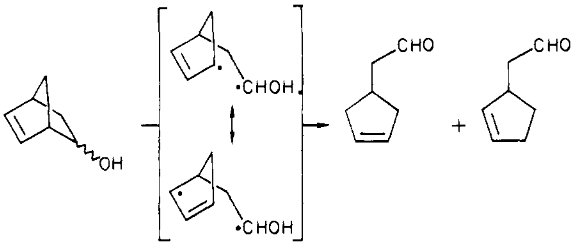
accurate value of the extinction coefficient of methanol in solution at 185 nm is not available.[17] If the value is between that of the vapor and the liquid, the decrease in the rate can be largely attributed to the fraction of the light that is absorbed by the methanol.

In order to obtain more extensive data, the photolysis of these homoallylic alcohols was extended to monochromatic radiation at 214 nm.[18] It was possible to use methanol as a solvent although it absorbed ~60% of the radiation in the path length that was used.[19] The results (Table II) show that in **1** methanol speeds up the fragmentation to give methylenecyclohexane by a factor of more than five (after correction for absorption by the solvent) whereas in the rigid bicyclic alcohols it *slows* the rate to about 30–40% (corrected) of its value in pentane. The acceleration of the former would be in keeping with the protonation mechanism that was suggested by Kropp and his co-workers[5,7] which would be favored when a hydroxylic species is available to capture the trans olefin. The decelerating effect on the reactions of the bicyclic alcohols clearly rules out a common mechanism for these two classes of compounds.

Some mechanistic details such as the differences in behavior between exo and endo alcohols and formation of both Δ^2- and Δ^3-aldehydes deserve comment. If the excitation of an endo alcohol such as **2** led to a concerted process as depicted in eq 2, only the Δ^3-aldehyde would be formed. Such a concerted reaction is obviously not feasible in the exo isomers. It is therefore necessary to postulate a diradical path as well which is shown in eq 4.[20] The diradical pathway alone would not explain the differing ratios of aldehydes from the exo and endo isomers. Note that the endo alcohols which have two routes for reaction according to this hypothesis also react faster than the exo alcohols. The slowing down of these reactions in methanol is an intriguing phenomenon. The type II process in a variety of ketones is known to be speeded up in hydroxylic solvents.[21] At first sight, it seems reasonable that the inverse of this process should be slowed down by a hydroxylic solvent. But since no epimerization of the starting compounds was detected, there is no reason to believe that the intermediate biradical reverts to the starting material. The effect of the hydroxylic solvent may therefore be on the starting material rather than on the intermediate.



(4)

The photoreactions seen in these rigid, bicyclic ene alcohols at 185 nm are not characteristic of olefins which usually react via carbene intermediates.[22] Alcohols do undergo a variety of scission processes at 185 nm,[17] but in the present examples the reaction paths seem few and narrowly channelled. Thus, some interaction between the olefin and alcohol chromophores in the excited state can be inferred even if it is not evident from the ultraviolet spectra.

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Joel Studebaker, R. Srinivasan,* Jose A. Ors, Thomas Baum
IBM Thomas J. Watson Research Center
Yorktown Heights, New York 10598

Received March 3, 1980

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[18] The source was a Phillips 93106E zinc lamp. It was surrounded by an annulus which contained the solution to be photolyzed.

[19] "UV Atlas of Organic Compounds", Plenum Press, New York, 1966, Vol. I, M-1.

[20] The epimerization **2** ⇄ **3** or **4** ⇄ **5** under the influence of light was not observed. Further fragmentation of the diradicals to give cyclopentadiene and acetaldehyde is seen in the mass spectrum but cannot be taken as an indication of stepwide cleavage.

