

Poly(siloxane)-supported decacarbonyldimanganese(0) catalyst for terminal olefin hydrosilylation reactions: the effect of the support on the catalyst selectivity, activity and stability

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Abstract

A new class of supported carbonyl manganese catalyst was prepared by treating the dimeric decacarbonyldimanganese(0), $\text{Mn}_2(\text{CO})_{10}$, with insoluble aminated poly(siloxane) surface. Solid state FT-IR spectra indicated that the supported catalyst is a dimeric complex that is substituted with two amine ligands, one at each Mn atom. The supported manganese complex was investigated as catalyst for the hydrosilylation reaction of terminal olefins. Contrary to the homogeneous $\text{Mn}_2(\text{CO})_{10}$ catalytic system, the supported manganese complex was completely selective toward the hydrosilylation reaction with no detectable olefin isomerization or other side-reaction products. Furthermore, the catalyst was selective to produce the linear hydrosilylation product rather than the branched one. No lowering in catalyst activity due to the support was observed. A good proportion of the catalyst activity after separation and reuse was retained for at least four times. Highly reproducible catalytic activity measurements were obtained with catalytic samples taken from same prepared batch. Different prepared batches showed lower reproducibility. The effect of different reaction parameters, such as the solvent effect, the temperature effect, the concentration effect and the added-ligand effect have also been studied. Laine's kinetic studies indicated that the cluster remained intact during the reaction. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Interest in silica [1–3], alumina [1,2], polystyrene [4–8], and other solid-supported organometallic catalysts has been one of the focal areas to organometallic chemists since mid 1970s. It is assumed that supported organometallic catalysts combine the advantages of

both homogeneous and heterogeneous catalysts. Among the advantages of using supported catalysis are: the ease of catalyst recovery, the ease of handling the supported catalyst, and the ease of chemical modification of the active sites [9]. The accessibility of the catalyst active sites to reactant molecules makes the supported catalysts more active compared to other heterogeneous ones. Supported mononuclear and cluster catalysts are known [10–12]. Different classes of supported catalysts have been described for

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several organic and organometallic reactions. Examples are hydroformylation [12], hydrogenation [13–17], *O*-silylation [18,19], isomerization [11,20,21] and other reactions [22–26] of unsaturated organic systems.

Olefin hydrosilylation reactions are known to occur with the aid of homogeneous and supported catalysts [27,28]. These reactions are conventionally known to be accompanied by other side reactions, such as olefin isomerization [28–33]. The development of catalysts with higher activity and selectivity toward hydrosilylation is undoubtedly needed. Researchers have always been active in developing new selective catalyst systems for hydrosilylation reactions. In many cases more expensive catalysts have been employed for this purpose [29–33]. In these laboratories, work is underway to develop highly active and selective homogeneous and supported catalytic systems for different classes of reactions. We have reported on the use of modified poly(siloxane) surfaces as support for different classes of organometallic complex catalysts [29–38]. Terminal olefin hydrosilylation is one of our areas of interest. In this study, the dimeric decacarbonyldimanganese(0) complex, $\text{Mn}_2(\text{CO})_{10}$, was chemically anchored to the insoluble aminated poly(siloxane) matrix via the anchoring ligand $(\text{C}_2\text{H}_5\text{O})_3\text{Si}(\text{CH}_2)_3\text{NH}_2$. The influence of the support on the stability, activity and selectivity of the supported manganese dimer in the hydrosilylation reaction was the core target of this work.

2. Experimental

Chemicals and solvents were purchased from either Aldrich or Merck in the purest possible forms. The solvents were further purified and dried according to standard procedures [39].

The infrared spectra were measured on a Pye-Unicam SP200 IR spectrophotometer and/or a Shimadzu 8021 PC FT-IR spectrophotometer. Solid samples, such as the supported catalyst, were measured as KBr discs.

Liquid samples were measured as thin films between NaCl discs. Electronic absorption spectra were measured on a Pye-Unicam SP8-100 UV/Visible double beam spectrophotometer in quartz cuvettes.

2.1. Preparation of the solid support

The aminated solid surface was prepared as described earlier by Khatib and Parish [40]. Tetraethylorthosilicate, $(\text{C}_2\text{H}_5\text{O})_4\text{Si}$, (20.0 g, 0.096 mol) and distilled H_2O (4.75 g, 0.26 mol) were stirred together while cooling with ice for a few minutes. The amine anchoring ligand $(\text{C}_2\text{H}_5\text{O})_3\text{Si}(\text{CH}_2)_3\text{NH}_2$ (10.60 g, 0.048 mol) was added to the stirred mixture. Within a few minutes a white solid appeared, which was crushed and oven dried overnight. The solid was then ground and sieved, with the range 40–100 mesh taken for use as support.

