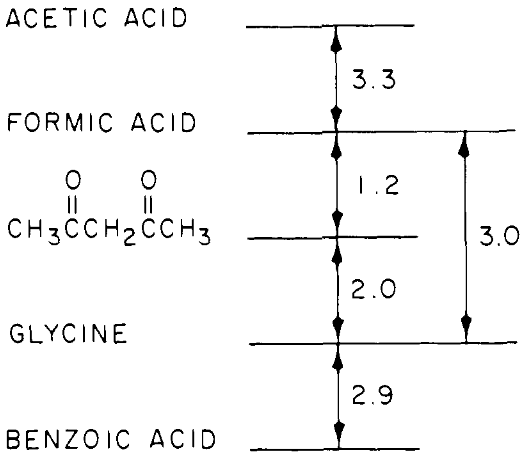

Figure 2. The acidity of glycine in the gas phase realtive to several reference acids. Each number listed is $\Delta G_{385}°$ (kilocalories/mole) for proton transfer reactions such as $A^- + BH = B^- + AH$. The strongest acid in this series is benzoic acid.

$$\text{glycine} = H^+ + H_2NCH_2COO^-, \quad \Delta G^0_{385} = 332.5 \text{ kcal/mol} \quad (6)$$

$$CH_3COOH = H^+ + CH_3COO^-, \quad \Delta G^0_{385} = 339.0 \text{ kcal/mol} \quad (7)$$

$$CH_3NH_2 = H^+ + CH_3NH^-, \quad \Delta G^0_{385} = 393.5 \text{ kcal/mol} \quad (8)$$

cine in the gas phase has a deprotonation energy more similar to acetic acid than methylamine. Thus, we conclude that the $(M - H)^-$ ion of glycine is due to loss of a proton from the carbonyl group to give the ionic structure shown in reaction 6.

The site of protonation and the site of deprotonation of glycine in the gas phase are established by the comparisons made above. Furthermore, glycine in the gas phase behaves in its acid/base chemistry like a nonionic α-aminocarboxylic acid rather than a zwitterion. Matrix isolation studies[9] and recent theoretical calculations[10] also indicate that the nonionic form is more stable than the dipolar form. We are currently investigating this problem in more detail by studying the effects of substituents on the gas-phase acidity and basicity of α-amino acids.

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(7) In recent months the preferred value for the gas-phase proton affinity of ammonia ($\Delta H_{298}°$ for $NH_4^+ = NH_3 + H^+$) has begun to inflate once again after an extended period of stability. The relative proton affinity scales reported by ref 6b and R. Yamdagni and P. Kebarle, *J. Am. Chem. Soc.*, **98**, 1320 (1976), have been shifted up in absolute value owing to revised values for certain of the reference compounds. In particular, revised values for $\Delta H_f°$ (t-$C_4H_9\cdot$) and the ionization potential of t-$C_4H_9\cdot$ have changed the proton affinity of isobutene from 193.0 to 197.4 kcal/mol, and this shifts the PA (NH_3) from the previously accepted value of 202.3 to 206.7 kcal/mol. Since this situation still seems to be unresolved, we have simply selected 207.0 kcal/mol as our reference value for ammonia. Conversion from $\Delta H_{298}°$ to $\Delta G_{382}°$ for the process $NH_4^+ = NH_3 + H^+$ can be accomplished by estimating the entropy of this reaction to be equal to $S°(H^+) + R \ln (3/12)$, where 3/12 is the ratio of the rotational symmetry numbers for NH_3 and NH_4^+, respectively. Thus, at 382 K, $\Delta G_{382}° = 207.0 - 0.382\,(26.043 + R \ln 3/12) = 198.1$ kcal/mol for the gas-phase basicity of ammonia. Of course, the relative values reported in Figure 1 are not affected by changes in the absolute values of the reference compounds.

(8) The value 329.6 kcal/mol for the absolute acidity of benzoic acid is due to equilibrium measurements by Cumming and Kebarle, *Can. J. Chem.*, **56**, 1 (1978), and the acidity of CH_3NH_2 was measured by G. I. Mackay, R. S. Hemsworth, and D. K. Bohme, *Can. J. Chem.*, **54**, 1624 (1976).