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Quenching of Emission and of Photochemistry of Pentacarbonyl(4-cyanopyridino)tungsten(0)

Sir:

Several complexes of the general formula $W(CO)_5L$, where L is an *n*-electron donor, have been found to luminesce at 77 K either as the pure solid or in rigid glasses.[1,2] The emission has been assigned to either a $^3E \rightarrow {}^1A_1$ ligand-field (LF) transition or a W → L charge-transfer (CT) transition, depending on the nature of L. As L becomes more electron withdrawing, the CT state lowers in energy, and for various 4-substituted pyridines as L has been inferred to be the lowest lying state.[3] $W(CO)_5L$ complexes have not been thought to luminesce in room temperature solution, presumably because of rapid ligand dissociation and nonradiative relaxation to ground state.[2,4] We report here what appears to be the first observation of emission from a $W(CO)_5L$ complex in room temperature solution. The finding makes possible quenching studies, and results are reported for anthracene as quencher.

$W(CO)_5$(4-CNpyr) (cyanopyridine) was prepared via the tetrahydrofuran complex, $W(CO)_5$(THF), according to a literature procedure.[3,5] Purification was achieved by chromatography on alumina, followed by recrystallization from toluene/isooctane solution. Anthracene was recrystallized from benzene prior to use. The solvent methylcyclohexane was purified by several distillations, to remove emitting or quenching impurities. Laser pulse excitation was at 353 or 530 nm, using a 20-ns pulse from a Nd glass laser.[6] The photomultiplier was an RCA 7265. Conventional photolyses were carried out with light from an interference filtered Hg lamp, and quantum yields were determined by means of Reineckate actinometry.[7]

Either 353- or 530-nm excitation of $W(CO)_5$(4-CNpyr) (5×10^{-5} to 1×10^{-4} M) in argon-flushed[8] methylcyclohexane produced a relatively weak emission (comparable in intensity to that found for various Cr(III) ammines in room temperature solution[9]). The decay time, τ, is 360 ± 30 ns at 25 °C, and the emission is in the 600–700-nm region with an uncorrected peak intensity at about 630 nm (reported values in EPA at 77 K are 33 μs and 602 nm[3]). On correction, using the manufacturers response data, the emission maximum shifts slightly, to 640 nm; the emission is broad and unstructured. The emission temperature dependence was determined both in the above solvent and with added 0.1 M ethanol (which has no detectable effects). Points for seven temperatures from 0 to 30 °C give good Arrhenius behavior, the least-squares line being $1/\tau = 3.56 \times 10^7 \exp(-1520/RT)$, R in cal; the apparent activation energy is thus small, and may relate to that of solvent viscosity. It might be noted that we see weak emission

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[8] Argon purging was necessary, as oxygen quenching was observable.

[9] Walters, R. T.; Adamson, A. W. *Acta Chem. Scand., Ser. A* **1979**, *A33*, 53.