2.2. Preparation of the supported manganese catalyst (I)

A 250 ml round-bottomed flask, equipped with a refluxing condenser, was charged with a known amount of $\text{Mn}_2(\text{CO})_{10}$, the aminated solid support and dioxane solvent. The mixture was flushed out with nitrogen, stirred and refluxed using a boiling water bath ($\sim 100^\circ\text{C}$). Two different batches have been prepared. The amount of each added substance in the preparation procedure is shown in Table 1. The treated solid was filtered while hot and washed with dioxane several times and dried at room temperature overnight. Precautions were taken to avoid exposure of the solid to air while filtering and

Table 1
Conditions for preparing supported Mn catalyst

Batch no.	Amount of $\text{Mn}_2(\text{CO})_{10}$ (g)	Amount of solid support (g)	Volume of dioxane (ml)	Mn-uptake % $\text{Mn}_2(\text{CO})_{10}$ (w/w)
1	0.60	6.00	70	10.0
2	0.40	4.00	47	10.0

Time of reflux 7.0 h.

washing, and inert nitrogen atmosphere was used for the preparation experiments. To calculate the amount of supported Mn complex, the amount of $\text{Mn}_2(\text{CO})_{10}$ remaining in the filtrate, which was measured spectrophotometrically, was subtracted from the added amount. Special calibration curves were made for these purposes. Batches of the supported catalyst **I** were qualitatively analyzed using FT-IR in the form of solid KBr discs.

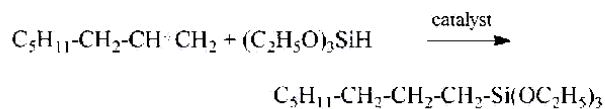
2.3. The catalytic experiments

All catalytic experiments were conducted in a 50 ml three-necked round-bottomed flask equipped with subaseal stoppers, a refluxing condenser, a thermostated bath and a magnetic stirrer.

In a typical experiment, the stirred thermostated reactor was charged with the catalyst, the solvent (enough to make total volume 10.0 ml), benzene (5.0 ml, as an internal reference standard), other added ligands, the olefin and the silane. The reaction was monitored by syringing out small aliquots after specified time intervals. Each aliquot was immediately chilled in a stoppered capillary tube, and quantitatively analyzed by IR spectrophotometry. Specially made calibration curves were used for this purpose. The kinetics of the hydrosilylation reaction were followed by monitoring the decay of the IR band at 2210 cm^{-1} characteristic for the Si–H bond in the silane reactant $(\text{C}_2\text{H}_5)_3\text{SiH}$, relative to the absorbance of benzene reference at 1860 cm^{-1} , with time. The reaction mixture was analyzed for other possible side reaction products such as isomerization, dehydrogenative-silylation, and other reactions, vide the results section.

3. Results

The poly(siloxane)-supported manganese catalyst, **I**, was employed as a catalyst for the



Scheme 1.

hydrosilylation reaction of 1-octene as shown in Scheme 1.

Addition of triethoxysilane $(\text{C}_2\text{H}_5\text{O})_3\text{SiH}$ to a stirred thermostated catalytic mixture of 1-octene, supported catalyst **I** and solvent, yielded the hydrosilylation reaction product, octyltriethoxysilane, shown in Scheme 1. This was manifested by IR spectral analysis of the reaction products. Fingerprint analysis of the reaction product with literature IR data [41,42] confirmed the occurrence of the hydrosilylation product. The intensity of the band at 1250 cm^{-1} , characteristic for the Si–C bond in the hydrosilylation product, was increasing progressively with time relative to the reference absorbance at 1860 cm^{-1} . At the same time the IR absorption band of $(\text{C}_2\text{H}_5\text{O})_3\text{SiH}$ at 2210 cm^{-1} , characteristic for the Si–H bond, decayed with time relative to the reference band. Within the working reaction temperature range ($40\text{--}70^\circ\text{C}$), no detectable olefin isomerization products were observed. No internal *cis*- or *trans*-olefin species were detected. Unlike the conventional homogeneous catalytic system, no bands at 960 cm^{-1} (characteristic for the *trans*-olefins) were observed throughout the course of the reaction. No dehydrogenative-silylation reaction products of the type $\text{R-CH}_2\text{=CHSi}(\text{C}_2\text{H}_5\text{O})_3$ with the characteristic band at 1400 cm^{-1} were detected. No hydrogen gas evolution was observed. No reaction between the silane and the supported amine ligand was detected.

Control experiments were conducted to decide what the actual catalyst was. In the absence of the supported catalyst **I** no reaction was detected. The naked poly(siloxane) surface did not catalyze the hydrosilylation reaction either. Therefore, under the described working conditions, the reaction was catalyzed exclusively by the supported catalyst **I**.

The rate of increase in the intensity of the product band at 1250 cm^{-1} was consistent with the rate of decay of the silane band at 2210 cm^{-1} and of the 1-octene band at 1650 cm^{-1} . Therefore, the reaction profiles were measured by following the disappearance of the band at 1250 cm^{-1} characteristic for the Si–H bond, and the extent of the hydrosilylation reaction was calculated based on the amount of the consumed $(\text{C}_2\text{H}_5\text{O})_3\text{SiH}$ as a limiting reactant. A typical presentation of the hydrosilylation reaction progress with time is shown in Fig. 1.

The hydrosilylation reaction was conducted under a variety of reaction conditions. The effects of temperature, solvent, reactant concentrations and catalyst amounts, on the rate of the hydrosilylation reaction, were investigated, together with catalyst recovery and reproducibility.

