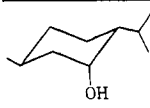
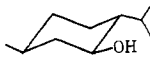
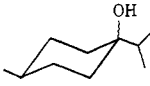
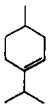
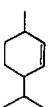
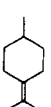


Table II. Product Composition in Solvolysis of Menthyl Tosylate (1-OTs)

| Products (mol %) ^b | —Reaction conditions ^a — | |
|---|-------------------------------------|----------------|
| | 70 T, 45° | 70 E, 70° |
|  | 3 | 13 |
|  | 30 | 22 |
|  | 3 ^c | 3 ^c |
|  | 27 | 37 |
|  | 12 | 13 |
|  | 4 | 0 |
| Ethers | 21 | 12 |

^a Initial concentrations 0.06–0.08 mol/l., buffered with 1 equiv of 2,6-lutidine. ^b Rounded off average values of two independent experiments with five–six glc analyses of each product mixture. All products were shown to be stable under the reaction conditions. ^c Stereochemistry at the tertiary carbon atom has not yet been established.

outcome of 2-adamantyl tosylate solvolysis.^{19,20} In analogy to adamantyl tosylate front side displacement from the solvent separated ion pair seems to be the preferred substitution path because of the steric hindrance to solvent approach from the rear.²³ This hindrance is apparently operative for the chair-like conformation of the intermediate but not for the half-chair transition state in which nucleophilic solvent participation is facilitated.¹¹ The necessary condition for the occurrence of this chair-like transition state is in our opinion the presence of substituent(s) in such positions which greatly hinder the formation of bent chair (C_2 symmetry) or half-chair (C_s symmetry) transition states.²⁴ These requirements are best met by two bulky equatorial substituents in positions 2,5 and 2,4 relative to the reacting center. With such an arrangement at least one substituent has to assume the unfavorable pseudoequatorial or pseudoaxial orientation if C_2 or C_s conformations are to be formed. The re-

(19) J. A. Bone and M. C. Whiting, *Chem. Commun.*, 115 (1970).

(20) Hüchel and Sommer²¹ observed a 100% retention of configuration in methanolysis of 5-methyl-2-*tert*-butylcyclohexyl tosylate. They interpreted this result in terms of an O–S fission of the tosylate. For Hüchel's work on menthyl and neomenthyl tosylates see ref 22.

(21) W. Hüchel and W. Sommer, *Justus Liebigs Ann. Chem.*, **687**, 102 (1968).

(22) W. Hüchel and C. M. Jennewein, *Justus Liebigs Ann. Chem.*, **683**, 100 (1965).

(23) J. L. Fry, C. J. Lancelot, L. K. M. Lam, J. M. Harris, R. C. Bingham, D. J. Raber, R. E. Hall, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **92**, 2538 (1970).

(24) A. Komornicky and J. W. McIver, *J. Amer. Chem. Soc.*, **95**, 4512 (1973).

sulting nonbonded interactions render this geometry less favorable than a front side displacement on the unperturbed chair form.²⁵ One substituent cannot prevent distortions of the chair conformation in the transition state as demonstrated in the case of 4-*tert*-butylcyclohexyl derivatives.³

Acknowledgments. We thank Professor V. J. Shiner, Jr., for stimulating discussions. D. E. S. is grateful for the hospitality of the Department of Chemistry, Indiana University, Bloomington, Ind., in the course of this work.

(25) This might also explain why 1-OTs is, under identical conditions, about 50 times less reactive than cyclohexyl tosylate.

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Reaction of Diiron Nonacarbonyl with Stereochemically Fixed Divinylcyclopropyl Systems in Norcaradienes

Sir:

Recently several examples of the reaction of diiron nonacarbonyl with various cisoid divinylcyclopropyl systems have been reported.¹ The products are either σ - π -allyl complexes or may be considered as resulting from initial formation of such an intermediate.

One example of the behavior of a transoid divinylcyclopropyl system with $Fe_2(CO)_9$ has been reported; namely, spiro[2,4]hepta-4,6-diene yields 6-methylfulvene diiron hexacarbonyl and an iron tricarbonyl complex of the starting diene.²

In order to contrast the behavior of cisoid relative to transoid divinylcyclopropyl systems, the reaction of spironorcaradienes with $Fe_2(CO)_9$ is particularly relevant because they possess both systems within the same molecule.

Accordingly, the reaction of spiro[2,4-cyclooctadiene-1,7'-norcaradiene-2',4'-diene] (4)³ and spiro[2,4-cyclopentadiene-2',5'-dimethyl-1,7'-norcaradiene-2',4'-diene] (5)⁴ with $Fe_2(CO)_9$ under various conditions was carried out. The products obtained are as shown in Scheme I.