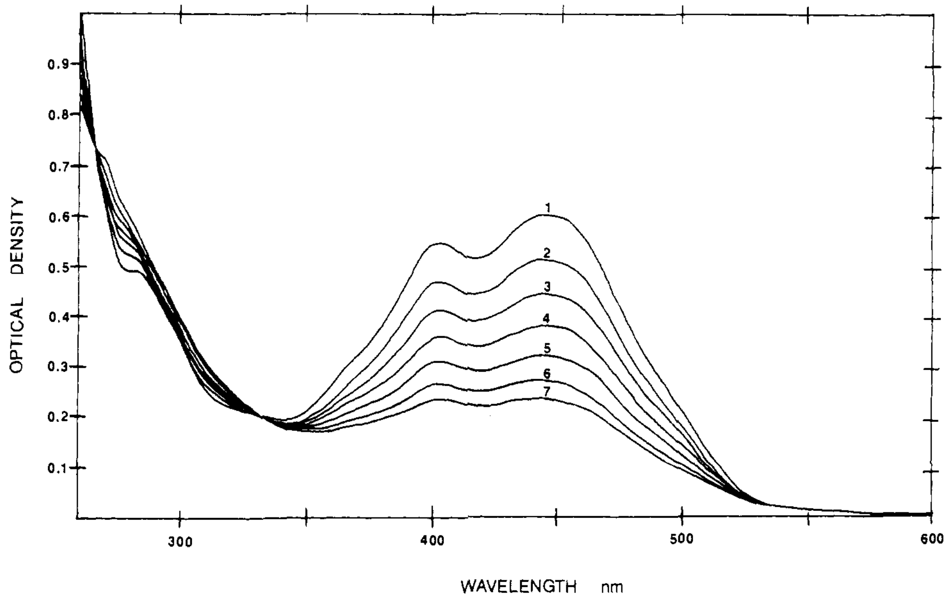

Figure 1. Photolysis of 7.3 × 10^{-5} M $W(CO)_5(4\text{-CNpyr})$ at room temperature in methylcyclohexane containing 0.1 M ethanol. Curve 1, initial spectrum. Curves 2–7, irradiation at 520 nm for equal time intervals.

from such complexes as $W(CO)_6$ and $W(CO)_5(C_2H_5OH)$, but of lifetime less than 20 ns, so that quenching studies were not attempted.

In the absence of some entering ligand, the photochemistry is complex. Photodissociation of the 4-cyanopyridine or similar ligands has been found to be the most efficient process for our excitation wavelength region,[3,10] and binuclear species such as $W_2(CO)_{11}$ or $W_2(CO)_{10}L$ may be formed.[11] Also, for example, evidence has recently been reported for the appearance of $Cr_2(CO)_{11}$ on flash photolysis of $Cr(CO)_6$ in perfluorocarbon solvents.[12] We observed an early loss of isosbestic points on photolysis of $W(CO)_5(4\text{-CNpyr})$ in methylcyclohexane, evidently due to secondary reactions to form such binuclear products. However, in the presence of excess entering ligand, in this case 0.1 M ethanol, the photosubstitution reaction to form $W(CO)_5(C_2H_5OH)$ appears to be uncomplicated by side or subsequent reactions. The spectral sequence on 520-nm irradiation is shown in Figure 1; there is a clean progression to near zero terminal absorbance in the 450–500-nm region. The quantum yield, ϕ, is 0.021 ± 10%, at 25 °C; such a low value is consistent with results reported for substituted pyridine ligands of this type,[3] and is apparently characteristic when the CT state lies below the LF state. The yield is independent of ethanol concentration in the 0.025–0.1-M range; preliminary observations show that at higher concentrations major changes occur both in the emission behavior and in the absorption spectrum, to be reported in detail in the full paper. It should be noted that the lack of dependence both of the emission lifetime and of ϕ on ethanol concentration in the dilute range is a good indication that ethanol is not a quencher in dilute solution, and does scavenge completely the photochemically produced $W(CO)_5$ intermediate. The yield is temperature dependent, the values at 10, 15, 20, and 30 °C being 0.0110, 0.0131, 0.0162, and 0.0265, respectively, corresponding to an apparent activation energy of 7.6 kcal mol^{-1}.

Quenching both of the photochemistry and of the luminescence is observed with anthracene. Stern–Volmer type plots of ϕ^0/ϕ and τ^0/τ, where superscript zero denotes absence of quencher, are linear against anthracene concentration, as shown in Figure 2, and are coincident. The slope yields a common bimolecular quenching rate constant of 4.0 × 10^9 M^{-1} s^{-1}. This value is at about the diffusion limit.