3.1. Temperature effect on the rate of hydrosilylation reaction

The reaction of 1-octene (1.0 M) with the triethoxysilane (0.5 M) catalyzed by **I** (0.01 M of Mn_2 in the total reaction mixture) in benzene

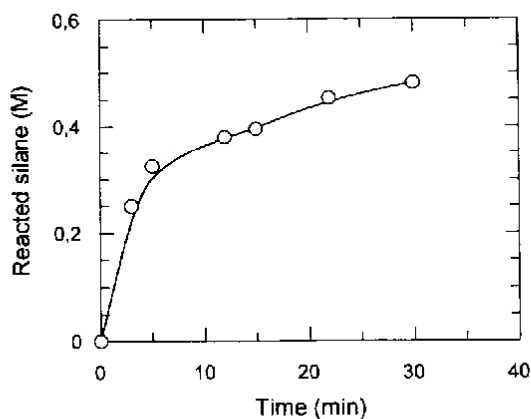


Fig. 1. Reaction profiles showing the consumption of the tertiary silane $(\text{EtO})_3\text{SiH}$ (initial concentration 0.5 M) with time during the hydrosilylation reaction of 1-octene (initial concentration 1.0 M). The reaction was conducted in dioxane (2.5 ml) and benzene (5.0 ml) at 70°C using a fresh sample of catalyst **I** (0.01 M concentration for the Mn dimer) taken from batch (II).

Table 2

The effect of temperature on the rate of the hydrosilylation reaction^a of 1-octene

Entry No.	T ($^\circ\text{C}$)	Value of TN with time			
		5 min	10 min	15 min	20 min
1	70	38	42	47	49 ^b
2	60	19	24	25	27
3	50	12	21	24	25
4	40	5	6	7	9

^aAll reactions were conducted in dioxane (2.5 ml), using $(\text{C}_2\text{H}_5\text{O})_3\text{SiH}$ (0.923 ml, 0.5 M) and supported catalyst **I** from batch 1 (0.3889 g, equivalent to 0.0389 g of $\text{Mn}_2(\text{CO})_{12}$, 0.01 M) and 1-octene (1.56 ml, 1.0 M).

^bReaction completion with 100% yield reached.

(5.0 ml) and dioxane (enough to make total reaction mixture 10 ml) was conducted at different temperatures. The reaction was clearly faster at higher temperatures. At 70°C turnover numbers (TN) up to 50 (reaction completion) were obtained for the catalyst within 20 min. At 40°C the TN value was no more than 9 after the same reaction time. Table 2 shows different values of catalyst TN for the hydrosilylation reaction at different temperatures.

The activation energy, E_a , for the reaction was calculated and found to be 84.2 kJ mol^{-1} using the Arrhenius method [43] which clearly showed a linear relation. The significant value of E_a indicates that the reaction is not a diffusion controlled process. At same temperature, the rate of the reaction was not significantly affected by the rate of stirring. Under the present working conditions the reaction proceeded to completion within 20 min, when carried out at 70°C . After complete consumption of the silane, no other reactions were detected.

3.2. Solvent effect on the rate of the reaction

Using benzene as an internal standard reference, several types of solvents with different polarities were used. Depending on the values of measured TN for the reaction, the rate of the reaction varied with different solvents in the order:

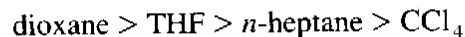


Table 3
Effect of type of solvent on the rate of the 1-octene hydrosilylation reaction^a

Entry	Solvent	Value of TN		
		10 min	15 min	20 min
1	dioxane	42	47	49 ^b
2	THF	31	37	39
3	<i>n</i> -heptane	24	26	28
4	CCl ₄	21	24	27

^aAll reactions were conducted in 2.5 ml solvent, using (C₂H₅O)₃SiH (0.923 ml, 0.5 M) and supported catalyst I from batch 1 (0.3889 g, containing 0.0389 g of Mn₂(CO)₁₀, 0.01 M) and 1-octene (1.56 ml, 1.0 M).

^bReaction completion with 100% yield reached.

Despite the fact that the variation in the rate does not strictly follow the polarity of the solvent, it shows a rough tendency. Generally, the reaction was faster with solvents that carry Lewis basic centers. After 10 min reaction time, the TN value was about 42 in case of dioxane, compared to a value of 21 in *n*-heptane. Table 3 shows values of TN measured for the catalyst after specified reaction times with different solvents. Although the dioxane solvent is non-polar, viz. it has a zero dipole moment, it has two σ -basic centers. Despite this behavior, no solid conclusions can be drawn regarding the solvent polarity effect on the catalyst activity.

3.3. Reactant concentrations effect

The initial rate of the hydrosilylation reaction was affected by changing the initial concentrations of the silane while keeping other reaction conditions constant. Plot of the measured ln(initial rate) vs. ln[initial (C₂H₅O)₃SiH] showed a linear relation with a slope equal to a unity. Fig. 2 summarizes these results. This indicates that the reaction was first order with respect to the silane. The reaction was also affected by the 1-octene concentration. A first order dependence with respect to the olefin was also observed by the method of initial rates, as shown in Fig. 3.

The effect of the amount of the supported dimeric catalyst on the rate of the reaction was

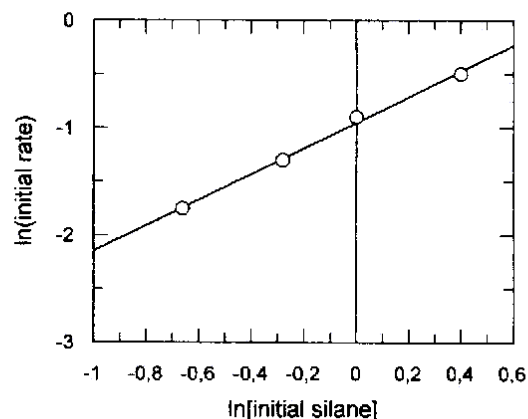


Fig. 2. Plot of ln(initial rate) vs. ln[initial silane] for the reaction of (EtO)₃SiH with 1-octene (1.0 M) in dioxane (variable to make total volume 10.0 ml) and benzene (5.0 ml) at 60°C using catalyst I (with 0.01 M manganese dimer) taken from batch 1.

investigated using the method of initial rates. Fig. 4 shows a first order reaction with respect to the catalyst.

