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Photoactivated Homogeneous Catalytic Hydrosilylation of Carbonyl Compounds

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The photocatalytic hydrosilylation of carbonyl compounds has been investigated. The catalytic species were generated by optical irradiation of homogeneous organometallic carbonyl compounds. It was found that photocatalysts which were effective for the hydrosilylation of terminal olefins were not necessarily active toward the model ketone substrates examined. Evidence for the photogeneration of thermal catalysts was also found. Differences in catalytic activity between different photogenerated catalysts have been exploited for the selective hydrosilylation of an aldehyde in the presence of a ketone.

INTRODUCTION

The photogeneration of thermal catalysts from homogeneous organometallic precursors has become a topic of current interest (*1–8*). For example, photoactivated catalytic polymerization (*9*), metathesis (*10*), hydrogenation, and hydrosilylation (*3, 11*) of olefins have been reported. In some cases, it has also been observed that "photocatalysis," where the reaction quantum yield is greater than unity, occurs. This latter point is important from a practical viewpoint because of the high cost of photons from artificial light sources such as mercury arc lamps or lasers.

The bulk of the photoactivated catalyzed reactions reported in the literature has been concerned with transformations of olefins. An exception was a preliminary report of Pittman and co-workers on the photocatalyzed hydrosilylation of acetophenone and cyclohexanone (*12*). This is of interest because of the importance of hydrosilylation of carbonyl compounds in organic synthesis (*13–17*). In this paper we describe our work on the photoactivated transition metal catalyzed hydrosilylation of carbonyl compounds.

EXPERIMENTAL

All organometallic compounds were obtained from Strem Chemical and were used without further purification. Acetone, heptanone, and butyraldehyde were purchased from Aldrich and distilled before use. Triethylsilane was purchased from Alfa, distilled, and stored over 3 Å molecular sieves.

The photoreactions were performed in the following manner: a pyrex tube equipped with a high vacuum stopcock (with a Teflon plug) was charged with 0.014 mol of carbonyl compound, 0.014 mol of triethylsilane, and 10^{-6} mol of catalyst. The reaction mixture was thoroughly degassed by four freeze-pump-thaw cycles. The evacuated tube was then irradiated in a Rayonet photoreactor equipped with RPR 3500 Å lamps ($\lambda = 350 \pm 20$ nm). The operating temperature of the photoreactor was measured to be 29°C. Under these conditions, only the organometallic catalyst absorbs light. After the photolysis, the tube contents were analyzed by gas chromatography. The light intensity at 365 nm for the quantum yield measurements was determined by benzophenone–benzhydrol acti-

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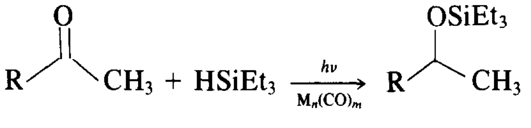
nometry. The 365-nm line was isolated by the use of Corning glass filters CS 0-52 and CS 7-60.

Samples for thermal reactions were prepared similarly and heated in a constant temperature oil bath.

RESULTS AND DISCUSSION

Table 1 shows the results of the photoreaction of acetone and 2-heptanone with triethylsilane in the presence of a transition metal carbonyl compound.



(1)

$R = CH_3, C_5H_{11}$
$M = Re, Ir, Os, Ru\ .\ .\ .$

Acetone is converted to the silyl ether in good yield only when the photoactivated catalyst precursor is a carbonyl compound of Re, Ir, Os, or Ru. $Ir_4(CO)_{12}$ and $Re_2(CO)_{10}$ are effective for hydrosilylating 2-heptanone. However, the catalysts derived from the Ru and Os clusters proved to be less effective in this case than for acetone hydrosilylation. Furthermore, $Mn_2(CO)_{10}$, which was reported to be an active photocatalyst for hydrosilylating acetophenone and cyclohexanone (*12*), is ineffective in hydrosilylation reactions of acetone and 2-heptanone. Apparently, the photoactivated catalytic hydrosilylation of ketones is very sensitive to the structure of the carbonyl substrate. Sensitivity to substrate structure has also been observed in the photocatalyzed hydrosilylation of olefins where only terminal olefins are reactive (*3*).