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Photoactivation of Cluster Catalysis: a Comparison of 1-Pentene Isomerization by Tetracarbonyl(triphenylphosphine)ruthenium and 1,1,1,2,2,2,3,3,3-Nonacarbonyl-1,2,3-tris(triphenylphosphine)-*triangulo*-triruthenium

Sir:

In this communication we register two potential advantages of cluster precursors to photochemically generated catalysts. We present preliminary results demonstrating that (1) lower energy irradiation can be used to activate catalysis by irradiation of a cluster compared with an appropriate mononuclear analogue and (2) the active species generated from the cluster can operate on the substrate to give a substantially different ratio of products. The latter result bears on the question of whether cluster species can do unique chemistry relative to their mononuclear fragments. We report a comparison of the photocatalyzed 1-pentene isomerization by $Ru_3(CO)_9(PPh_3)_3$ and $Ru(CO)_4(PPh_3)$.[1]

Before detailing the results concerning the 1-pentene isomerization, we will delineate some of the essential photochemical and spectral properties of the two catalyst precursors. Both complexes are thermally inert at 298 K, but each is photosensitive. The absorption spectra of the two complexes are included in Figure 1; $Ru(CO)_4(PPh_3)$ is a pale yellow substance with only tail absorption at wavelengths longer than 300 nm, while $Ru_3(CO)_9(PPh_3)_3$ exhibits an intense visible absorption maximum at 506 nm (ϵ ~14 000). The ultraviolet absorption of the C_{3v} $Ru(CO)_4(PPh_3)$ is logically a ligand field transition which terminates in the d_{z^2} orbital which is strongly σ antibonding.[2] Near-UV, 355 nm, irradiation in the presence of added 0.1 M PPh_3 in benzene yields $Ru(CO)_3(PPh_3)_2$ (ν_{CO} 1895 cm^{-1}),[3] and irradiation in the presence of 0.1 M $P(OMe)_3$ in benzene apparently yields $Ru(CO)_3(PPh_3)[P(OMe)_3]$ (ν_{CO} 1905 cm^{-1}) and *not* $Ru(CO)_4[P(OMe)_3]$. These results allow the conclusion that loss of CO is the principal result of near-UV irradiation of $Ru(CO)_4(PPh_3)$ (eq 1).

$$Ru(CO)_4(PPh_3) \xrightarrow[\Phi\,=\,0.32\pm0.02]{h\nu,\ 355\text{ nm}} Ru(CO)_3(PPh_3) + CO \quad (1)$$

When CO is purged from the solution, 1-pentene can scavenge $Ru(CO)_3(PPh_3)$ to yield a very substitution labile 1-pentene complex, but, in hermetically sealed samples of benzene solutions of 1.76 M 1-pentene, $Ru(CO)_4PPh_3$ undergoes little net reaction even at long irradiation times. Note that the coordinatively unsaturated species generated has the same empirical formula as $Ru_3(CO)_9(PPh_3)_3$. This fact is an important feature of the system under study, since we find that visible irradiation of $Ru_3(CO)_9(PPh_3)_3$ in the presence of L yields $Ru(CO)_3PPh_3L$, (eq 2). Based on this photochemistry

$$Ru_3(CO)_9(PPh_3)_3 \xrightarrow[L\,=\,CO,\ PPh_3;\ \Phi\,\approx\,10^{-2}]{h\nu,\ 514.5\text{ nm}} 3Ru(CO)_3PPh_3L \quad (2)$$

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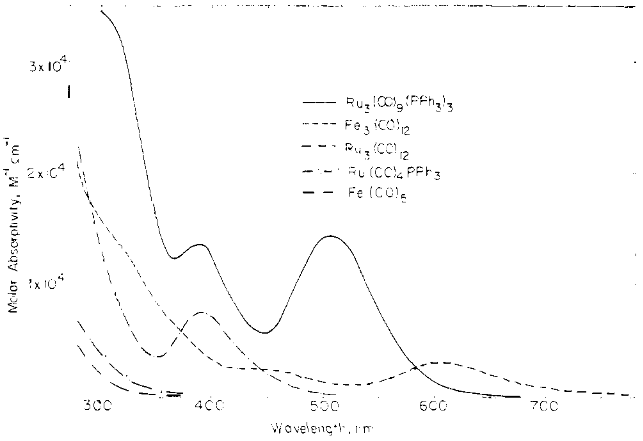


Figure 1. Comparison of the absorption spectra of various catalyst precursors in benzene solution at 298 K.