The Laine's kinetic technique [44,45] was used to see if the manganese dimeric species catalyzes the reaction while remaining intact. Plots of TN values vs. supported Mn₂(CO)₁₀ were made after different reaction times. Fig. 5 shows that the TN value is independent of the supported dimer catalyst concentration. This indicates that the dimer catalyzes the reaction

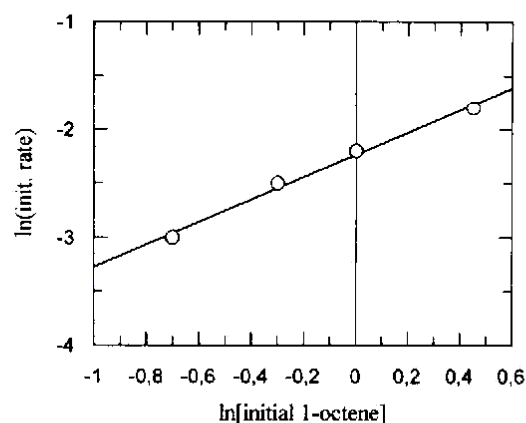


Fig. 3. Plot of ln(initial rate) vs. ln[initial octene] for the reaction of (EtO)₃SiH (0.5 M) with 1-octene in dioxane (variable to make total volume 10.0 ml) and benzene (5.0 ml) at 60°C using catalyst I (with 0.01 M manganese dimer) taken from batch 1.

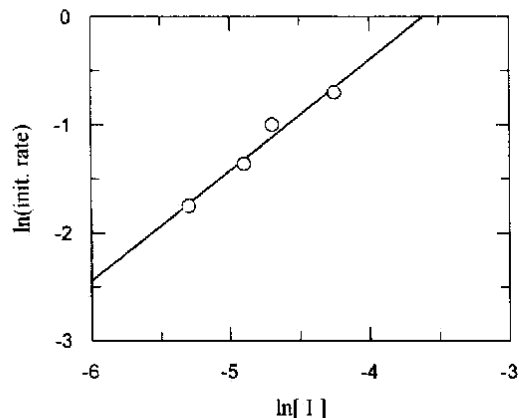


Fig. 4. Plot of $\ln(\text{initial rate})$ vs. $\ln[\text{catalyst I}]$ for the reaction of $(\text{EtO})_3\text{SiH}$ (0.5 M) with 1-octene (1.0 M) in dioxane (variable to make total volume 2.51 ml) and benzene (5.0 ml) at 60°C using catalyst I taken from batch 2.

while remaining intact, vide the discussion section.

The supported manganese catalyst showed relatively high reproducible catalytic activity for reaction runs conducted using same batch. Fig. 6 shows that the reaction was reproducible when carried out using a fresh sample taken from same batch. Different prepared batches of the supported catalyst I showed lower reproducibility in catalyzing the hydrosilylation reaction, as shown in Fig. 7.

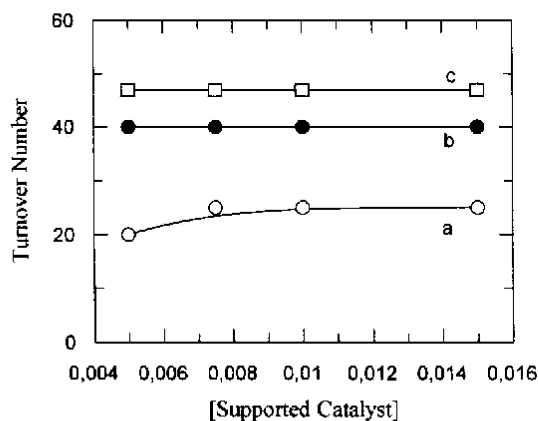


Fig. 5. Plot of value of turnover number vs. supported catalyst I (from batch 2) concentration for the reaction of $(\text{EtO})_3\text{SiH}$ 0.5 M with 1-octene (1.0 M) in dioxane (3.5 ml) and benzene (5.0 ml) at 60°C after (a) 5 min; (b) 20 min; (c) 25 min.

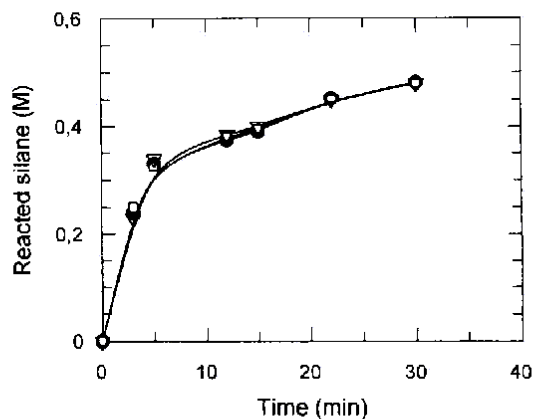


Fig. 6. High reproducibility of the catalyst I samples taken from same batch (2), in the reaction of $(\text{EtO})_3\text{SiH}$ (0.5 M) with 1-octene (1.0 M) in dioxane (2.5 ml) and benzene (5.0 ml) at 70°C using a fresh catalyst sample (0.01 M concentration for the Mn dimer) in each run.