(1) (a) R. Aumann, *Angew. Chem.*, **83**, 175 (1971); *Angew. Chem., Int. Ed. Engl.*, **10**, 189 (1971); (b) R. Aumann, *Angew. Chem.*, **83**, 177 (1971); *Angew. Chem., Int. Ed. Engl.*, **10**, 190 (1971); (c) R. Aumann, *Angew. Chem.*, **83**, 176 (1971), *Angew. Chem., Int. Ed. Engl.*, **10**, 188 (1971); (d) R. Aumann, *Angew. Chem.*, **84**, 583 (1972); *Angew. Chem., Int. Ed., Engl.*, **11**, 522 (1972); (e) R. M. Moriarty, C. -L. Yeh, and K. C. Ramey, *J. Amer. Chem. Soc.*, **93**, 6709 (1971); (f) A. Eisenstadt, *Tetrahedron Lett.*, 2005 (1972); (g) R. Aumann, *J. Organometal. Chem.*, **47**, C29 (1973); (h) R. M. Moriarty, C. -L. Yeh, K. -N. Chen, and R. Srinivasan, *Tetrahedron Lett.*, 5325 (1972); (i) D. Ehnholt, A. Rosan, and M. Rosenblum, *J. Organometal. Chem.*, **56**, 628 (1973).

(2) C. H. DePuy, V. M. Kobal, and D. H. Gibson, *J. Organometal. Chem.*, **13**, 266 (1968).

(3) D. Schönleber, *Angew. Chem.*, **81**, 83 (1969); *Angew. Chem., Int. Ed. Engl.*, **8**, 76 (1969).

(4) Compound 5 is a new compound preparation by the irradiation (medium-pressure 450-W Hanovia mercury lamp) of diazocyclopentadiene in *p*-xylene for 4 hr. It is a low melting yellow crystalline solid which decomposes upon exposure to air: nmr ($CDCl_3$, δ ppm) 1.92 (s, 6 H, CH_3 's), 3.07 (s, 2 H, cyclopropyl protons), 5.81 (s, cyclohexadiene protons), 6.09 (m, 2 H, cyclopentadiene α -protons), 6.39 (m, 2 H, cyclopentadiene β -protons). Synthesis of 4 and 5 is extremely dangerous. A serious explosion occurred in the distillation at 27° (0.25 mm) of diazocyclopentadiene.

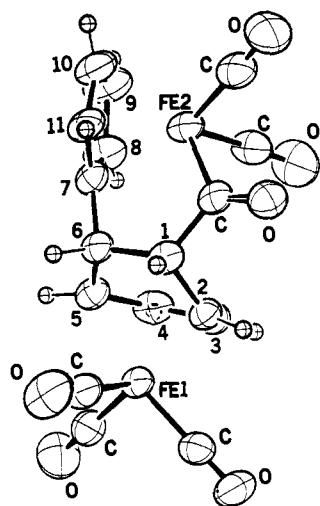
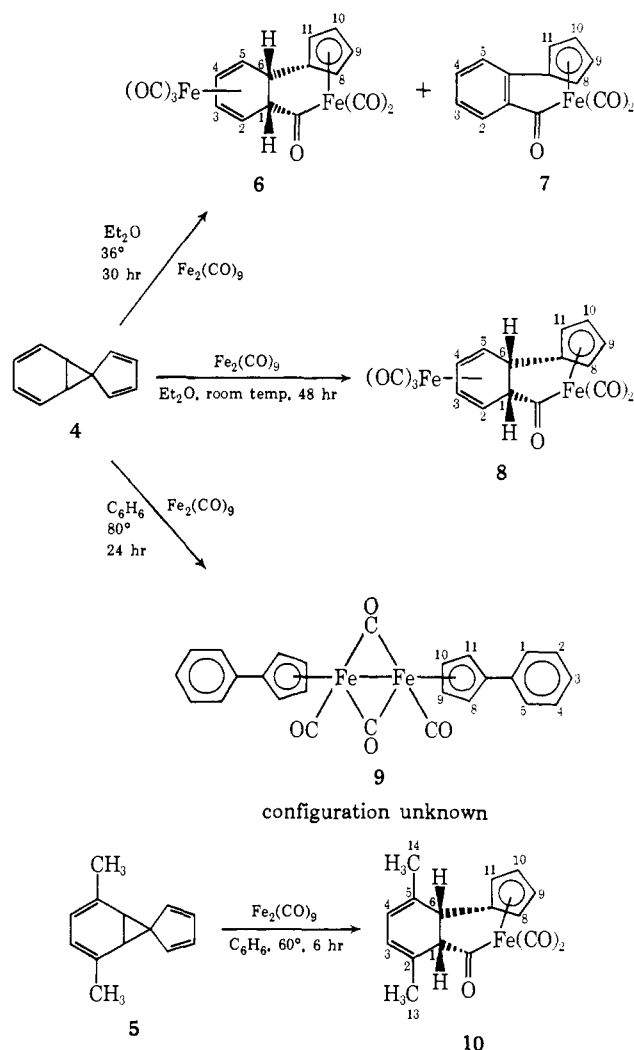


Figure 1. Molecular geometry of complex 6.

