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PHOTOACTIVATION OF CLUSTER CATALYSIS: A COMPARISON OF 1-PENTENE--ETC(U)

NOV 78 J L GRAFF, R D SANNER, M S WRIGHTON

N00014-75-C-0880

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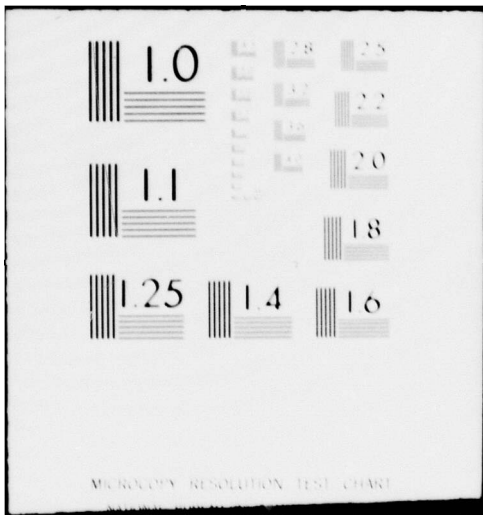
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4. TITLE (and Subtitle) Photoactivation of Cluster Catalysis: A Comparison of 1-Pentene Isomerization by Tetracarbonyl(tri-phenylphosphine)ruthenium and 1,1,1,2,2,2,3,3,3-Nonacarbonyl-1,2,3-tris(triphenylphosphine)-triangulo-triruthenium		5. TYPE OF REPORT & PERIOD COVERED Technical
7. AUTHOR(s) James L. Graff, Robert D. Sanner, and Mark S. Wrighton		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS Massachusetts Institute of Technology Cambridge, Massachusetts 02139 Mark S. Wrighton, Principal Investigator		8. CONTRACT OR GRANT NUMBER(s) N00014-75-C-0880
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Chemistry Program Office, Code 472 Arlington, Virginia 22217		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 051-579; This document has been approved for public release & sale; its distribution is unlimited
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE November 29, 1978
		13. NUMBER OF PAGES -9-
		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

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18. SUPPLEMENTARY NOTES

Prepared for publication in the Journal of the American Chemical Society

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

photocatalysis, cluster catalysis, olefin isomerization, ruthenium clusters, iron clusters

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The photocatalyzed isomerization of 1-pentene to trans- and cis-2-pentene by $Ru(CO)_4PPh_3$ and $Ru_3(CO)_9(PPh_3)_3$ is reported along with data for $Ru_3(CO)_{12}$, $Fe_3(CO)_{12}$, and $Fe(CO)_5$. The primary photoprocess in $Ru(CO)_4PPh_3$ is dissociative loss of CO giving a coordinatively unsaturated species having the same empirical formula as $Ru_3(CO)_9(PPh_3)_3$; the trinuclear species undergoes Ru-Ru bond rupture and ultimate declusterification subsequent to photo-excitation giving a quantitative yield of $Ru(CO)_4PPh_3$ under CO or

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$\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ in the presence of PPh_3 . The crucial result is that the cluster yields a different catalytically active species compared to $\text{Ru}(\text{CO})_4\text{PPh}_3$, since the initial ratio of trans- and cis-2-pentene is different for the two photocatalysts. The photocatalysis and primary photoprocesses suggest that the isomerization from the $\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3$ results from an active form of the cluster. By way of contrast, $\text{Fe}(\text{CO})_5$ and $\text{Fe}_3(\text{CO})_{12}$ yield the same initial ratio of photocatalytic products, implicating a common, mononuclear catalytic species. Since the clusters are good visible absorbers compared to the mononuclear species, photoactivation of cluster catalysis can be effected with low energy visible light, initial product ratios are independent of wavelength, but quantum yields for olefin isomerization are somewhat larger in the visible compared to near-uv excitation.

