords binding the sandwich to C, Si, P, Fe, Mn, Mo, etc., and can provide a useful mean of attaching the redox catalyst $\mathbf{1}^+ \rightleftharpoons \mathbf{1}$ onto surfaces and electrodes. $Fe(CO)_5$, $Cr(CO)_6$, and $Mo(CO)_6$ react with **2** in 1 h at 80 °C in benzene to give air-sensitive complexes[15] insoluble in most solvents except CH_3CN with which they are extracted. In ^1H NMR δ_{Cp} is intermediate between that of **2** (3.4 ppm) and those found for **4–9** (4.7 ppm). The quadrupole splittings (QS) observed in the Mössbauer spectra (2.00 mm s^{-1}) are closer to those of the cations **4–9** (2.02 mm s^{-1}) than to that of **2** (1.88 mm s^{-1}). Thus these binuclear complexes are best formulated as zwitterionic metallates with some π character (eq 4).

$$\mathbf{2} + M(CO)_n \rightarrow \underset{\mathbf{11\text{–}13}}{CpFe^+[\eta^6\text{-}C_6Me_5CH_2M^-(CO)_{n-1}]} \quad (4)$$

11 (Fe, $n = 5$, purple, 64%); **12** (Cr, $n = 6$, orange 83%); **13** (Mo, $n = 6$, bright red, 75%)

We have also synthetized C–C bonds by nucleophilic addition of the CH_2 group onto cationic hydrocarbon ligands activated by cationic organoiron moieties.[17] **2** reacts with $CpFe(CO)_3{}^+PF_6{}^-$[18] at −78 °C in 5 min in THF to give the soluble binuclear cation **14** in which the two oxidation states of iron, 0 and II, are deduced from the Mössbauer and NMR parameters (eq 5).[19] However,

$$\mathbf{2} + CpFe(CO)_3{}^+ \xrightarrow{-78\ °C} \underset{\mathbf{14}}{CpFe^+\text{-}\eta^6,\eta^4\text{-}C_6Me_5CH_2C_5H_5Fe(CO)_3} \quad (5)$$

the same reaction at 20 °C gives Fp_2 and $\mathbf{1}^+$, the products resulting from electron transfer[20] and H-atom abstraction from the solvent.

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(9) Crystal data and refinement results: $C_{17}H_{22}Fe$; orthorhombic; a = 8.267 (3), b = 14.669 (5), c = 11.843 (3) Å; space group $P2_12_12_1$; Z = 4. A crystal of 2.07 × 10^{-2} mm^3 limited by the faces (010), (00$\bar{1}$), ($\bar{1}$00), ($\bar{1}$21), (012), (120) mounted under inert (extremely dry) atmosphere in a glass capillary was used to collect X-ray diffraction data on a Nonius-CAD4 diffractometer by using graphite-monochromated Mo Kα radiation and ω–2θ scans; 1484 [$I > 3\sigma(I)$] data with $2\theta < 60°$ were used in subsequent refinement. Atoms were located throughout direct method (MULTAN) and difference Fourier syntheses. Structure was refined to a final residual R index on F_o of 0.049 (R_w = 0.046), with anisotropic thermal parameters for all nonhydrogen atoms. All the hydrogen atoms were precisely located and refined with fixed isotropic thermal parameters.

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(14) We already know that **2** reacts with CO_2 and CS_2 to give zwitterions and that deprotonation of $CpFe^+$ alkylarene complexes gives species which are alkylated by CH_3I "in situ" at −50 °C.[4,5] Similar alkylations of alkylarene by CH_3I induced by $Cr(CO)_3$ were reported earlier. (a) Jaouen, G.; Meyer, A.; Simonneaux, G. *J. Chem. Soc., Chem. Commun.* **1975**, 813–814. (b) Simonneaux, G.; Jaouen, G. *Tetrahedron* **1979**, *35*, 2249–2254.

(15) All complexes **3–20** were obtained in crystalline forms and satisfactorily analyzed (C, H, metals). ^1H, ^{13}C NMR, and IR spectra were consistent with the proposed structures and high purities. For CH_2, δ (Me_4Si, CD_3CN) ranges from 2.0 to 4.9 (^1H) and from −6 to 80 (^{13}C). ^{13}C NMR spectra could not be recorded for **12** and **13** due to lack of solubility.

(16) Green, J. C., personal communication.

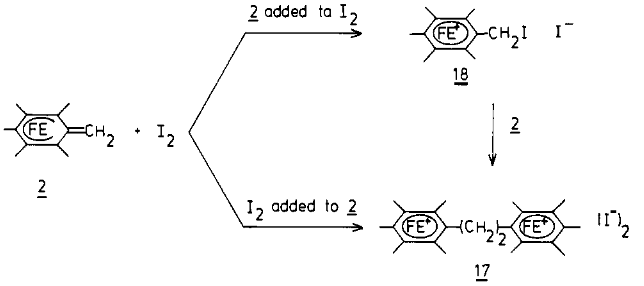
(17) (a) Davies, S. G.; Green, M. L. H.; Mingos, D. M. P. *Tetrahedron* **1978**, *34*, 3047–3077. (b) Eisenstein, O.; Hoffmann, R. *J. Am. Chem. Soc.* **1980**, *102*, 6148–6149.