Scheme I



Complex 6 was obtained in 28% yield by fractional crystallization of the crude product from CHCl_3 -hexane (1:5) and subsequent chromatographic purification on alumina, mp 160° dec. *Anal.* Calcd for $\text{C}_{17}\text{H}_{10}\text{O}_6\text{Fe}_2$: C, 48.34; H, 2.37. Found: C, 48.25; H, 2.41. Nmr (δ , ppm, CDCl_3) 2.85–3.50 (m, 4 H, protons 1, 6, 2, and 5), 4.50–5.80 (m, 6 H, protons 3, 4, 8, 9, 10, and 11); ir (KBr), 1630 cm^{-1} , acyl carbonyl,

1965–1985, 2005, and 2032 cm^{-1} terminal carbonyls.

The structure of 6 was determined unambiguously by means of an X-ray structural analysis. The complex crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ (C_{2h}^5 ; no. 14): $a = 6.562$ (1), $b = 21.690$ (5), $c = 11.399$ (2) Å; $\beta = 96.78$ (2) $^\circ$; $V = 1611$ Å 3 ; $\rho_{\text{obsd}} = 1.71$; $\rho_{\text{calcd}} = 1.739\text{ g cm}^{-3}$ for $Z = 4$. X-Ray diffraction data ($2\theta_{\text{max}} = 50^\circ$, Mo $K\alpha$ radiation) were collected with a Picker FACS-1 diffractometer, and the structure was solved *via* Patterson, Fourier, and least-squares refinement methods. All atoms (including hydrogens) were located, the final discrepancy indices being $R_F = 5.0\%$ and $R_{wF} = 4.2\%$ for 2852 independent reflections. The molecular geometry is shown in Figure 1.

Atom Fe(1) is bonded to four atoms of the six-membered ring, with $\text{Fe}(1)\text{--C}(2) = 2.098$ (3), $\text{Fe}(1)\text{--C}(3) = 2.049$ (3), $\text{Fe}(1)\text{--C}(4) = 2.048$ (3), and $\text{Fe}(1)\text{--C}(5) = 2.097$ (3) Å. Distances within this cis-diene system are $\text{C}(2)\text{--C}(3) = 1.428$ (4), $\text{C}(3)\text{--C}(4) = 1.387$ (5), and $\text{C}(4)\text{--C}(5) = 1.429$ (4) Å (*cf.* ref 5).

Atom Fe(2) is bonded symmetrically to the five-membered ring, individual distances ranging from $\text{Fe}(2)\text{--C}(7) = 2.068$ (3) to $\text{Fe}(2)\text{--C}(9) = 2.128$ (4) Å. The iron-(σ -acyl) linkage of 1.960 (3) Å is contracted significantly from the accepted $\text{Fe}\text{--C}(\text{sp}^3)$ distance of 2.098 (2) Å 6 in $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{R}$ species (in agreement with previous considerations of metal-(σ -acyl) linkages 7).

Complex 7, obtained in 5% yield from the mother liquors of 6, was purified by column chromatography on alumina and recrystallization from CHCl_3 -hexane (1:5). The structure is based on its composition (*Anal.* Calcd for $\text{C}_{11}\text{H}_8\text{OFe}$: C, 60.00; H, 2.85. Found: C, 60.14; H, 2.89), molecular weight (Rast) (calcd, 280; found, 290), and the aromatic and typical AB nmr spectrum [δ , ppm, CDCl_3] 4.92 (t, 2 H, protons 8 and 11), 5.43 (t, 2 H, protons 9 and 10), 7.25–7.78 (m, 4 H, protons 2, 3, 4, and 5)]. The $\text{C}=\text{C}$ aromatic stretching frequency occurred in the ir (KBr) at 1595 cm^{-1} , the acyl carbonyl appeared at 1635 cm^{-1} , and the terminal carbonyls occur at 1990 and 2060 cm^{-1} .

