mental analyses[5] are in good agreement with the stoichiometry $\{(C_5(CH_3)_5)_2Zr\}_2(N_2)_3$.

The molecular weight determined cryoscopically for a solution containing 53.3 mg of **2** per gram of benzene was 820 ± 100, indicating a binuclear solution structure as suggested by its stoichiometry (807 is calculated for **2**). The ^1H nmr spectrum[7] for **2** in toluene-d_8 at 25° shows a single, somewhat broadened, resonance centered at δ 1.75 ppm. Below *ca.* 5° this signal splits into two resonances of nearly equal intensity at 1.74 and 1.76 ppm, indicative of the presence of two isomers of **2** which are in rapid equilibrium on the nmr time scale above this temperature. The full details of this equilibrium are presently under investigation utilizing ^{13}C and ^{15}N nmr and ir spectroscopy and will be reported in a forthcoming paper. The infrared spectrum of **2** (Nujol mull) exhibits, in addition to those bands characteristic of $[\eta\text{-}C_5(CH_3)_5]$ rings, two strong bands at 2041 and 2006 cm^{-1} and a band of medium intensity at 1556 cm^{-1} which shift upon substitution of doubly labeled $^{15}N_2$[8] to 1972, 1937, and 1515 cm^{-1}, respectively. These three bands are thus attributed to NN stretching frequencies for **2**. The 1556-cm^{-1} band, the position of which suggests a major reduction in the N≡N bond order, could possibly be due to a bridging N_2 in a noncentrosymmetric structure, *e.g.*

$$(C_5(CH_3)_5)_2Zr\cdots N\equiv N\cdots Zr(C_5(CH_3)_5)_2$$
$$\qquad\qquad\quad N_2 \quad N_2$$

The X-ray crystal structure determination for **2**, in progress at the time of this writing, should settle the questions concerning the mode(s) of Zr–N_2 bonding in this dimer.

Treatment of **2** with a 10 *M* excess of HCl at −80° in toluene yields, after subsequent warming to room temperature, a mixture of **1**, N_2, H_2, ($Zr:N_2:H_2$ = 1.000:0.998:0.158),[9] and a white crystalline solid identified as pure $N_2H_4\cdot 2HCl$.[10] Equation 4 is consequently implicated as a major reaction pathway wherein the four reducing equivalents available in the dimer are utilized in the reduction of 1 of the 3 mol of N_2 to N_2H_4.

$$\{(C_5(CH_3)_5)_2Zr\}_2(N_2)_3 + 4HCl \longrightarrow 2(C_5(CH_3)_5)_2ZrCl_2 + 2N_2 + N_2H_4 \quad (4)$$

Chatt, *et al.*, have observed protonation of one of the ligated dinitrogens in complexes of the type *trans*-$[M(Ph_2PCH_2CH_2PPh_2)_2(N_2)_2]$, M = Mo, W; however, the release and/or further reduction of the resulting $[N_2H_2]$ moiety has not been realized.[11] Shilov and coworkers have previously reported the formation of unstable dark blue complexes of the type $[(C_5H_5)_2TiR]_2N_2$ and $[(C_5H_5)_2Ti]_2N_2$ on reduction of $(C_5H_5)_2TiCl_2$ and $(C_5H_5)_2TiCl$ with RMgX in the presence of N_2.[12,13] Protonation under conditions similar to those reported herein produces a near quantitative yield of hydrazine for $[(C_5H_5)_2TiR]_2N_2$ and a mixture of N_2 and N_2H_4 or N_2 and NH_3 for $[(C_5H_5)_2Ti]_2N_2$. The exact nature of these dinitrogen complexes is as yet unknown, however.

2 appears to be the best characterized dinitrogen complex capable of liberating *reduced* N_2 on simple protonation and thus represents a first stage of dinitrogen activation well suited for further study. We are presently investigating the essential features of this reaction with respect to whether diimide is an intermediate in hydrazine formation and/or whether the reduction involves a μ-dinitrogen.