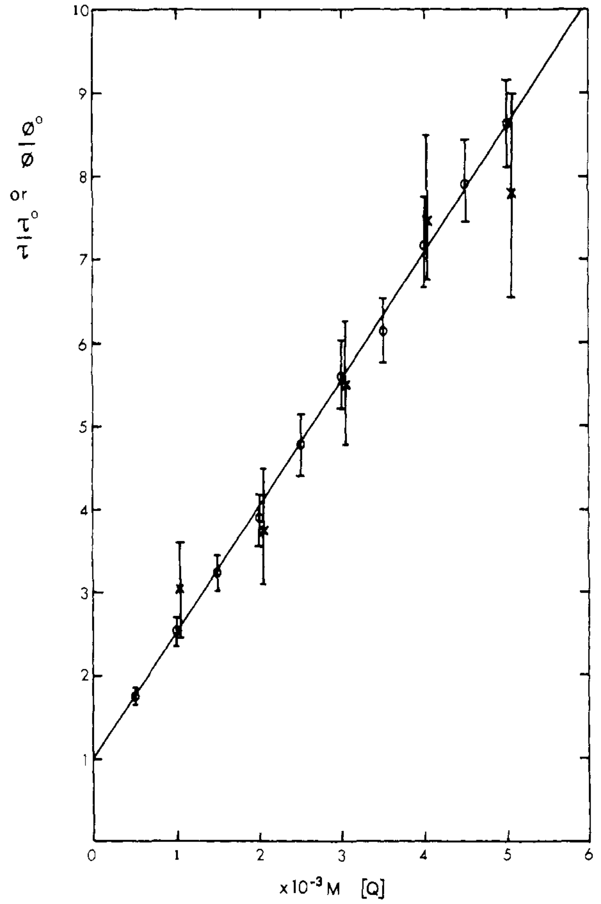

Figure 2. Quenching of 7.5 × 10^{-5} M $W(CO)_5(4\text{-CNpyr})$ processes at room temperature by anthracene in argon-purged methylcyclohexane containing 0.1 M ethanol (O, τ^0/τ, X, ϕ^0/ϕ). Error lines show the deviations from the average of three separate experiments.

Our results strongly indicate, of course, that the emitting state of $W(CO)_5(4\text{-CNpyr})$ is implicated in the photochemistry, that is, that chemical reaction occurs either from *or* via this state. The simplest possiblity is the former one. We can write $\phi = k_{cr}/(k_r + k_{nr} + k_{cr})$ where k_{cr}, k_r, and k_{nr} are the rate constants for chemical reaction for radiative return to the ground state and for the nonradiative return, respectively. Since ϕ is small, $\phi \simeq k_{cr}/k_{nr}$ (k_r taken to be negligible), so that $E_\phi^* = 7.6$ kcal $mol^{-1} \simeq E_{cr}^* - E_{nr}^*$. In the one-state scheme, $1/\tau = k_r + k_{nr} + k_{cr} \simeq k_{nr}$, when $E_{nr}^* \simeq 1.5$ kcal mol^{-1} and $E_{cr}^* \simeq 9.1$ kcal mol^{-1}. The photo-

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chemical reaction presumably occurs by breaking the W–L bond, to form the intermediate $W(CO)_5$, which is then scavenged by the ethanol (in our case).[2] It is at least debatable whether the W–L bond-breaking reaction should be activated to the extent of 9 kcal mol^{-1}.

An attractive alternative is a two-state scheme in which chemical reaction occurs from a LF state lying above the emitting CT state (in our case), and in steady-state equilibrium with it. The observed E_ϕ* is now attributed primarily to the energy difference between the two states. In this scheme, excitation leads, through the intersystem crossing, to a triplet CT state, ^{3}CT.[13] This state is emitting, but not highly chemically reactive. The higher lying LF state, presumably also a triplet, does react efficiently, but the overall quantum yield is small because of the competition with nonradiative relaxation of ^{3}CT. The detailed kinetics for such a system have been discussed.[14–16]

The above type of two-state scheme has been proposed in explanation of the photochemical behavior of $Ru(NH_3)_5L^{2+}$ complexes,[17] as well as for that of the present type of carbonyl complexes.[2,18,19] It has the appealing feature of accounting for the increase in ϕ for cases where L is such that the CT absorption band lies at higher energy than the LF one. We hope, through current solvent dependence studies, and through variations in L, to gain leverage in distinguishing between the one- and two-state types of schemes.