Complex 8, obtained in 35% yield by column chromatography of the crude reaction product on neutral alumina (elution with CHCl_3) is an isomer of 6 as shown by molecular weight (Rast) (calcd, 422; found, 426). *Anal.* Calcd for $\text{C}_{17}\text{H}_{10}\text{O}_6\text{Fe}_2$: C, 48.34; H, 2.37. Found: C, 48.56; H, 2.44. The acyl carbonyl appeared in the ir (KBr) at 1667 cm^{-1} and the terminal carbonyls appeared at 1964 – 1985 , 2003 , and 2025 cm^{-1} . The nmr spectrum (δ , ppm, CDCl_3) showed absorption at 2.58 (m, 1 H, proton 1), 3.12 (m, 1 H, proton 2), 3.38 (m, 1 H, proton 5), 4.08 (m, 1 H, proton 6), 4.58–5.38 (m, 6 H, protons 3, 4, 8, 9, 10, and 11). We propose that 6 and 8 stand in the relationship of stereoisomers corresponding to different locations of the $\text{Fe}(\text{CO})_3$ unit with respect to the cyclohexadiene group.

The structural assignment of di- μ -carbonyl-dicar-

(5) F. A. Cotton, V. W. Day, B. A. Frenz, K. I. Hardcastle, and J. M. Troup, *J. Amer. Chem. Soc.*, **95**, 4522 (1973); see Table VI on p 4526.

(6) M. R. Churchill and S. W. -Y. Ni Chang, *J. Amer. Chem. Soc.*, **95**, 5931 (1973).

(7) M. R. Churchill, *Perspect. Struct. Chem.*, **3**, 91 (1970); see Table 10 on p 154.

bonylbis(η^5 -phenylcyclopentadienyl)diiron (**9**) rests upon its composition (*Anal.* Calcd for $C_{26}H_{18}O_4Fe_2$: C, 61.66; H, 3.56. Found: C, 61.44; H, 3.50.), molecular weight (Rast) (calcd, 506; found, 510), and nmr spectrum (δ , ppm, $CDCl_3$) [4.63 (t, 2 H, protons 8, 11), 5.19 (t, 2 H, protons 9, 10), 7.49 (m, protons 1, 2, 3, 4, and 5)]. The ir spectra showed bridging carbonyl at 1770 and 1800 cm^{-1} , and terminal carbonyl at 1998, 1970, and 1955 cm^{-1} .

Complex **10**, formed in 75% yield from spiro-[2,4-cyclopentadiene-2',5'-dimethyl-1,7'-norcaradiene] (**5**) had mp 138° dec. The composition (*Anal.* Calcd for $C_{18}H_{14}O_3Fe$: C, 61.90; H, 4.52. Found: C, 61.76; H, 4.69.) and nmr spectrum [δ , ppm, $CDCl_3$] 1.70 (s, 3 H, protons on 13), 1.88 (s, 3 H, protons on 14), 2.87 (d, 1 H, proton 1), 4.53 (m, 1 H, proton 6), 4.65 (m, 1 H, proton 8), 4.74 (m, 1 H, proton 11), 5.04 (m, 1 H, proton 9), 5.30 (q, 1 H, proton 10), 5.72 (s, 2 H, protons 3 and 4)] are in agreement with expectation. The mass spectrum of **10** showed the parent molecular ion at m/e 310 (27%) and peaks for successive loss of CO, 282 (10%) and 254 (44%), and base peak for $C_{13}H_{14}Fe$ at 226. The ir spectrum showed strong terminal carbonyl stretching absorptions at 1960–1985 and 2020 cm^{-1} and acyl carbonyl stretching frequency at 1640 cm^{-1} .

The fact that the cyclohexadiene system is uncomplexed in **10** indicates that its complexation is not a necessary prerequisite for the opening of the cyclopropyl ring. In the full paper the mechanism of the reaction of the divinylcyclopropyl system with $Fe_2(CO)_9$ will be discussed in light of these results.

Acknowledgment. This work was made possible by financial support from the National Science Foundation (Grant GP 33018, to M. R. C.) and also by a generous allocation of time on the IBM 370/158 computer at the Computer Center, University of Illinois, Chicago Circle.

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Luminescence Quenching of Dicyanobis(1,10-phenanthroline)ruthenium(II) by Cupric Ion in Aqueous Solutions. Dynamic and Static Processes

Sir:

We wish to report on the quenching of the charge-transfer (CT) luminescence of $Ru(phen)_2(CN)_2$ (phen = 1,10-phenanthroline) by Cu^{2+} (H_2O , $\sim 22^\circ$). This system demonstrates what we believe to be the first unequivocal evidence for both static and dynamic quenching of a metal complex exhibiting CT luminescence.¹ Static quenching appears to proceed by coordination of $Ru(phen)_2(CN)_2$ to the Cu^{2+} by a CN-bridge, and it was possible to determine the equilibrium constant, K_{eq} , by luminescence measurements only.