Table I. Photocatalyzed 1-Pentene Isomerization[a]

catalyst precursor	irrdn, λ (nm)	% convn	Φ	trans/cis
$Ru(CO)_4PPh_3$[b]	355	5.7	3.1	2.3
		14.9	2.7	2.0
$Ru_3(CO)_9(PPh_3)_3$	355	5.3	0.6	4.3
		10.0	0.9	3.4
	436	6.7	1.2	3.0
		13.7	1.9	2.9
	550	6.9		3.3
		12.0		3.5
$Ru_3(CO)_{12}$	355	7.7	5.5	5.7
		13.8	5.0	6.2
	436	8.4	13	5.5
		14.6	12	7.0
$Fe(CO)_5$[b]	355	6.2	91	2.8
		14.1	107	2.8
$Fe_3(CO)_{12}$	355	7.3	27	3.0
		13.4	26	2.8
	436	8.5	41	2.9
		17.0	33	2.8
	550	8.7		3.0
		13.9		2.9

[a] All experiments were carried out at 298 K in a degassed 1.76 M 1-pentene-benzene solution containing 1×10^{-3} M catalyst precursor. Quantum yields, Φ, are ±20%, and the ratio of *trans*- to *cis*-2-pentene products (trans/cis) is ±5%. Irradiation at 550 or 436 nm was carried out using an appropriately filtered 550-W Hanovia Hg lamp and at 355 nm using a GE Blacklite. Light intensities at 436 or 355 nm were in the range of 1×10^{-6} to 1×10^{-7} einstein/min. All analyses were carried out using vapor-phase chromatography and each entry represents the average of at least two analyses. [b] Note that for these species 1×10^{-3} M does not completely absorb all incident photons at 355 nm in the 1.0-cm path-length ampules used to contain the samples. The Φ's have not been corrected in any way to account for this transmission of incident light. We take Φ to be the number of 1-pentene molecules isomerized per *incident* photon.

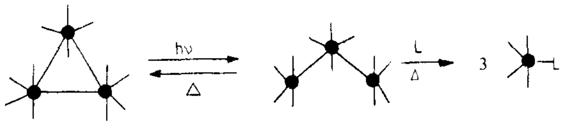
and the low energy of the first absorption feature, we attribute the lowest energy absorption band to a transition which involves the Ru orbitals and likely terminates in one which is strongly σ antibonding with respect to the Ru-Ru bonds.[1,4] In the presence of 1.76 M 1-pentene, irradiation of $Ru_3(CO)_9(PPh_3)_3$ in benzene solution only gives slow conversion to mononuclear complexes ($\Phi < 10^{-4}$). We note that $Fe(CO)_5$ and $Fe_3(CO)_{12}$ are related to each other in the way that $Ru(CO)_4(PPh_3)$ and $Ru_3(CO)_9(PPh_3)_3$ are. The absorption spectra of $Fe(CO)_5$ and $M_3(CO)_{12}$ are included in Figure 1, and some of their photochemistry is given in reactions 3 and

$$Fe(CO)_5 \xrightarrow[355\text{ nm},\ \phi \approx 1.0]{h\nu} Fe(CO)_4 + CO \qquad (3)$$

$$M_3(CO)_{12} \xrightarrow[\substack{L=CO,\text{ alkene} \\ \phi \approx 10^{-2}}]{h\nu} M(CO)_4L \qquad (4)$$

$$M = Fe, Ru$$

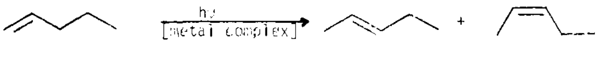
4.[1,5,6] From the quantum yields given in eq 1–4 it appears that the clusters are qualitatively less efficiently decomposed than the mononuclear complexes. Further, for the irradiation of the Ru-phosphine complexes in the presence of 1-pentene we observe only very slow conversion to any product. Though the detailed mechanism of reactions 2 and 4 is not clear, it can be speculated that cleavage of a M-M bond is the primary chemical result of light absorption in the trinuclear species,



(5)

reaction 5, followed by (i) rapid reformation of the M-M bond (giving low quantum yields) or (ii) dissociative and/or associative processes leading to the mononuclear products. The possibility that the ring-opened trinuclear species might interact with substrates prompted the comparison of photocatalytic properties of mononuclear and trinuclear species.