3.4. Supported vs. homogeneous $\text{Mn}_2(\text{CO})_{10}$ catalytic systems

In addition to the supported catalyst experiments, the hydrosilylation reaction of 1-octene was conducted homogeneously using the $\text{Mn}_2(\text{CO})_{10}$ system and derivatives. The homogeneous $\text{Mn}_2(\text{CO})_{10}$ is known to be soundly selective to hydrosilylation reaction when con-

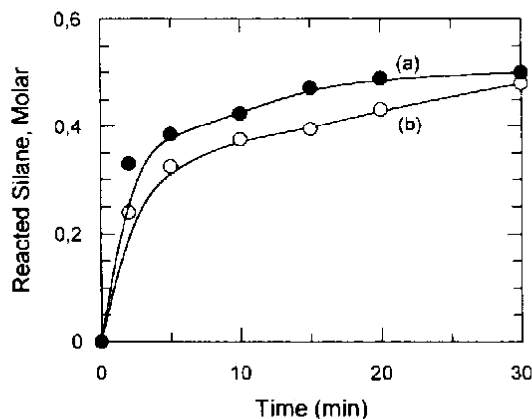


Fig. 7. Lower reproducibility of the catalyst I samples taken from different batches, in the reaction of $(\text{EtO})_3\text{SiH}$ (0.5 M) with 1-octene (1.0 M) in dioxane (2.5 ml) and benzene (5.0 ml) at 70°C using a fresh catalyst sample (0.01 M concentration for the Mn dimer) in each run. (a) batch 1; (b) batch 2.

ducted at lower temperatures, ca. 40°C, [29]. At higher temperatures, however, the homogeneous system showed lower selectivity to hydrosilylation. Table 4 shows that at 70°C the homogeneous $\text{Mn}_2(\text{CO})_{10}$ catalyst system yields the isomerization product *trans*-2-octene as a reaction product, in addition to the hydrosilylation reaction product. The isomerization reaction was manifested by the appearance of the *trans*-2-octene IR band at 960 cm^{-1} . Internal olefins do not have the tendency to undergo hydrosilylation reactions [29] and are expected to remain unreacted in the reaction mixture. In case of the homogeneous $\text{Mn}_2(\text{CO})_{10}$ system, the product distribution showed that the hydrosilylation-to-isomerization mole ratio was no better than 1:1 for reactions conducted at 70°C. Addition of dissolved $(\text{C}_2\text{H}_5\text{O})_3\text{Si}(\text{CH}_2)_3\text{NH}_2$ ligand to the homogeneous $\text{Mn}_2(\text{CO})_{10}$ solution in a 1:1 molar ratio (catalyst mixture **II**) caused a big difference in the behavior of the $\text{Mn}_2(\text{CO})_{10}$ catalyst system. The resulting catalytic mixture showed a better selectivity toward the hydrosilylation reaction, and the product distribution was about 6:1 in favor of the hydrosilylation reaction product. This indicates that the enhanced selectivity is due to the added ligand. When the anchoring ligand was added in a higher ratio,

$\text{Mn}_2(\text{CO})_{10}/2\text{L}$, (catalyst mixture **III**), the product distribution was further enhanced to become 9:1 in favor of the hydrosilylation reaction product. Table 4 also shows that the aminated poly(siloxane)-supported manganese catalyst, **I**, completely favors the production of the hydrosilylation reaction as a sole product, with no isomerization.

In addition to the selectivity enhancement, the supported catalyst system showed two other good features. First, the supported system showed a comparable catalytic activity to that of the $\text{Mn}_2(\text{CO})_{10}$ homogeneous system. Therefore, the pronounced selectivity of the supported system did not happen at the expense of the catalyst activity as generally observed in other supported catalyst systems [19,22–26]. Table 4 shows that within 20 min both the homogeneous and the supported catalysts gave comparable values of **TN**, ca. 10, for the hydrosilylation reaction conducted at 40°C. Second, the supported catalyst system proceeded with the hydrosilylation reaction to completion, whereas the homogeneous system failed to reach completion. Table 4 shows that after 20 min reaction time the homogeneous catalyst reaction profiles leveled at about 15 value for **TN**, without any tendency to reach completion, whereas

Table 4
Comparison of the catalytic selectivity of **I** with that of the homogeneous catalysts

Entry	Catalyst	Temperature (°C)	TN	Percent conversion	Time (min)	Hydrosilylation/ isomerization mole ratio
1	$\text{Mn}_2(\text{CO})_{10}$ (homog.)	70	50 ^a	100	20	5:5
2	mixture II	70	50 ^b	100	20	6:4
3	mixture III	70	50 ^c	100	20	9:1
4	I	70	50 ^d	100	20	10:0
5	$\text{Mn}_2(\text{CO})_{10}$ (homog.)	40	10 ^a	20	20	9:1
6	$\text{Mn}_2(\text{CO})_{10}$ (homog.)	40	15 ^a	30	> 120	8.5:1.5
7	I	40	10 ^d	20	20	10:0
8	I	40	45 ^d	90	> 120	10:0

All reactions were conducted in benzene/dioxane solvent system, using $(\text{C}_2\text{H}_5\text{O})_3\text{SiH}$ (0.923 ml, 0.50 M), 1-octene (1.56 ml, 1.0 M).

^aUsing 0.01 M $\text{Mn}_2(\text{CO})_{10}$.