(1) Fujita and Kobayashi² have suggested a combinational quenching of $Ru(bipy)_3^{2+}$ by $Co(C_2O_4)_3^{4-}$ based only on intensity data. Failure to correct for trivial effects³ probably accounts for their observations, however.

(2) J. Fujita and H. Kobayashi, *Ber. Bunsenges. Phys. Chem.*, **76**, 115 (1972).

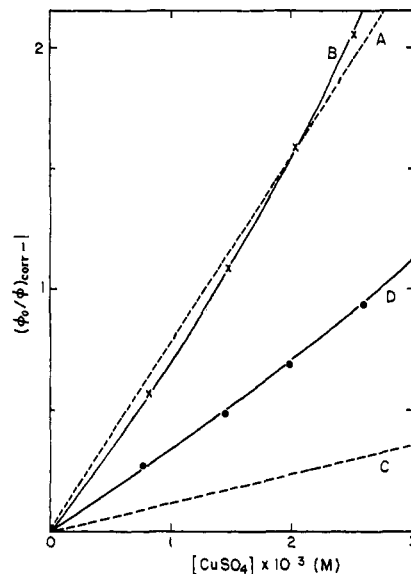


Figure 1. Intensity Stern-Volmer quenching plots for deactivation of aqueous $Ru(phen)_2(CN)_2$ by $CuSO_4$. Values obtained in deoxygenated solutions (\times 's) and in O_2 -saturated solutions (\bullet 's): A, Stern-Volmer plot with $K_{SV} = 780 M^{-1}$; B, combination static and dynamic quenching with $K_{SV} = 325 M^{-1}$ and $\beta K_{eq} = 270 M^{-1}$; C, Stern-Volmer plot with $K_{SV} = 130 M^{-1}$; D, combination static and dynamic quenching with $K_{SV} = 55 M^{-1}$ and $\beta K_{eq} = 270 M^{-1}$. See text for details. $[Ru(phen)_2(CN)_2] \sim 2 \times 10^{-5} M$. $\lambda_{exc} = 480 nm$.

The first indication that quenching was not simply diffusional, as it is with most metal complex quenchers³⁻⁶ and O_2 ,⁷ was the apparent slight upward curvature to the intensity, ϕ , Stern-Volmer (SV) quenching plot ($\phi_0/\phi - 1$ vs. $[Q]$) in deoxygenated solutions. See Figure 1. The effect was not large, however, and the data were fit fairly well by normal SV kinetics with $K_{SV} \sim 780 M^{-1}$ (curve A). That this simple explanation was incorrect was established by making a decay time, τ , SV plot ($\tau_0/\tau - 1$ vs. $[Q]$) under similar conditions; this procedure yields the true K_{SV} free of any contribution from static quenching. A linear plot resulted with $K_{SV}^{N_2} = 335 M^{-1}$ ($k_2 \sim 5 \times 10^8 M^{-1} sec^{-1}$) in considerable disagreement with the ϕ -derived value. Thus, both static and dynamic quenching pathways seemed to be operative.

As an additional test of the inadequacies of the diffusion only model, we measured the ϕ -quenching by $CuSO_4$ in an O_2 -saturated solution (Figure 1). Under these conditions τ of the donor is reduced by a factor of 6.15 by oxygen quenching.⁷ Since $K_{SV} = k_2\tau_0$ and k_2 should be unaffected by oxygen, the K_{SV} of $\sim 780 M^{-1}$ for a deoxygenated solution should be reduced by a factor of 6.15 to $\sim 130 M^{-1}$ for the O_2 -saturated ones if all quenching were diffusional; line C is the required experimental curve. The extreme disagreement between C and the data again argues for a combinational model.

(3) J. N. Demas and A. W. Adamson, *J. Amer. Chem. Soc.*, **95**, 5159 (1973).

(4) H. Gafney and A. W. Adamson, *J. Amer. Chem. Soc.*, **94**, 8238 (1972).

(5) F. Bolletta, M. Maestri, and F. Moggi, *J. Phys. Chem.*, **77**, 861 (1973).

(6) F. Bolletta, M. Maestri, L. Moggi, and V. Balzani, *J. Amer. Chem. Soc.*, **95**, 7864 (1973).

(7) J. N. Demas, D. Diemente, and E. W. Harris, *J. Amer. Chem. Soc.*, **95**, 6864 (1973).