The cluster species $M_3(CO)_{12}$ (M = Fe, Ru) and $Ru_3(CO)_9(PPh_3)_3$ all photocatalyze reaction 6 upon *visible*



(6)

light excitation which is not absorbed by the Fe or Ru mononuclear complexes. This establishes one important advantage for the cluster vs. mononuclear precursors. The ability to initiate the catalytic action in the visible may allow catalysis of a wider range of substrates in that many organic substances are sensitive to ultraviolet light.

The particulars of the 1-pentene isomerization according to eq 6 are given in Table I. All of the catalyst precursors are capable of moving high concentrations of 1-pentene toward the thermodynamic ratio[7] of the linear pentenes, demonstrating turnover numbers (number of 1-pentene molecules consumed per metal atom initially present) which are at least 10^3. Further, observed initial quantum yields, Φ (number of 1-pentene molecules isomerized per *incident* photon), are high and often exceed unity, evidencing the photogeneration of a thermally active catalyst which turns over a number of times.

The critical result is that the initial ratio of *trans*- to *cis*-2-pentene depends on the catalyst precursor used. In particular, there is a marked difference between photocatalysis by $Ru(CO)_4(PPh_3)$ and $Ru_3(CO)_9(PPh_3)_3$. This result reveals that, whatever the actual catalytic species are, they are different for the two precursors. The initial ratio of the 2-pentenes from the clusters appears to be independent of the excitation wavelength, but modest differences in quantum yield are found. The data from the photochemical reactions, catalytic chemistry, and the comparison with $Ru(CO)_4PPh_3$ compel us to conclude that $Ru_3(CO)_9(PPh_3)_3$ yields a *cluster* as the actual active species. While it is our opinion that the catalytically active species results from the formation of the diradical in eq 5, it is possible that the catalyst actually results from loss of CO or PPh_3 as the primary photoprocess. The similarity of the ratio of 2-pentenes from $Fe(CO)_5$ and $Fe_3(CO)_{12}$ is consistent with catalytic action only from mononuclear species. Infrared spectral studies show that, for all of the clusters studied here, mononuclear catalysts, or at least precursors to catalysts, must ultimately result upon prolonged visible light irradiation.

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Site Specificity in the Singlet Oxygen-Trisubstituted Olefin Reaction

Sir:

We report that the reaction of singlet oxygen with simple trisubstituted olefins shows a general preference for hydrogen abstraction on the more highly congested side of double bonds.

Many experimental aspects of the singlet oxygen reaction are well known.[1] Singlet oxygen is, for example, strongly electrophilic, showing a clear preference for highly substituted, electron-rich olefins;[2] the overall reaction occurs in the classical "ene" manner with invariable shift of the double bond;[3] and very low isotope effects are found variously reported from 1.05 to 1.96.[4] Despite this considerable body of data, no mechanistic rationalization is generally agreed upon. Concerted ene pathway[3,5] perepoxide intermediates,[2,6] diradicals,[7] and gradations in between all find experimental and theoretical support.

Studies of site specificity in the singlet oxygen ene reactions have received little attention. It is generally recognized that methyl and methylene hydrogens are reactive, and that isopropyl C-H and certain conformationally inaccessible hydrogen atoms are not.[3,8] Other more subtle features remain unexplored.