^bUsing 0.01 M $\text{Mn}_2(\text{CO})_{10}$ with 0.01 M ligand.

^cUsing 0.01 M $\text{Mn}_2(\text{CO})_{10}$ with 0.02 M ligand.

^dSupported catalyst **I** (taken from batch 2, 0.389 g, equivalent to 0.039 g $\text{Mn}_2(\text{CO})_{10}$, 0.01 M).

Table 5
Retention of catalytic activity of **I** after recovery in hydrosilylation reactions

Entry	Catalyst sample	Values of TN with time			
		5 min	10 min	20 min	30 min
1	fresh	31	38	44	48
2	1st recovery	26	31	37	42
3	2nd recovery	22	26	30	31
4	3rd recovery	17	22	25	26

All reactions were conducted in benzene/dioxane using $(C_2H_5O)_2SiH$ (0.923 ml, 0.50 M), 1-octene (1.56 ml, 1.0 M) and **I** (taken from batch 2, 0.389 g, equivalent to 0.039 g $Mn_2(CO)_{10}$, 0.01 M) at 70°C.

the supported catalyst proceeded to completion giving a TN of higher than 45 after 2 h reaction time or longer.

The catalytic activity of the supported catalyst was significantly retained after recovery. Table 5 shows that the catalyst retained more than 50% of its activity after the third time recovery (fourth use).

4. Discussion

The main objective of this work was to develop an active, easy-to-recover, recyclable inexpensive catalytic system with a high selectivity toward olefin hydrosilylation reaction with the exclusion of other side reactions such as isomerization and dehydrogenative-silylation. The supported catalyst **I** described here partly satisfied this objective.

Treatment of the white colored aminated poly(siloxane) surface with the yellowish-green solution of $Mn_2(CO)_{10}$ in dioxane produced the light-brown colored supported manganese complex **I**. Throughout the course of treatment, the solution coloration continued to fade away with time until it completely disappeared after ca. 6 h. Under our working conditions the whole amount of the added $Mn_2(CO)_{10}$ was anchored to the support, and the uptake was up to 10% w/w. High metal uptakes are known for poly(siloxane) surface systems [36,40]. The yellow-to-brown color change is an indication of a

chemical change in the $Mn_2(CO)_{10}$ complex. The treated solid was isolated and washed several times with hot dioxane. The filtrate fractions showed no detectable amounts of $Mn_2(CO)_{10}$. This is an additional evidence that the manganese complex is attached to the surface via primary chemical bonding rather than merely physical adsorption. Solid state FT-IR spectra were used to further confirm the chemical anchoring of $Mn_2(CO)_{10}$ on the support surface. The spectra were soundly conclusive and indicated chemical bonding between $Mn_2(CO)_{10}$ and the supported amine ligand. The FT-IR spectra were measured for the supported catalyst **I** prepared by heating $Mn_2(CO)_{10}$ with the aminated poly(siloxane) surface. For comparison purposes, FT-IR spectra were also measured for solid mixtures of $Mn_2(CO)_{10}$ and aminated surface, system **IV**, without prior heating of the mixture. In this way it was possible to look directly at the solid state FT-IR spectra of the $Mn_2(CO)_{10}$ in system **IV** without chemical change. Typically the spectrum of $Mn_2(CO)_{10}$ should have three stretching bands for CO at 2044 (m), 2013 (s) and 1983 (m) cm^{-1} [42] as shown in entry (1) of Table 6. For system **I**, the spectra showed significant deviations from those of $Mn_2(CO)_{10}$. System **I** showed three well defined carbonyl stretching bands, one with a medium intensity at 2045 cm^{-1} , another strong band at 2036 cm^{-1} and a third with a very strong intensity at 1928 cm^{-1} in addition to a poorly defined shoulder at 1983 cm^{-1} as shown in entry (2) of Table 6. For system **IV**, three carbonyl stretching bands were observed: one with medium intensity at 2045 cm^{-1} , another strong band at 2036 cm^{-1} and a third poorly defined medium intensity shoulder at 1983 cm^{-1} as shown in entry (3) of Table 6. This shows that system **IV**, with no chemical reaction, is same as $Mn_2(CO)_{10}$. On the other hand, system **I** is different from the original $Mn_2(CO)_{10}$ complex.

The solid state FT-IR spectra discussed above indicate chemical bonding of $Mn_2(CO)_{10}$ with the supported amine ligand. Literature [46–49]

Table 6
FT-IR spectral data for different solid or solution systems

Entry	Compound	IR Bands
1	$\text{Mn}_2(\text{CO})_{10}$	2044 (m), 2013 (s), 1983 (m) ^a
2	I (solid state), fresh sample	2045 (m), 2036 (s), 1980 ^b , 1928 (vs)
3	IV unreacted $\text{Mn}_2(\text{CO})_{10}$ /support	2045 (m), 2036 (s), 1983 ^b
4	untreated aminated surface (solid state)	no bands in the region
5	$\text{Mn}_2(\text{CO})_{10}$ (in dioxane)	2050 (m), 2020 (s), 1980 (m)
6	V solution phase (in dioxane)	2050 (m), 2020 (s), 1980 (m)
7	VI $\text{Mn}_2(\text{CO})_{10}$ /ligand 1:1 (precipitate)	2023 (s), 1912 (vs)
8	VII $\text{Mn}_2(\text{CO})_{10}$ /ligand 1:2 (precipitate)	2023 (s), 1912 (vs)
9	recovered I after use (solid state)	2045 (m), 2036 (s), 1980 ^b , 1928

The solid state spectra were measured as KBr discs.