(5) Calculated for $C_{20}H_{30}N_3Zr$: C, 59.54; H, 7.44; N, 10.41; Zr, 22.61. Found: C, 59.75; H, 7.36; N, 10.18; Zr, 22.77.

(6) Although **3** has not been completely characterized at present, its nmr spectrum strongly suggests that the predominant species in solution has the structure $(C_5(CH_3)_5)(C_5(CH_3)_4CH_2)ZrH$, apparently formed *via* a *reversible* ring methyl hydrogen abstraction by the Zr center for the tautomer $(\eta\text{-}C_5(CH_3)_5)_2Zr$. A completely analogous tautomeric behavior has recently been established for $(\eta\text{-}C_5(CH_3)_5)_2Ti$ (ref 2).

(7) Spectra were recorded on a Varian HR-220 (CW) spectrometer. ^1H chemical shifts were calculated from their positions relative to the residual aromatic protons in toluene-d_8 and converted to values relative to (and downfield of) TMS at δ 0.

(8) Bio-Rad "$^{15}N_2$" with a composition (mass spectrum) of $^{15}N\equiv{}^{15}N$, 93.3%; $^{15}N\equiv{}^{14}N$, 6.3%; $^{14}N\equiv{}^{14}N$, 0.37%.

(9) Identical treatment of **3** with HCl yields only **1** and H_2 in a 1.00:1.01 mole ratio, respectively.

(10) Isolated *via* extraction of the residue (after removal of toluene) with 6 *M* HCl and identified by its infrared spectrum and a mixture melting point determination.

(11) J. Chatt, G. A. Heath, and R. L. Richards, *J. Chem. Soc., Chem. Commun.*, 1010 (1972).

(12) A. E. Shilov, A. K. Shilova, E. F. Kvashina, and T. A. Vorontsova, *Chem. Commun.*, 1590 (1971).

(13) Y. G. Borodko, I. N. Ivleva, L. M. Kachapina, S. I. Salienko, A. K. Shilova, and A. E. Shilov, *J. Chem. Soc., Chem. Commun.*, 1178 (1972).

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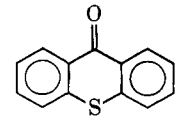
Solvent Effects on Thioxanthone Fluorescence

Sir:

Thioxanthone, **1**, is a commonly used triplet sensitizer,[1] with a lowest π,π* triplet at 65.5 kcal/mol.[2]



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While using thioxanthone as a triplet sensitizer in alcohols, we have noted strong luminescence visible to the eye. We wish to report an investigation of this phenomenon which demonstrates that the quantum yield of fluorescence of thioxanthone varies by more than three orders of magnitude as a function of solvent and suggests that caution should be exercised in using thioxanthone as a triplet sensitizer in alcoholic solvents.[3]

Broad structureless fluorescence is observed from solutions of thioxanthone in all solvents used.[4] The rela-

(1) See, for example, (a) G. S. Hammond, *et al.*, *J. Amer. Chem. Soc.*, **86**, 3197 (1964); (b) D. Valentine, Jr., and G. S. Hammond, *ibid.*, **94**, 3449 (1972); (c) S. Hosaka and S. Wakamatsu, *Tetrahedron Lett.*, 219 (1968); (d) O. L. Chapman and G. Wampfler, *J. Amer. Chem. Soc.*, **91**, 5390 (1969); (e) C. D. DeBoer and R. H. Schlessinger, *J. Amer. Chem. Soc.*, **94**, 655 (1972); (f) R. W. Yip, A. G. Szabo, and P. K. Tolg, *J. Amer. Chem. Soc.*, **95**, 4471 (1973).

(2) W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Amer. Chem. Soc.*, **86**, 4537 (1964).

(3) Caution should also be exercised at high thioxanthone concentrations because of self quenching. See ref 1d–f.

(4) A few reports of thioxanthone fluorescence have appeared previously. See (a) E. Sawicki, T. W. Stanley, W. C. Elbert, and M. Morgan, *Talanta*, **12**, 605 (1965); (b) H.-D. Dell, J. Fiedler, and R. Kamp, *Z. Anal. Chem.*, 253, 357 (1971).