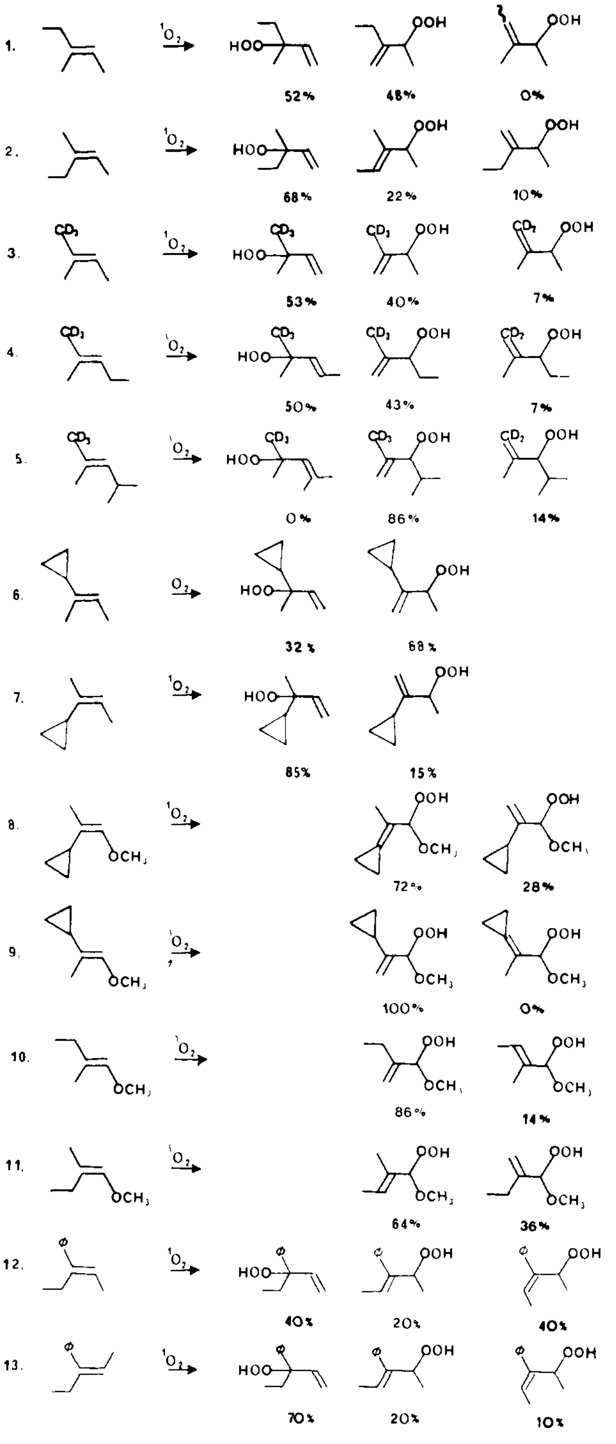
In this paper we report a general type of selectivity in the reactions of trisubstituted olefins. This selectivity does not appear to have been previously recognized and may hold important implications in the mechanism of the reaction.

In a series of trisubstituted olefins shown in Chart I, we find a strong preference for regiospecificity favoring hydrogen abstraction on that side of an olefin with two substituents. Olefins **1** and **2** clearly illustrate this point. The same trend is also noted in compounds **3**, **4**, and **5**, where reaction at the labeled site on the monosubstituted side is slight.[9] This heightened reactivity is demonstrated again in compound **6** and impressively so in **7**, even though one of the groups (cyclopropyl) is unreactive.

The presence of polar substituents does not alter this basic relationship (**8** and **9**, taken from Conia et al.[10] and **10** and **11** from this work). The fact that the cyclopropyl can be induced to react in **8** is probably a superposition of our effect and Goddard's anomeric effect explanation, recently published.[7]

This trend persists in reactions of styrene derivatives **12** and **13**, where reactivity of the methylene and methyl hydrogens is clearly dependent on their environment.

Chart I. Regioselectivity in the Reaction of Singlet Oxygen with Trisubstituted Olefins[a]



[a] The photooxidations were carried out at −10 °C, in acetone-d_6 with Rose Bengal as sensitizer. A Sylvania 275-W sun lamp was used for these experiments. Analyses were carried out by direct NMR examination of the hydroperoxide immediately after reaction. Reduction with dimethyl sulfide is then followed by NMR examination of the alcohol. Where appropriate the measurements were checked by gas chromatography. Entries 1 and 3 were also photooxidized in benzene-d_6 with tetraphenylporphyrin. Precisely identical results were obtained.

We cannot accommodate these results into a simple six-center concerted ene mechanism. Indeed, steric considerations in a concerted transition state would appear to favor results precisely opposite to ours. As shown below our results would require favoring the transition state (a) with pseudoaxial R

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