The solution spectra were measured in dioxane.

^aFrom literature, Ref. [42].

^bA medium intensity shoulder.

showed that $\text{Mn}_2(\text{CO})_{10}$ reacts with amines while retaining the dimeric nature of the complex. The resulting supported manganese complex **I** (Scheme 2) could be one or a combination of the following species:

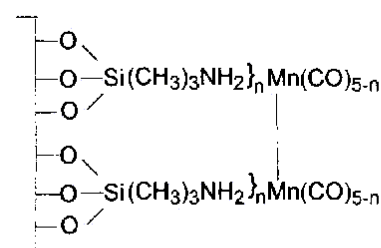
1. a mono-substituted dimer in which one surface amine is bound only to one Mn atom, leaving the other Mn atom free of amine;
2. a di-substituted dimer in which two amines are bound to one Mn atom, leaving the other Mn atom free of amines;
3. a di-substituted dimer in which one surface amine ligand is bound to each Mn atom.

In (1) and (2) the surface amine(s) is (are) bound only to one Mn atom, leaving the other Mn atom free of any bonding to the supported amine. Thus, more than one type of carbonyl IR stretching will be observed. Similarly, in (3), where each Mn atom is bound to a surface amine, two types of carbonyl groups exist. The carbonyl groups that are trans to the amine groups are expected to absorb at lower stretching frequency than the carbonyl groups trans to the carbonyl groups. This is because the amine ligand has no ability to compete for the Mn–C π -bonding. These carbonyl groups will therefore have high Mn–C back donation. This lowers the bond order in the carbonyl group, and consequently lowers the C–O stretching fre-

quency to 1936 cm^{-1} . The carbonyls that are trans to one another, will have higher competition for Mn–C π -bonding. In this case the Mn–C back donation will be lowered, and consequently the carbonyl stretching will occur at higher frequency, 2050 cm^{-1} . Thus, the solid state spectra measured for **I** is in agreement with the di-substituted dimer described in (3).

Additional control experiments were conducted using naked aminated poly(siloxane) in KBr and analyzed with FT-IR. No bands for the naked poly(siloxane) solid were detected in the region, as shown in entry (4) of Table 6.

The complex $\text{Mn}_2(\text{CO})_{10}$ is known to react with amines in organic solvents [46,47]. One



Supported Catalyst **I**
($n = 0$ or 1)

Scheme 2.

mole of $\text{Mn}_2(\text{CO})_{10}$ reacts with one mole of NH_3 to yield the mono-substituted product [$\text{Mn}_2(\text{CO})_9(\text{NH}_3)$]. The substitution reaction is believed to occur via a fragmentation/re-association process [48,49]. The overall reaction of two moles of amines with one mole of $\text{Mn}_2(\text{CO})_{10}$ would also yield one mole of the dimer [$\text{Mn}_2(\text{CO})_8(\text{NH}_3)_2$], in which one amine is bound to each Mn atom in the dimer [46–49].

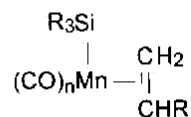
To confirm the discussions about the supported manganese complex **I**, $\text{Mn}_2(\text{CO})_{10}$ was allowed to react with the dissolved ligand $(\text{C}_2\text{H}_5\text{O})_3\text{Si}(\text{CH}_2)_3\text{NH}_2$ in refluxing dioxane in different dimer-to-ligand molar ratios. With dimer/ligand 1:0 no change in the solution IR spectra was observed, as shown in entry (5) of Table 6. Using a 1:1 molar ratio, the reaction yielded a light yellow-brown precipitate. The solution phase, **V**, spectra showed no difference from the $\text{Mn}_2(\text{CO})_{10}$ spectra, entry (6) of Table 6. The precipitate, **VI**, was isolated by filtration and analyzed by FT-IR spectra as solid KBr disc. The solid state spectra showed a strong band at 2023 cm^{-1} and a very strong band at 1912 cm^{-1} , entry (7) of Table 6. Similarly, and in a separate experiment, $\text{Mn}_2(\text{CO})_{10}$ was reacted with the in situ ligand using a 1:2 $\text{Mn}_2(\text{CO})_{10}$ to ligand molar ratio, respectively. A light yellow-brown solid, **VII**, precipitated. The solution portion showed IR spectra, entry (6) of Table 6, that resemble the spectra of unreacted $\text{Mn}_2(\text{CO})_{10}$. The FT-IR spectra were measured for the isolated precipitate as KBr disc. One strong band at 2023 cm^{-1} and another very strong band at 1912 cm^{-1} were observed and are shown in entry (8) of Table 6.

The solid state FT-IR spectra of the two precipitates **VI** and **VII** were identical and showed a new strong band at 1912 cm^{-1} in addition to the 2023 cm^{-1} band, as shown in entries (7) and (8) of Table 6. This lowering in the C–O bond stretching frequency indicates that $\text{Mn}_2(\text{CO})_{10}$ reacts with the ligand. The resemblance of the IR spectra of the two resulting precipitates indicates that the di-substitution process is the dominant one in both cases. The

FT-IR spectrum measured for the remaining solutions (**V**), in both experiments of $\text{Mn}_2(\text{CO})_{10}$ -to-ligand 1:1 and 1:2 molar ratios, entry (6) of Table 6, showed the presence of the dimeric $\text{Mn}_2(\text{CO})_{10}$ species remaining unchanged. This was more pronounced in the 1:1 molar-ratio reaction mixture, where significant amount of $\text{Mn}_2(\text{CO})_{10}$ remained unreacted due to the consumption of two moles ligand per one mole reacted $\text{Mn}_2(\text{CO})_{10}$. This was observed by FT-IR spectra measured for the solution portion of the reaction mixture.