Table I. Solvent Effects on Thioxanthone Fluorescence

Solvent	Φ_f^{rel} [a]	λ^{fl}_{max}, [b] nm
C_6H_{14}	0.019	395
$(C_2H_5)_2O$	0.048	398
CCl_4	0.070	400
C_6H_6	0.18	405
$(CH_3)_2CO$	0.30	405
CH_3CN	1.00	409
CH_2Cl_2	1.33	409
$CHCl_3$	3.39	413
t-C_4H_9OH	7.20	418
i-C_3H_7OH	12.3	423
C_2H_5OH	14.2	428
CH_3OD	22.5	430
CH_3OH	23.4[c]	431
CF_3CH_2OH	90.2	439

[a] Quantum yield of fluorescence measured relative to thioxanthone in acetonitrile at 25.0 ± 0.2° with λ_{ex} = 340 nm. Solutions were not degassed. Fluorescence yield measurements were carried out using a Hitachi-Perkin-Elmer MPF-2A spectrofluorometer and are not corrected for changes in solvent refractive index. Error is ±5%. [b] Wavelength of maximum fluorescence intensity, ±1 nm. [c] The absolute fluorescence quantum yield for thioxanthone in methanol is 0.12. We would like to thank Mr. Frank Grum of the Eastman Kodak Company for this measurement. For a description of the apparatus and techniques used, see L. Costa, F. Grum, and D. J. Paine, *Appl. Opt.*, **8**, 1149 (1969).

tive quantum yield of fluorescence, Φ_f^{rel}, and the wavelength of the fluorescence maximum, λ_{max}^{fl}, are found to be a strong function of solvent as shown in Table I. It is clear that increasing the hydrogen bonding ability and/or the polarity of the solvent leads to an increase in Φ_f^{rel} and a red shift of λ_{max}^{fl}, *e.g.*, for alcohol solvents Φ_f^{rel} and λ_{max}^{fl} increase in the order *tert*-butyl alcohol < isopropyl alcohol < ethanol < methanol < trifluoroethanol, while for substituted methanes the order is hexane < acetone < acetonitrile < dichloromethane < chloroform. Although hydrogen bonding ability of the solvent appears to be the major factor, *i.e.*, acetone < chloroform, solvent polarity, as measured by dielectric constant, also appears to affect the Φ_f^{rel} and λ_{max}^{fl} values.[5]

An expression for Φ_f, the quantum yield of fluorescence from the S_1 state of thioxanthone, is given in eq 1, where k_f is the unimolecular rate constant for fluorescence and k_{st} is the unimolecular rate constant for intersystem crossing to the T_1 state.[6] From eq 1 we see that

$$\Phi_f = \frac{k_f}{k_f + k_{st}} = k_f\tau_f \quad (1)$$

$$\tau_f = \frac{1}{k_f + k_{st}} \quad (2)$$

an increase in Φ_f can be due to an increase in k_f and/or a decrease in k_{st}. The value of the rate constant for fluorescence from S_1, k_f, is related to the probability of excitation of S_1 and can be calculated from the electronic absorption spectrum.[7] We have observed only minimal solvent effects on the k_f values derived from the electronic absorption spectrum of thioxanthone ($\epsilon_{max} \sim 5000$). This suggests that changes in the intersystem crossing rate are the source of the observed solvent effects on Φ_f^{rel}.

If Φ_f^{rel} increases with increasing polarity and hydrogen bonding ability because k_{st} decreases, then the fluorescence decay time, τ_f, defined by eq 2, must increase as Φ_f^{rel} increases. On the other hand, if the increase in Φ_f^{rel} is due to increases in k_f, then τ_f will decrease as Φ_f^{rel} increases. The relative fluorescence quantum yields and fluorescence lifetimes for thioxanthone in alcohol solutions are given in Table II. The increase in

Table II. Solvent Effects on Φ_f^{rel} and τ_f

Solvent	Φ_f^{rel} [a]	τ_f, [b] nsec
t-C_4H_9OH	7.2	≤1.0
i-C_3H_7OH	12.3	1.3
C_2H_5OH	14.2	1.7
CH_3OH	23.4	2.4
CF_3CH_2OH	90.2	7.3