The data in Table 1 also show that $Fe_3(CO)_{12}$, $Co_2(CO)_8$, and $Co_4(CO)_{12}$ which are known to be effective photoactivated catalysts for the hydrosilylation of olefins are found to be relatively poor catalysts for catalyzed photohydrosilylation of acetone. Also, while the photocatalyzed hydrosilylation of olefins results in a high yield of fully reduced product (*3*), only trace amounts of 2-propanol or 2-heptanol are detected in reaction (1).

Thermal reactions were performed in the dark at 29 and 80°C. As shown in Table 2, only a small amount of reaction occurred at 29°C which is the operating temperature of the photochemical reactor. Optical excitation, therefore, is a crucial component of these reactions. However, more reaction to the silyl ether is observed at 80°C. $Fe_3(CO)_{12}$ which is a poor photocatalyst (5% yield) improved somewhat when thermally activated. The only effective photocatalysts which exhibited thermal activa-

TABLE 1

Photoactivated Catalyzed Hydrosilylation of Acetone and 2-Heptanone

Catalyst	% Yield[a,b]	
	Acetone	2-Heptanone
$Re_2(CO)_{10}$	89	86
$Os_3(CO)_{12}$	83	15
$Ru_3(CO)_{12}$	87	14
$Ir_4(CO)_{12}$	86	85
$Fe_3(CO)_{12}$	5	Trace
$Co_2(CO)_8$	25	
$Co_4(CO)_{12}$	30	
$Cr(CO)_6$	25	
$Mo(CO)_6$	1	
$Mn_2(CO)_{10}$	5	
$W(CO)_6$	5	

[a] Yields were determined by quantitative gas chromatography with toluene as the internal standard. The percentage yield is an average of three runs.

[b] Reaction time = 20 hr.

TABLE 2

Catalytic Hydrosilylation of Acetone

Catalyst	T (°C)	Time (hr)	% Yield[a]
$Re_2(CO)_{10}$	29	20	<1
$Re_2(CO)_{10}$	80	20	10
$Ru_3(CO)_{12}$	29	20	<1
$Ru_3(CO)_{12}$	80	20	100
$Fe_3(CO)_{12}$	29	20	<1
$Fe_3(CO)_{12}$	80	20	34
$Co_4(CO)_{12}$	29	20	<1
$Co_4(CO)_{12}$	80	20	3
$Ir_4(CO)_{12}$	29	20	<1
$Ir_4(CO)_{12}$	80	20	6
$Os_3(CO)_{12}$	29	20	<1
$Os_3(CO)_{12}$	80	20	76

[a] Based on consumption of $HSiEt_3$.

TABLE 3

Quantum Yields of Product Formation for the Photocatalytic Hydrosilylation of Acetone

Catalyst	Φ[a]
$Re_2(CO)_{10}$	6.1
$Os_3(CO)_{12}$	3.3
$Ru_3(CO)_{12}$	1.1

[a] Φ = mole product produced/mole photons; $I = 1.98 \times 10^{-6}$ einsteins/min; λ = 365 nm; average of three runs.

tion at 80°C were $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$. The ruthenium cluster has also been reported to be a thermal catalyst for the synthesis of vinylsilanes from olefins and hydrosilanes (*17*).

As mentioned earlier, a good indication of photocatalysis as opposed to mere photoassistance is a quantum yield of reaction greater than unity. In other words, each photon absorbed by the catalyst or catalyst precursor should result in the production of more than one product molecule. Quantum yields for three "photocatalysts" are shown in Table 3. The order of quantum efficiency is found to be $Re_2(CO)_{10} > Os_3(CO)_{12} > Ru_3(CO)_{12}$.

The catalytic utilization of photons is clearly happening for the cases of $Re_2(CO)_{10}$ and $Os_3(CO)_{12}$. An interesting point is that, in contrast to the data in Table 3, the quantum efficiency for the photohydrosilylation of 1-hexene is $Ru_3(CO)_{12} > Os_3(CO)_{12}$ (*3*).

