Preliminary communication

HYDROSILATION CATALYSIS VIA SILYLMANGANESE CARBONYL COMPLEXES: THERMAL vs. PHOTOCHEMICAL ACTIVATION

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Summary

Thermal and photochemical activation of $Ph_3SiMn(CO)_5$ leads to different catalyst systems, both of which promote the addition of organosilicon hydrides to terminal alkenes. In the thermal case, major catalytic activity is due to triphenylsilyl radicals generated from Si—Mn bond homolysis. Upon photolysis, however, there is no evidence of Si—Mn homolysis during catalyst activation. These studies represent the first well-defined example of disparate behavior upon photochemical vs. thermal activation of the same catalyst precursor.

In the course of our studies on transition metal promoted hydrosilation, we have examined the catalytic activity of complexes containing Group IVA—manganese bonds toward substrate mixtures of alkenes and organosilicon hydrides. Thermolysis and photolysis of silylpentacarbonylmanganese(I) catalyst precursors with these reagents lead to very different product mixtures, implying that disparate catalytic species are generated via two types of stimulus upon the same molecule. We communicate here our preliminary data that suggest a radical mechanism for thermal hydrosilation and a coordination mechanism for photoinduced hydrosilation employing triphenylsilylpentacarbonylmanganese(I) as the soluble metal catalyst. These observations provide the first evidence for a premise often enunciated in the organometallic photochemical literature: the fact that photogenerated catalysts are milder and more selective than their thermally generated counterparts [1].

Metallic catalyst precursors used in these studies include triphenylsilylpentacarbonylmanganese(I) [2,5,6] triphenylstannylpentacarbonylmanganese(I) [3,5,6] and an immobilized silylpentacarbonylmanganese(I) species formed by treatment of trichlorosilylpentacarbonylmanganese(I) [4,5] with Cab-O-Sil fumed silica in THF/H₂O solvent. Hydrosilation substrates are pentene-1 and

heptamethylcyclotetrasiloxane. The latter cyclic, monohydridic siloxane is abbreviated as HMCTS or D_4H in subsequent text and formulae [7].

Incorporation of 0.1 mol % of the triphenylsilyl complex into equimolar mixtures of HMCTS and pentene-1 followed by heating at 180°C in sealed, evacuated ampoules forms the products shown in eq. 1, while irradiation of identical samples at 3500 Å in a Rayonet Photochemical Reactor yields only the saturated adduct [9] and carbon monoxide (eq. 2).
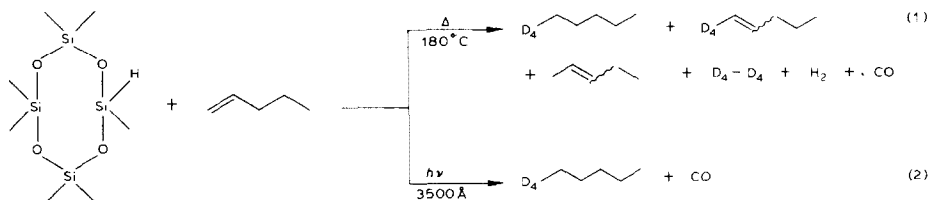
On complete disappearance of HMCTS in the thermal reaction, the product distribution is typically 55% alkylsiloxane, 25% alkenylsiloxanes, and 20% silicon—silicon bonded material. Approximately 10% of the remaining pentene-1 is converted to *cis*-(7%) and *trans*-pentene-2(3%). Turnover number defined as mol HMCTS lost per mol manganese are 10^2—10^3, while the average turnover rate defined as mol HMCTS lost per mol manganese per minute during complete HMCTS consumption is 2.0. For the photochemical reaction, quantum yield defined as mol HMCTS lost per mol photons is 1.6 [10]. The observed catalysis is photoassisted since all activity ceases in the dark subsequent to irradiation [11]. All products in eq. 1 and 2 are unambiguously identifiable by GLC/MS [12] or low resolution mass spectroscopic analysis [13].

Catalytic production of hydrogen and D_4—D_4 (eq. 1) suggests that radical species result from precatalyst decomposition at 180°C, and that these species take part in hydrosilation. Other observations supporting this hypothesis are given below:

(A) Thermal hydrosilation (HMCTS + pentene-1) catalyzed by triphenylsilylpentacarbonylmanganese(I) is slowed by a factor of four in the presence of di-t-butyl nitroxide (3 mol R_2NO per mol Mn), and no discernible hydrogen or D_4—D_4 is produced.

(B) Bis(triphenylsilyl)mercury [14], an alternative source of $[Ph_3Si\cdot]$ [15], promotes hydrosilation as effectively as triphenylsilylpentacarbonylmanganese(I) at 180—200°C. Product mixtures contain alkylsiloxane (ca. 90%) and D_4—D_4 (10%) at 40% conversion.

(C) Triphenylstannylpentacarbonylmanganese(I) is a poor catalyst for HMCTS + pentene-1 hydrosilation at 180°C (turnover 0.05% of that observed in silylmanganese catalysis). Since $[Ph_3Sn\cdot]$ is less likely than $[Ph_3Si\cdot]$ to abstract hydrogen from HMCTS [16], catalysis is predicted to be less efficient in the stannylmanganese system.

(D) Immobilized Si—Mn(CO)$_5$ material forms dimanganese decacarbonyl when heated, neat, in vacuo at 180°C.

Observation (B) suggests that interaction of $[Ph_3Si^{\cdot}]$ and alkylsiloxane may be responsible for D_4—D_4 and alkenylsiloxane production [19], and that $[\cdot Mn(CO)_5]$ or $[\cdot Mn(CO)_4]$ may promote alkene isomerization (eq. 1).