[a] See footnote *a* in Table I. [b] Fluorescence decay time, measured by single photon counting. Absolute error ±15%. Relative error ±5%.

both Φ_f^{rel} and τ_f with increasing solvent polarity and hydrogen bonding ability demonstrates that the changes in fluorescence efficiency in alcohols are predominantly due to changes in the intersystem crossing rate, k_{st}. The thioxanthone fluorescence lifetime in alcoholic solvents is sufficiently long that care must be taken to ensure that singlet sensitization or quenching does not occur when thioxanthone is used as a triplet sensitizer.

The most likely reason for the large solvent effect on k_{st} is that the solvent is changing the states which are involved in the intersystem crossing process.[8] Calculations by El-Sayed[9] for azaaromatic and Plotnikov[10] for carbonyl compounds indicate that intersystem crossing will be as much as 10^3 times faster when there is a change in configuration, *e.g.*, $^1\pi,\pi^* \rightarrow {}^3n,\pi^*$ or $^1n,\pi^* \rightarrow {}^3\pi,\pi^*$, than when the singlet and triplet states are of the same configuration, *e.g.*, $^1n,\pi^* \rightarrow {}^3n,\pi^*$ or $^1\pi,\pi^* \rightarrow {}^3\pi,\pi^*$.[11] Furthermore, it is well known that increasing solvent polarity or hydrogen bonding ability stabilizes π,π^* states and destabilizes n,π^* states.[12] We therefore propose that, as shown in Scheme I, intersystem crossing in thioxanthone occurs predominantly from $^1\pi,\pi^*$ (S_1) to $^3n,\pi^*$ (T_2) in nonpolar poor hydrogen bonding solvents, *e.g.*, hexane, and therefore is fast.[13] As the solvent becomes more polar or a better hydrogen bonder,

(5) Qualitatively similar, although much smaller in magnitude, solvent effects have been observed for a limited range of solvents on the intensity and wavelength maximum of fluorescence of acridone, a compound analogous to **1** but with the sulfur replaced by a nitrogen. See (a) H. Kokubun, *Z. Elektrochem.*, **62**, 599 (1958); (b) E. J. Bowen and J. Sahu, *J. Chem. Soc.*, 3716 (1958); (c) H. Kokobun, *Z. Phys. Chem. (Frankfurt am Main)*, **17**, 281 (1958); (d) H. Kokobun and M. Kobayashi, *ibid.*, **41**, 245 (1964).

(6) Internal conversion to the ground state is usually an unimportant pathway for radiationless deactivation of ketone excited singlet states. This appears to be the case for thioxanthone, since the sum of the quantum yields of fluorescence (0.12) and intersystem crossing (0.82) in methanol is close to unity (J. C. Dalton and F. C. Montgomery, unpublished results).

(7) For recent applications see J. C. Dalton and N. J. Turro, *J. Amer. Chem. Soc.*, **93**, 3569 (1971); and H. E. Zimmerman and A. A. Baum, *J. Amer. Chem. Soc.*, **93**, 3546 (1971).

(8) For a detailed discussion of the effect of the relative ordering of n,π^* and π,π^* singlet and triplet states on molecular luminescence characteristics see (a) R. N. Nurmukhametov, V. G. Plotnikov, and D. N. Shigorin, *Russ. J. Phys. Chem.*, **40**, 622 (1966); (b) V. Plotnikov, *Opt. Spektrosk.*, **23**, 20 (1967).

(9) M. A. El-Sayed, *J. Chem. Phys.*, **38**, 2834 (1963).

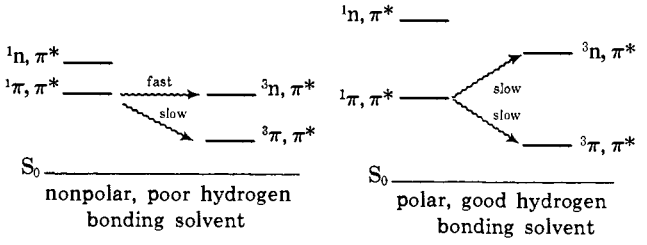
(10) V. G. Plotnikov, *Opt. Spektrosk.*, 22, 401 (1967).