One cause of a reaction quantum yield greater than unity is the photogeneration of a thermal catalyst. That is, an appreciable dark reaction subsequent to a short irradiation time would be observed. The evidence in the literature for such an occurrence is contradictory. For example, photocatalysis has been claimed for the isomerization and hydrosilylation of terminal olefins by photolysis of $Cr(CO)_6$, $Fe(CO)_5$, and the iron group trinuclear dodecacarbonyl cluster compounds (*3, 5, 6*). However, data were presented only in one case for a dark reaction after optical activation. Later work indicated that the lifetimes of these catalysts were on the order of 7 to 28 sec (*18, 19*). Despite this short lifetime after excitation, very large quantum yields and turnover numbers were obtained (*18*). Appreciable dark reactions, however, have been observed by other workers (*7, 12*).

We have seen that, in some cases, sub-

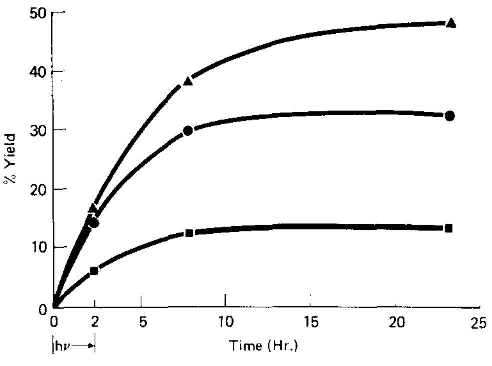
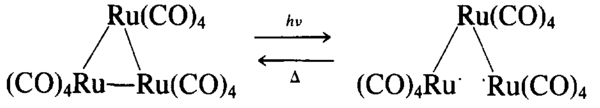


Figure 1

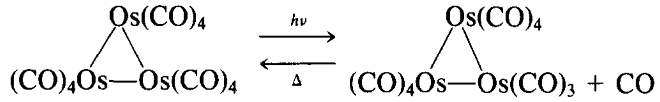
FIG. 1. Photogeneration of thermal catalysts for the hydrosilylation of acetone. The excitation source is turned off after 2 hr and the subsequent reaction occurs in the dark: $Re_2(CO)_{10}$, ▲; $Os_3(CO)_{12}$, ●; $Ru_3(CO)_{12}$, ■.

stantial dark reactions subsequent to irradiation occur. Figure 1 shows that after 2 hr of irradiation, the reaction continued when the excitation source is turned off. The most active catalytic species is that derived from $Re_2(CO)_{10}$ which showed some activity even after 10 hours in the dark. The order of catalytic activity $Re_2(CO)_{10} > Os_3(CO)_{12} > Ru_3(CO)_{12}$ may be a partial reflection of the greater quantum yield of decomposition of $Re_2(CO)_{10}$ ($\Phi = 0.6$) relative to the cluster compounds ($\Phi = 0.03$) (*1, 3*).

A comparison of $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ is interesting because a clue to their different catalytic activities may be found by examining their primary photophysical reactions. Gray and co-workers (*20*) have reported that fragmentation via metal–metal bond cleavage is a principal pathway for $Ru_3(CO)_{12}$ but not for $Os_3(CO)_{12}$ where Os–CO dissociation is favored.



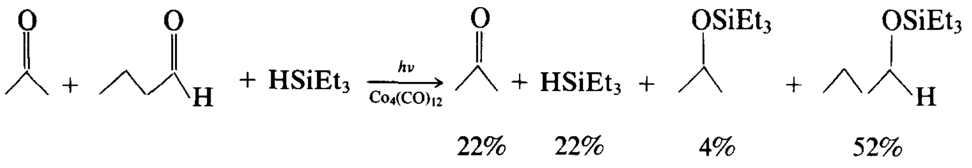
(2)



(3)

It can be speculated, therefore, that the relative activities of the photogenerated thermal catalyst in these two cases may be a reflection of the catalytic abilities of a ruthenium diradical complex and an osmium cluster containing a 16 electron center. Differences in the nature and rate of declusterification to other catalytic species cannot, of course, be ruled out.