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⁹ TECHNICAL REPORT NO. 12

⁶ 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.

by

¹⁰ James L. Graff, Robert D. Sanner, and Mark S. Wrighton

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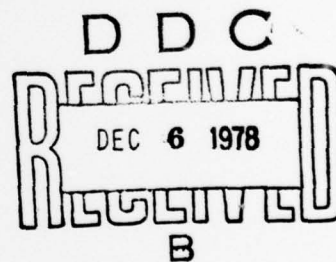
¹⁴ TR-12

¹² 14 p. Journal of the American Chemical Society

¹¹ 29 Nov 78

Massachusetts Institute of Technology
Department of Chemistry
Cambridge, MA

November 29, 1978



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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

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Abstract: The photocatalyzed isomerization of 1-pentene to trans- and cis-2-pentene by $\text{Ru}(\text{CO})_4\text{PPh}_3$ and $\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3$ is reported along with data for $\text{Ru}_3(\text{CO})_{12}$, $\text{Fe}_3(\text{CO})_{12}$, and $\text{Fe}(\text{CO})_5$. The primary photoprocess in $\text{Ru}(\text{CO})_4\text{PPh}_3$ is dissociative loss of CO giving a coordinatively unsaturated species having the same empirical formula as $\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3$; the trinuclear species undergoes Ru-Ru bond rupture and ultimate declusterification subsequent to photoexcitation giving a quantitative yield of $\text{Ru}(\text{CO})_4\text{PPh}_3$ under CO or $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ in the presence of PPh_3 . The crucial result is that the cluster yields a different catalytically active species compared to $\text{Ru}(\text{CO})_4\text{PPh}_3$, since the initial ratio of trans- and cis-2-pentene is different for the two photocatalysts. The photocatalysis and primary photoprocesses suggest that the isomerization from the $\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3$ results from an active form of the cluster. By way of contrast, $\text{Fe}(\text{CO})_5$ and $\text{Fe}_3(\text{CO})_{12}$ yield the same initial ratio of photocatalytic products, implicating a common, mononuclear catalytic species. Since the clusters are good visible absorbers compared to the mononuclear species, photoactivation of cluster catalysis can be effected with low energy visible light; initial product ratios are independent of wavelength, but quantum yields for olefin isomerization are somewhat larger in the visible compared to near-uv excitation.

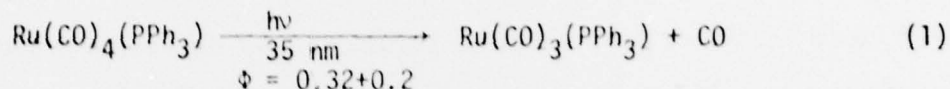
Photoactivation of Cluster Catalysis: A Comparison of 1-Pentene Isomerization by Tetracarbonyl(triphenylphosphine)ruthenium and 1,1,1,2,2,2,3,3,3-Nonacarbonyl-1,2,3-tris(triphenylphosphine)triangulo-triruthenium

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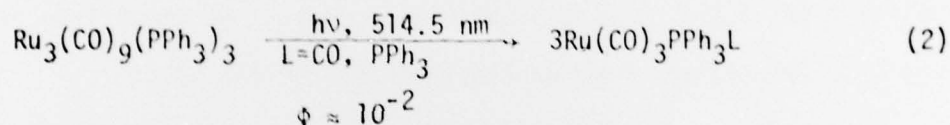
In this communication we wish to register two potential advantages of cluster precursors to photochemically generated catalysts. We wish to present preliminary results demonstrating that (1) lower energy irradiation can be used to activate catalysis by irradiation of a cluster compared to an appropriate mononuclear analogue and (2) that 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 $\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3$ and $\text{Ru}(\text{CO})_4(\text{PPh}_3)$.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 is included in Figure 1; $\text{Ru}(\text{CO})_4(\text{PPh}_3)$ is a pale yellow substance with only tail absorption wavelengths longer than 300 nm, while $\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3$ exhibits an intense visible absorption maximum at 506 nm ($\epsilon \sim 14,000$). The ultraviolet absorption of the C_{3v} $\text{Ru}(\text{CO})_4(\text{PPh}_3)$ 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 $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ ($\nu_{\text{CO}}=1895 \text{ cm}^{-1}$),³ and irradiation in the presence of 0.1M $\text{P}(\text{OMe})_3$ in benzene apparently yields $\text{Ru}(\text{CO})_3(\text{PPh}_3)(\text{P}(\text{OMe})_3)$ ($\nu_{\text{CO}}=1905 \text{ cm}^{-1}$) not $\text{Ru}(\text{CO})_4(\text{P}(\text{OMe})_3)$. These results allow the conclusion that