(11) See, however, T. Azumi, *Chem. Phys. Lett.*, **25**, 135 (1974).

(12) See, for example, C. A. Parker, "Photoluminescence of Solutions," Elsevier, New York, N. Y., 1968, p 33.

(13) The lowest triplet state, T_1, is known to be π,π^* (ref 2). The large extinction coefficient for the longest wavelength band in the thioxanthone electronic absorption spectrum and the red shift in λ^{fl}_{max} strongly imply that the S_1 state is π,π^* also (*vide infra*).

Scheme I



the energy of the $^3n,\pi^*$ state (T_2) will become greater than that of the $^1\pi,\pi^*$ state (S_1) meaning that intersystem crossing from S_1 to T_2 will require a larger activation energy and will become slower. The greater the solvent polarity or hydrogen bonding ability, the larger the energy difference between T_2 and S_1, the greater the activation energy and the lower the rate constant for intersystem crossing from S_1 to T_2 will be. This predicts that the intersystem crossing rate will decrease continuously as a function of increasing solvent polarity or hydrogen-bonding ability, until only the slow intersystem crossing from S_1 (π,π^*) to T_1 (π,π^*) remains.[14] In solvents of intermediate polarity and hydrogen bonding ability, the observed intersystem crossing rate will equal the sum of the rates of intersystem crossing to T_2 and T_1. (The solvent effect of k_{st} can also be explained by an analogous argument involving the extent of mixing of n,π^* character into the vibrationally excited level of the π,π^* triplet isoenergetic with the π,π^* singlet.)

The explanation given above for the enormous effect of solvent on the Φ_f^{rel} values also accounts for the solvent effect on $\lambda^{fl}{}_{max}$. Since the S_1 state is π,π^*, presumably with substantial amounts of intramolecular charge transfer character,[15] its energy should decrease in going to solvents of greater polarity or hydrogen-bonding ability causing $\lambda^{fl}{}_{max}$ to red shift, as is observed. If the lowest singlet of thioxanthone in nonpolar solvents were the n,π^* singlet, then increasing solvent hydrogen-bonding ability would be expected to cause an initial blue shift in $\lambda^{fl}{}_{max}$. The absence of such a blue shift suggests that S_1 is π,π^* in all solvents.

In summary, we have observed substantial solvent effects on the fluorescence efficiency and lifetime and the position of the fluorescence maximum of thioxanthone. The Φ_f^{rel} and τ_f changes are attributed to solvent effects on the rate of intersystem crossing caused by changes in relative energies of the $^1\pi,\pi^*$ (S_1) state and $^3n,\pi^*$ (T_2) state. The sensitivity of $\lambda^{fl}{}_{max}$ to solvent character may make thioxanthone useful in fluorescence labeling experiments as a probe for molecular environment.[16]

Acknowledgment. We would like to thank Dr. William H. Saunders Jr. for helpful assistance with this research.

(14) A similar explanation has been suggested for the stronger fluorescence of acridone in alcohol relative to hexane and solvent effects on fluorenone fluorescence lifetimes and efficiencies. See (a) ref 8a; (b) L. A. Singer, *Tetrahedron Lett.*, 923 (1969); (c) R. A. Caldwell, *ibid.*, 2121 (1969); (d) B. M. Monroe and R. P. Groff, *ibid.*, 3955 (1973).

(15) V.-K. H. Giovanelli, J. Dehler, and G. Hohlneicher, *Ber. Bunsenges. Phys. Chem.*, 75, 864 (1971).

(16) For a recent review of an application of fluorescence probes, see G. M. Edelman and W. O. McClure, *Accounts Chem. Res.*, 1, 65 (1968).