So far, we have only considered photocatalytic reactions of ketones. The results for *n*-butyraldehyde are shown in Table 4. The most striking aspect of the data is that catalyst precursors which are ineffective for hydrosilylating acetone are active for *n*-butyraldehyde, e.g., $Co_4(CO)_{12}$. Furthermore, *n*-butyraldehyde can be hydrosilylated selectively in the presence of acetone when $Co_4(CO)_{12}$ is the catalyst precursor. However, a good catalyst for acetone photocatalyzed hydrosilylation, $Ir_4(CO)_{12}$, is practically inactive in the presence of the aldehyde (<4% overall yield). The normalized gas chromatographic data for $Co_4(CO)_{12}$ photoactivated catalysis is shown below. (The mole ratio of acetone : butyraldehyde : triethylsilane is 1 : 1 : 2):



Further work is needed to determine the scope and utility of this reaction.

CONCLUSION

Photocatalysts which are effective for the hydrosilylation of terminal olefins are not necessarily active toward carbonyl compounds. Catalytic activity was found to be very sensitive to the nature of the substrate. The structure of the catalyst derived

TABLE 4

Photoactivated Catalyzed Hydrosilylation of *n*-Butyraldehyde[a]

Catalyst	% Yield[b]
$Ir_4(CO)_{12}$	7
$Re_2(CO)_{10}$	53
$Co_4(CO)_{12}$	90
$Cr(CO)_6$	9
$Fe_3(CO)_{12}$	8
$Co_2(CO)_6(PPh_3)_2$	87

[a] Reaction time = 20 hr.

[b] Based on consumption of $HSiEt_3$; average of three runs.

by optical irradiation of transition metal carbonyl compounds is not known but it is clear that the effect of irradiation is to generate a thermal catalyst.

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REFERENCES

1. Geoffroy, G. L., and Wrighton, M. S., "Organometallic Photochemistry." Academic Press, New York, 1979.
2. Wrighton, M. S., Ginley, D. S., Schroeder, M. A., and Morse, D. L., *Pure Appl. Chem.* **41,** 671 (1975).
3. Austin, R. G., Paonessa, R. S., Giordano, P. J., and Wrighton, M. S., *Adv. Chem. Ser.* **168,** 189 (1978).
4. Asinger, F. Y., Fell, B., and Schrage, K., *Chem. Ber.* **98,** 372 (1965).
5. Schroeder, M. A., and Wrighton, M. S., *J. Organometal. Chem.* **128,** 345 (1977).
6. Wrighton, M. S., and Schroeder, M. A., *J. Amer. Chem. Soc.* **96,** 6235 (1974).
7. Faltynek, R. A., *Inorg. Chem.* **20,** 1357 (1981).
8. Peterson, J. R., Bennett, D. W., and Spicer, L. D., *J. Catal.* **71,** 223 (1981).
9. Ballard, D. G. H., and Lienden, P. W. V., *Makromol. Chem.* **154,** 177 (1972).
10. Agapiou A., and McNalis, E., *J. Amer. Chem. Soc.* **97,** 437 (1975).
11. Graff, J. L., Sanner, R. D., and Wrighton, M. S., *J. Amer. Chem. Soc.* **101,** 273 (1979).
12. Pittman, C. U., Absi-Halabi, M., and Trielking, B., *ACS Nat. Meeting Abstr.* **181** (1981).
13. Ojima, I., and Kogure, T., *Tetrahedron Lett.* 5085 (1972).
14. Hayashi, T., Yamamoto, K., and Kumada, M., *Tetrahedron Lett.* 3 (1975).
15. Ojima, I., Kogure, T., and Kumagai, M., *J. Org. Chem.* **42,** 1671 (1977).
16. Murai, S., and Sonoda, N., *Angew. Chem. Int. Ed. Engl.* **18,** 837 (1979).
17. Seki, Y., Takeshita, K., Kawamoto, K., Murai, S., and Sonoda, N., *Angew. Chem. Int. Ed. Engl.* **19,** 928 (1980).
18. Mitchener, J. C., and Wrighton, M. S., *J. Amer. Chem. Soc.* **103,** 975 (1981).
19. Chase, D. B., and Weigert, F. J., *J. Amer. Chem. Soc.* **103,** 977 (1981).
20. Tyler, D. R., Altobelli, M., and Gray, H. B., *J. Amer. Chem. Soc.* **102,** 3022 (1980).