(18) $CpFe(CO)_3{}^+$ is conveniently synthesized from ferrocene and CO: Roman, E.; Astruc, D. *Inorg. Chem.* **1979**, *18*, 3284–3285.

(19) **14**: ^1H NMR (δ, Me_4Si) (acetone–d_6) 4.46 (Cp), 2.46 and 2.47 (Me_5), 2.535 (d, CH_2, J = 7 Hz), 1.10 (t, CH, J = 7 Hz), 3.20 (m, CHα), 5.76 (m, CHβ); ^{13}C NMR (δ, Me_4Si) (CD_3CN) 79.1 (Cp), 18.2, 17.8, and 17.7 (Me_5), 100.4, 100.2, and 98.9 (C_6), 87.7 (quaternary), 43.8 (CH_2), 56.7 (CH), 59.2 (*CH*α), 85.7 (CHβ), 213.1 (CO). Mössbauer parameters (mm/s): IS 0.45, Fe(II) and 0.0, Fe(0); QS 2.0, Fe(II) and 1.52, Fe(0).

(20) For electron transfers in organometallic reactions, see ref 2. Also: Kochi, J. K. *Acc. Chem. Res.* **1974**, *7*, 351–360.

Scheme I



Now reaction of **2** with $\mathrm{CpFe(CO)_2(C_2H_4)^+}$ at −80 °C in THF specifically gives the nucleophilic addition product (**15**) onto the ethylene ligand,[17b] crystallized as the PF_6 salt[15] (eq 6).

$$2 + \mathrm{CpFe(CO)_2(C_2H_4)^+} \xrightarrow{-78\ ^\circ\mathrm{C}} \underset{\mathbf{15}}{\mathrm{CpFe^+\text{-}\eta^6\text{-}C_6Me_5(CH_2)_3Fe(CO)_2Cp}} \quad (6)$$

While nucleophilic substitution fails with free or complexes halogenoarenes, **2** adds to $\mathrm{CpFe(\eta^6\text{-}PhCl)}$ mostly ortho to Cl[21] in 5 min at −18 °C to give **16**, the nucleophilic addition product[15] (eq 7).

$$2 + \mathrm{CpFe(\eta^6\text{-}PhCl)} \xrightarrow[\mathrm{THF}]{-18\ ^\circ\mathrm{C}} \underset{\mathbf{16}}{\mathrm{CpFe^+\text{-}\eta^6,\eta^5\text{-}C_6Me_5CH_2\text{-}\mathit{o}\text{-}C_6H_5ClFeCp}} \quad (7)$$

The reaction of **2** with TCNQ in THF also provides electron transfer followed by H· abstraction from the solvent giving the green salt 1^+ $\mathrm{TCNQ^{-}\cdot}$ (eq 8) identified by its characteristic Mössbauer (1^+)[22] and optical spectra ($\mathrm{TCNQ^{-}\cdot}$).[23]

$$2 + \mathrm{TCNQ} \xrightarrow{\mathrm{THF}} 2^+\mathrm{TCNQ^{-}\cdot} \xrightarrow[\text{(solvent)}]{\mathrm{H}\cdot} 1^+\mathrm{TCNQ^{-}\cdot} \quad (8)$$

These electron-transfer reactions of **2** are consistent with the low-ionization potential (6.21 V from He(I) PES) recorded by J. Green.[16] Their synthetic goal—the coupling of **2** via the radical $\mathrm{CpFe^+(\eta^6\text{-}C_6Me_5CH_2)\cdot}$—was frustrated by the abstraction of H·. However, when a THF solution of I_2 is added to **2** at 20 °C, the sparingly soluble binuclear bication **17**[15] is obtained immediately and quantitatively. If, on the other hand, a solution of **2** in THF is added to I_2 at 20 °C, the iodo complex **18** is formed quantitatively [Scheme I, similar reactions with Cl_2 and Br_2 in the same conditions give $\mathrm{CpFe(\eta^6\text{-}C_6Me_5Ch_2Cl)}$(**19**), and $\mathrm{CpFe(\eta^6\text{-}C_6Me_5CH_2Br)}$ (**20**)];[15] further reaction of **2** with **18** gives **17**. Thus the formation of **17** from **2** and I_2 is not a coupling of two radicals but a double nucleophilic substitution of I^-.

Since **2** is easily accessible by short contact of **1** with air, the chemistry presented here can be achieved in a straightforward manner from the readily available complex $\mathrm{CpFeC_6Me_6}$.[22,24]

Acknowledgment. We thank Dr. M. L. H. Green for helpful discussions, Dr. J. C. Green (Oxford) for communicating the IP value of **2**, P. Michaud and J. P. Mariot from Professor F. Varret's group (Le Mans) for providing the fitted Mössbauer spectra, and D. Catheline for skillful experimental assistance. Financial support by the CNRS (ATP No. 3801) is also gratefully acknowledged.