We can report on results with other potential quenchers. The emission is quenched by 9-methylanthracene and by 1,2-benzanthracene, but not by 1,2,5,6-dibenzanthracene or ferrocene. The respective triplet-state energies are 16.2,[20] 16.5,[20] 18.3,[20] and 18.6 kK.[21] The triplet-state energy for anthracene is 14.7 kK.[20] With the assumption that quenching occurs by energy transfer, the above results indicate that the energy of the emitting state of $W(CO)_5$(4-CNpyr) lies between 16.5 and 18.3 kK, or somewhat above the energy corresponding to the emission maximum, 15.6 kK. In terms of the two-state scheme, we would place the reactive ligand-field state at about 7.6 kcal mol^{-1} or 2.6 kK above an emitting state energy of about 17 kK, or at 19.6 kK or 510 nm. This might, for example, be assigned as the energy of the ^{3}E state.[22]

Quenching of emission and of photochemistry has been observed for various Cr(III) ammines,[23] and recently for $Rh(NH_3)_5Cl^{2+}$[24] and $Rh(NH_3)_5Br^{2+}$.[25] Emission and emission quenching have been reported for rhenium tricarbonyl complexes.[26] The present case appears to be the first one involving a group 6 carbonyl complex and appears also to be novel in that quenching of photochemistry is also observed.

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Alistair J. Lees, Arthur W. Adamson*
Department of Chemistry
University of Southern California
Los Angeles, California 90007

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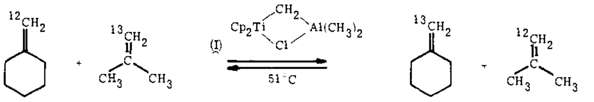
Titanium Metallacarbene–Metallacyclobutane Reactions: Stepwise Metathesis

Sir:

The mechanism of the olefin metathesis reaction[1] has been examined through model and labeling studies. These studies support a mechanism involving the interconversion of metal–olefin–carbene complexes and metallacyclobutanes.[2] Numerous questions concerning the structure of the intermediates, the factors controlling the stereochemistry of the reaction,[3] and the role of the cocatalyst in the active systems remain to be answered.

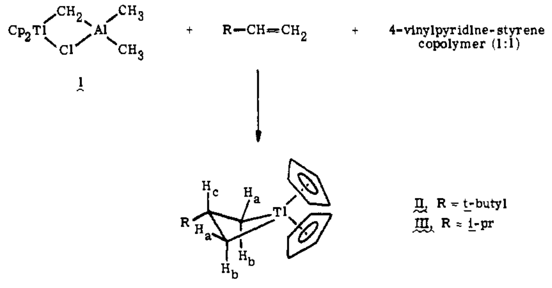
Parshall and Tebbe[4] recently reported a slow but well-defined catalyst (I) for the degenerate metathesis of isobutene and methylenecyclohexane (eq 1). Reaction was extensive after 47 h and was selective for exchange of terminal methylene groups. Ethylene and propylene were reported to undergo a methanation reaction instead of metathesis.[5]



(1)

As part of a study of the factors controlling the stereochemistry of metathesis with unsymmetrical analogues of I,[6] (η^5-C_5Me_5)(η^5-C_5H_5)$TiCH_2 \cdot AlClMe_2$ and (η^5-1,2,4-$C_5Me_3H_2$)(η^5-C_5H_5)$TiCH_2 \cdot AlClMe_2$, the methanation reaction was reexplored. We have now isolated a metallacyclobutane[7] from the true metathesis system I,[4] which provides answers to a few of the questions mentioned above.

The reaction of the "Tebbe" reagent (I) with neohexene in THF gave intractable products. However, when the reaction was run in benzene containing 1 equiv of pyridine, there was produced a near quantitative yield of a single metallocene product (II) and the pyridine–dimethylchloroaluminum adduct (eq 2). The two products could be separated with difficulty by repeated recrystallization from hexane–THF. It was subsequently found that



(2)

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