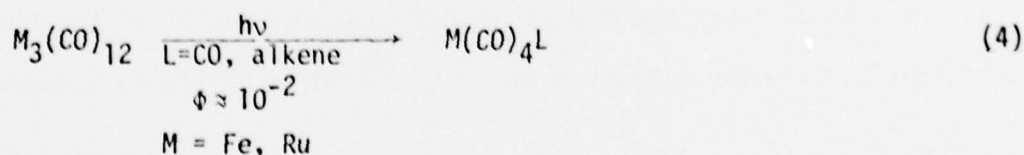
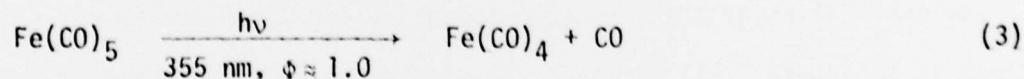
loss of CO is the principal result of near-uv irradiation of $\text{Ru}(\text{CO})_4(\text{PPh}_3)$, equation (1). When CO is purged from the solution, 1-pentene can scavenge



$\text{Ru}(\text{CO})_3(\text{PPh}_3)$ to yield a very substitution labile 1-pentene complex. But in hermetically sealed benzene solutions of 1.76M 1-pentene, $\text{Ru}(\text{CO})_4\text{PPh}_3$ undergoes little net reaction even at long irradiation times. Note that the coordinatively unsaturated species generated has the same empirical formula as $\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3$. This fact is an important feature of the system under study, since we find that visible irradiation of $\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3$ in the presence of L yields $\text{Ru}(\text{CO})_3\text{PPh}_3\text{L}$, equation (2). Based on this photochemistry and the low energy of the first

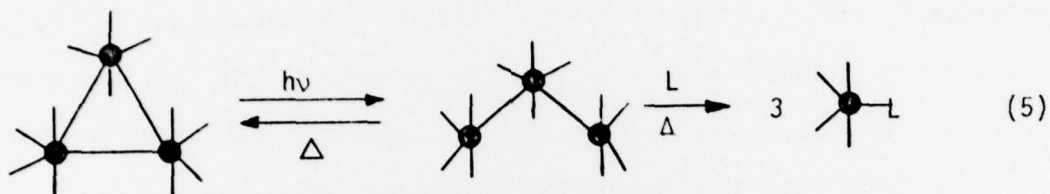


absorption feature, we attribute the lowest energy absorption band to a transition which involves the Ru orbitals and likely terminates in one which is strongly σ -antibonding with respect to the Ru-Ru bonds.^{1,4} In the presence of 1.76M 1-pentene, irradiation of $\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3$ in benzene solution only yields slow conversion to mononuclear complexes ($\phi < 10^{-4}$). We note that $\text{Fe}(\text{CO})_5$ and $\text{Fe}_3(\text{CO})_{12}$ are related to each other in the way that $\text{Ru}(\text{CO})_4(\text{PPh}_3)$ and $\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3$ are. The absorption spectra of $\text{Fe}(\text{CO})_5$ and $\text{M}_3(\text{CO})_{12}$ are included in Figure 1, and some of their photochemistry is given in reactions (3) and (4).^{1,56} From the quantum yields given in (1)-(4) it appears that



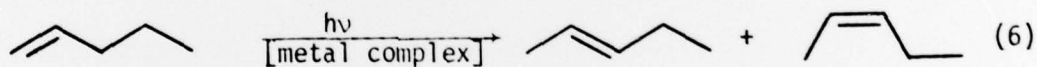
the clusters are qualitatively less efficiently decomposed than the mononuclear complexes. Further, for the irradiation of the Ru phosphine complexes in the

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, 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 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 the Table. All of the catalyst precursors are capable of moving high concentrations of 1-pentene toward the thermodynamic ratio⁷ 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 $\text{Ru}(\text{CO})_4(\text{PPh}_3)$ and $\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3$. 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 $\text{Ru}(\text{CO})_4\text{PPh}_3$ compel us to conclude that $\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3$ 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 equation (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 $\text{Fe}(\text{CO})_5$ and $\text{Fe}_3(\text{CO})_{12}$ 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.

Acknowledgements. We thank the Office of Naval Research for support of this research. MSW acknowledges support as a Dreyfus Teacher-Scholar Grant recipient, 1975-1980.