Preliminary experiments have shown that neither of these premises is valid. Reaction of the saturated HMCTS-pentene adduct and $Ph_3SiMn(CO)_5$ (mol ratio 100/1) at 180°C forms polymeric organosiloxanes carrying unaltered, saturated, pentyl side chains [20]. Decacarbonyldimanganese(0) fails to isomerize pentene-1 at 180°C, a temperature at which [·$Mn(CO)_x$] should be present [21,22]. It is apparent, therefore, that radical chemistry alone cannot account for all of the eq. 1 products.

By comparison, photoassisted hydrosilation proceeds chiefly via a coordination mechanism as proposed by Chalk and Harrod for platinum- and cobalt-catalyzed thermal reactions [23,24]. Irradiation of the immobilized Si—$Mn(CO)_5$ catalyst and excess triphenylphosphine in cyclohexane fails to produce bis(triphenylphosphino)octacarbonyldimanganese(0) or any other soluble metallic species [25,27]. Photoassisted hydrosilation is not inhibited by di-t-butyl nitroxide. These observations strongly support maintenance of the Si—Mn bond in the active photoassistance agent.

We have shown that triphenylsilylpentacarbonylmanganese(I) can act as a hydrosilation catalyst via two different mechanisms. Photochemical activation provides a milder, more selective catalyst than the silyl radical and other species generated thermally. Work is in progress toward characterizing all products resulting from precatalyst thermolysis, and the active photoassistance agent in eq. 2. Of longer range interest is the generality and viability of radical-induced hydrosilation. Except for a recent report by Jackson et al. [28] the literature suggests that only halide-substituted organosilicon hydrides can efficiently hydrosilate alkenes in the presence of radical initiators. These questions as well as the overall importance of dual or multiple activation mechanisms for transition metal catalysts are under study, and will be elaborated in due course.

References and notes

1   M.S. Wrighton, D.S. Ginley, M.A. Schroeder and D.L. Morse, Pure Appl. Chem., 41 (1975) 671.
2   W. Jetz, P.B. Simons, J.A.J. Thompson and W.A.G. Graham, Inorg. Chem., 5 (1966) 2217.
3   R.D. Gorsich, J. Am. Chem. Soc., 85 (1962) 2486.
4   W. Jetz and W.A.G. Graham, J. Am. Chem. Soc., 89 (1967) 2773.
5   In CH_2Cl_2 solution: $Ph_3SiMn(CO)_5$ 2098(w), 1998(vs) cm^{-1}; $Ph_3SnMn(CO)_5$ 2096(m), 1999(vs) cm^{-1}; $Cl_3SiMn(CO)_5$ 2124(w), 2043(sh), 2035(vs), 2010(s) cm^{-1}.
6   In CH_2Cl_2 solution: mol. wt. $Ph_3SiMn(CO)_5$ 454, calc. 454 amu; $Ph_3SnMn(CO)_5$ 542, calc. 542 amu.
7   An 8-membered ring of alternating $SiMe_2$ and O groups is represented as D_4 in organosilicon shorthand nomenclature. D_4 defines 4 difunctional methylsilicone units in a ring. D_4H represents the same ring structure with seven methyls and one hydrogen. See eq. 1 and ref. 8.
8   M.D. Curtis and P.S. Epstein, Advan. Organomet. Chem., 19 (1981) 213.
9   Yield is quantitative based on HMCTS disappearance.
10   Photon flux by ferrioxalate actinometry = 1.2×10^{-5} einstein/min.
11   R.A. Faltynek, Inorg. Chem., 20 (1981) 1357.
12   Mass spectra of liquid compounds obtained via electron impact or chemical ionization measurements.
13   Mass spectra of gaseous products obtained via low resolution electron impact measurements.
14   R.A. Jackson, Chem. Comm., (1966) 827.
15   Unlike alkylsilylmercury complexes, triphenylsilylmercury generates silyl radicals on thermolysis. See ref. 14.
16   Dissociation energies for Me_3E—H: Sn—H 70 kcal/mol = 293 kJ/mol [17]; Si—H 90 kcal/mol = 377 kJ/mol [18].

17 R.A. Jackson, The Chemical Society (London). Special Publication No. 24, 1970, p. 295.
18 R. Walsh, Acc. Chem. Res., 14 (1981) 246.
19 We thank a referee for raising this question.
20 Field desorption mass spectroscopy suggests that D_4 units are linked through $H_2C\cdot + \cdot CH_2$ coupling in the polymers.
21 N.J. Coville, A.M. Stolzenberg, and E.L. Muetterties, J. Am. Chem. Soc., 105 (1983) 2499.
22 Isomerization catalysis is the only possible test for manganese activity. Inclusion of organosilicon hydride under these conditions leads to $R_3SiMn(CO)_5$.
23 A.J. Chalk and J.F. Harrod, J. Am. Chem. Soc., 87 (1965) 16.
24 A.J. Chalk and J.F. Harrod, J. Am. Chem. Soc., 89 (1967) 1640.
25 Triphenylphosphine is necessary in this experiment to form insoluble $Mn_2(CO)_8(PPh_3)_2$ [26]. If formed, $Mn_2(CO)_{10}$ in solution will not survive secondary photoreactions prior to detection.
26 A.G. Osborne and M.H.B. Stiddard, J. Chem. Soc., (1964) 634.
27 It is likely that immobilized $Si-Mn(CO)_4PPh_3$ centers form during photolysis. Characterization is in progress.
28 N.M.K. El-Durini and R.A. Jackson, J. Organomet. Chem., 232 (1982) 117.