Supplementary Material Available: Atomic and thermal parameters (1 page). Ordering information is given on any current mashead page.

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Photochemical Formation of the Ketone Tautomer of 3,4-Dihydro-9-hydroxy-2(1*H*)-anthracenone from 2,3-Benzospiro[4.5]deca-2,6-diene-1,8-dione

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Although the ketone tautomer of 1-naphthol (**4**) has been detected by IR spectroscopy at 77 K as an intermediate in the photoreaction of naphthalene 1,2-oxide,[1] most ketone tautomers of phenols are not isolable at room temperature because of the strong driving force for rearomatization.[2] We now report the first isolation of the ketone tautomer of a naphthol derivative as an intermediate for the unique photochemical formation of 3,4-dihydro-9-hydroxy-2(1*H*)-anthracenone (**2**) from 2,3-benzospiro[4.5]deca-2,6-diene-1,8-dione (**1**).

When a solution of spiro diketone **1**[7,8] in benzene or methanol was irradiated through a Pyrex filter with a medium-pressure mercury lamp (Hanovia 450W) for 80 min at 25 °C, an air-labile product **2** (mp 122–123 °C) was obtained in 13 and 20% yields, respectively (Scheme I). The structure of **2**, 3,4-dihydro-9-hydroxy-2(1*H*)-anthracenone, was determined from its spectral characteristics and elemental analysis.[8] The elemental analysis and mass spectrum (70 eV, M^+, *m/e* 212) suggested that it was formulated as $C_{14}H_{12}O_2$. Its UV (C_2H_5OH) spectrum shows strong absorption bands at 243 (log ε, 4.40), 275 (3.74), and 325 nm (sh). This absorption pattern is similar to that of **4**.[3] In its ^{1}H NMR ($CDCl_3$) spectrum, the resonances of three methylene groups, the hydroxyl group, and aromatic ring protones appear at 2.73 (t, 2 H, J = 6.5 Hz), 3.18 (t, 2 H, J = 6.5 Hz), 3.70 (s, 2 H), 6.07 (s, 1 H, exchangeable with D_2O), and 7.23–8.20 ppm (m, 5 H).[9] The chemical shifts and coupling pattern of the resonances of aromatic ring protones are similar to that of **4**.[4] Its ^{13}C NMR (50% $Me_2SO\text{-}d_6$ in $CDCl_3$) spectrum shows the presence of 14 carbon atoms at 210.0, 149.1, 135.6, 132.9, 126.9, 125.6, 124.1 (×2), 121.9, 117.1, 114.9, 38.9, 38.3, and 28.7 ppm.[9] Its IR (Nujol) spectrum shows carbonyl absorption band at 1695 cm^{-1}. These results support **2** or **2′** for the structure. The method using a NMR shift reagent [Eu(fod)$_3$] allows us to assign the structure as **2**.[5] On the other hand, when a ether solution of **1** was irradiated through a Pyrex filter under nitrogen bubbling with a medium-pressure mercury lamp (Hanovia 450W) at 0 °C for 80 min, colorless compound **3** was crystallized out on the reaction tube: 23% yield; colorless fine needles, mp 132–133 °C. The structure of **3** is evident from elemental analysis[8] and spectral data: mass spectrum (70 eV), M^+, *m/e* 212; IR (Nujol) 1712, 1640

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(5) In the plots of the induced shifts vs. the shift reagent/substrate mole ratios (*E*/*S*) for **2**, the shift of the hydroxyl proton *a* was greater than the aromatic proton *b* (see **2** in Scheme **I**).

(6) The rate of the thermal reaction of **3** to **2** was measured in a chloroform–ethanol (10:1) solution. The Arrhenius plot of the first-order rate constants provides a straight line from which activation parameters were calculated as follows: E_a = 10.18 kcal/mol, log A = 5.27, $\Delta S^\ddagger$ = −36.4 (eu, 295 K).

(7) **1** was prepared by the treatment of 2-(hydroxymethyl)-1-indanone with methyl vinyl ketone and followed by acid (HCl) catalyzed aldol condensation of 2-formyl-2-(3-oxobutyl)-1-indanone formed: 13.6%; mp 84–85 °C; IR (Nujol) 1705, 1665 cm^{-1}; ^{1}H NMR ($CDCl_3$) 1.80–3.30 (m, 4 H), 3.27 (s, 2 H), 6.10 (d, 1 H, J=10.3 Hz), 6.61 (d, 1 H, J=10.3 Hz), 7.23-7.90 ppm (m, 4 H);[9] UV λ_{max} (ethanol) 206 (log ε, 4.30), 250 (4.16), 290 nm (3.37).[8]

(8) Satisfactory CHN elemental analyses were obtained for **1**–**3**.

(9) Tetramethylsilane (Me_4Si) is used for an internal standard.

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