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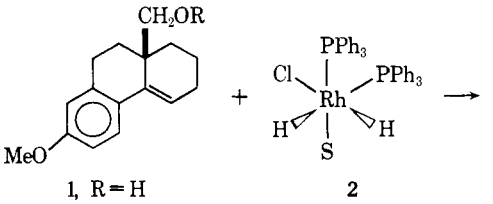
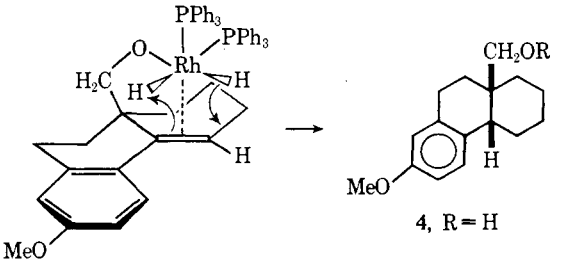
Control of Hydrogenation Stereochemistry by Intramolecular Anionic Coordination to Homogeneous Catalysts[1]

Sir:

Hydrogenation of olefins in the presence of homogeneous catalysts[2] holds potential for stereochemical control of the reduction process through coordination to the catalyst by polar functional groups within the molecule.[1b] This potential has so far remained unrealized,[3] in part because instances to which this idea might be applied usually involve alkenes whose degree of substitution would be expected to depress their rates of reduction severely.[4] However, several entries in the literature of this subject suggest that reduction of olefins may be accelerated by an assisting coordination to the catalyst of certain very polar functional groups within the molecule,[5-7] and that increasing the electron density on such a functional group may further favor this coordination.[6a,c]





We have applied the above principles to the reduction of compound **1**, which can serve as a model precursor for many polycyclic systems of interest. The trisubstituted styrene bond of **1** is expectedly unreactive[2c,4] toward hydrogenation with $(Ph_3P)_3RhCl$ at atmospheric pressure and room temperature, and even at 100 psi and 50°. However, treatment of alkali metal salts of **1** in benzene with hydrogen and 0.036 equiv of $(Ph_3P)_3RhCl$ under the latter conditions, leads to olefin

(1) (a) Part IV in the series Stereochemical Control of Reductions. (b) Part III: H. W. Thompson and R. E. Naipawer, *J. Amer. Chem. Soc.*, 95, 6379 (1973).

(2) (a) R. E. Harmon, S. K. Gupta, and D. J. Brown, *Chem. Rev.*, 73, 21 (1973); (b) F. J. McQuillin, *Progr. Org. Chem.*, 8, 314 (1972); (c) J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc. A*, 1711 (1966); (d) S. Montelatici, A. van der Ent, J. A. Osborn, and G. Wilkinson, *ibid.*, 1054 (1968).

(3) (a) *Cf.* A. J. Birch and K. A. M. Walker, *J. Chem. Soc. C*, 1894 (1966); Y. K. Sawa, N. Tsuji, K. Okabe, and T. Miyamoto, *Tetrahedron*, 21, 1121 (1965); (b) *cf.* H. J. Brodie, C. E. Hay, and T. A. Wittstruck, *J. Org. Chem.*, 37, 3361 (1972); (c) *cf.* Y. J. Abul-Hajj, *Steroids*, 18, 281 (1971).

(4) A. S. Hussey and Y. Takeuchi, *J. Amer. Chem. Soc.*, 91, 672 (1969); *J. Org. Chem.*, 35, 643 (1970).

(5) R. E. Harmon, J. L. Parsons, D. W. Cooke, S. K. Gupta, and J. Schoolenberg, *J. Org. Chem.*, 34, 3684 (1969).

(6) (a) W. S. Knowles, M. J. Sabacky, and B. D. Vineyard, *Ann. N. Y. Acad. Sci.*, 172, 232 (1970); (b) W. S. Knowles and M. J. Sabacky, *Chem. Commun.*, 1445 (1968); (c) T. P. Dang and H. B. Kogan, *Chem. Commun.*, 481 (1971); (d) J. D. Morrison, R. E. Burnett, A. M. Aguiar, C. J. Morrow, and C. Phillips, *J. Amer. Chem. Soc.*, 93, 1301 (1971).

(7) F. H. Jardine, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc. A*, 1574 (1967); S. Siegel and D. W. Ohrt, *Tetrahedron Lett.*, 5155 (1972).