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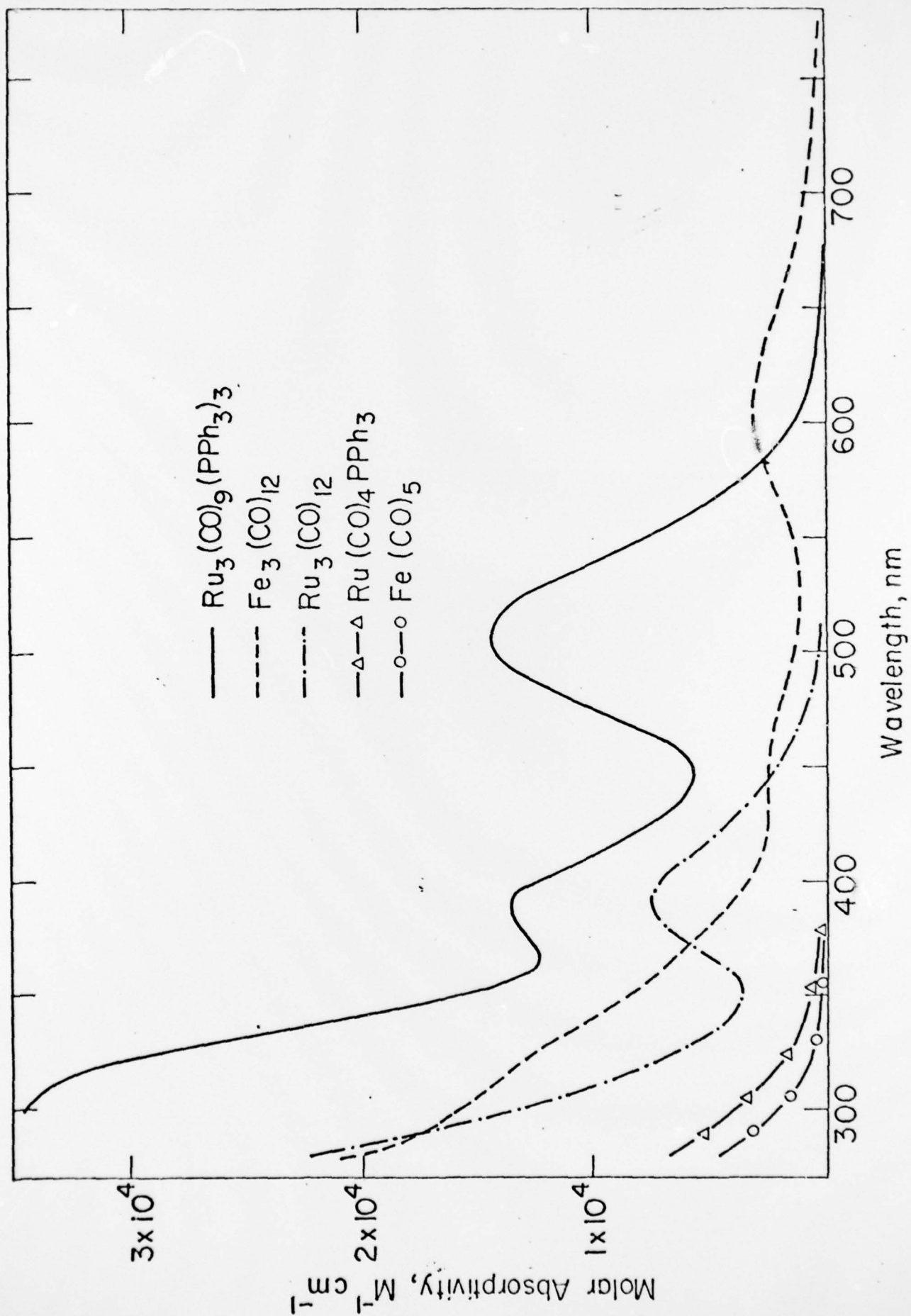
Table. Photocatalyzed 1-Pentene Isomerization.^a

Catalyst Precursor	Irrdn λ , nm	% Conv.	ϕ	(trans/cis)
Ru(CO) ₄ PPh 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

^aAll experiments carried out at 298°K in degassed, 1.76 M 1-pentene, benzene solution containing 1×10^{-3} M catalyst precursor. Quantum yields, ϕ , are $\pm 20\%$, and the ratio of trans- to cis-2-pentene products, (trans/cis), is $\pm 10\%$. 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 1×10^{-6} - 1×10^{-7} ein/min. All analyses were carried out using vapor phase chromatography and each entry represents the average of at least two analyses.

^bNote 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.

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



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