Relative selectivity enhancement in supported catalysts has been reported for other hydrosilylation reactions [29–33,50]. In this work, the high selectivity of **I** towards hydrosilylation is due to the amine ligand bound to the Mn atom. No solid mechanism can be suggested for the reaction at this stage. However, from literature [29–33,51–55], the Mn complex-catalyzed hydrosilylation reaction occurs via a series of steps, that involve the following.

- (1) Oxidative addition of the $\text{R}_3\text{Si-H}$ bond to form a Mn–H addendum and a coordinated silyl group, with a partial positive charge at Si atom.
- (2) Activation of the olefin molecule to form an intermediate that has both the olefin and the silyl groups bound to the Mn atom. The intermediate is shown in Scheme 3. The coordinated olefin is the one with a higher negative charge at carbon atom.
- (3) An insertion of the olefin between Mn and the silyl group via a nucleophilic attack of the coordinated olefin molecule at the coordinated Si atom to yield the coordinated alkyl-silyl compound.
- (4) A reductive elimination of the alkyl-silyl group and the hydride to yield the product.



Scheme 3.

On the other hand, olefin isomerization (side) reaction occurs via an alternative process that would by-pass step (3), [29]. In this case the coordinated olefin undergoes insertion between the Mn atom and the hydride via an electrophilic attack. The ability of coordinated olefins to behave as nucleophiles and as electrophiles is known [56]. It is possible to control the path of the reaction to the desired direction, simply by increasing or decreasing the partial charge at the coordinated olefin. The presence of the amine ligand, a good σ -donor and a poor π -acceptor, would increase the negative charge at the coordinated olefin molecules bound to the Mn atom. This increases the nucleophilicity of the coordinated olefin and encourages the olefin attack at coordinated silyl group. The selectivity of **I** to hydrosilylation is therefore attributed to the presence of the amine ligand. In the absence of the amine ligand, as with the in situ $\text{Mn}_2(\text{CO})_{10}$ case, the Mn atom is surrounded by π -acidic carbonyl groups. The coordinated olefin will thus have higher ability to behave as electrophile and will consequently yield the isomerization side reaction.

Parallel to the high selectivity of the supported catalyst **I**, the in situ mixture of $\text{Mn}_2(\text{CO})_{10}$ /ligand showed similar behavior. Again, the higher selectivity arising from the addition of the amine ligand can be understood. It was pointed earlier that the supported manganese complex is a di-substituted species. Evidence to this was observed from the FT-IR investigations of the in situ mixtures of $\text{Mn}_2(\text{CO})_{10}$ /ligand, *vide supra*. The fact that the 1:1 dimer-to-ligand ratio catalytic system showed enhanced selectivity is attributed to the partial formation of the di-substituted dimeric catalyst. This species selectively catalyzes the hydrosilylation reaction. The remaining unreacted $\text{Mn}_2(\text{CO})_{10}$ species in turn catalyzes both the hydrosilylation and the isomerization reactions unselectively. With a higher used ligand-to-dimer molar ratio, the 2:1 system, a higher fraction of the $\text{Mn}_2(\text{CO})_{10}$ is converted into the di-substituted product and a lower fraction of

unsubstituted $\text{Mn}_2(\text{CO})_{10}$ remains. In this catalytic mixture, higher selectivity was observed, as shown in Table 4.

These discussions are in favor, though not unequivocally, of the di-substituted dimer at two Mn atoms. Although this model helps to explain the selectivity of **I** towards hydrosilylation, it should be noted that knowing the exact nature of **I** was not the theme of this study. The application of **I** as a selective catalyst for hydrosilylation is the major theme. In any case, the presence of the amine group bound to the dimer is the reason for the enhancement of the selectivity towards the hydrosilylation reaction. Work is now underway to understand the exact nature of the supported complex **I** in these laboratories.

Mechanistic pathways based on cluster fragmentation and re-association have been proposed for the homogeneous counterparts of **I** [29]. These mechanisms may account for several results observed here. No definite evidence in favor of intact cluster catalysis or fragmentation is available yet. The Laine's kinetic studies here indicated that the cluster remained intact during the reaction process throughout a period of 45 min, as shown in Fig. 4. From Laine's kinetic model [44,45], it is stated that a decrease in turnover frequency (TF) with increasing total cluster concentration indicates cluster fragmentation to catalytically active species of lower nuclearity. On the other hand the increase in TF with increasing cluster concentration indicates association of the cluster to higher nuclearity catalytic species. If the TF remains constant with increasing cluster concentration then the cluster is believed to remain intact during the reaction. Fig. 4 shows that, within the working range of the used catalyst concentrations, the value of TF remains constant throughout a period of 45 min. This indicates that the dimeric supported catalyst remains intact during the reaction. Despite these findings, one cannot at this stage propose unequivocal mechanisms for the catalysis of the hydrosilylation reaction by **I**. Concrete evidence in favor of intact or frag-

mented cluster catalyst is not available yet. All what can be said is that the presence of the amine ligand enhances the catalyst selectivity toward the hydrosilylation reaction.

In addition to its high selectivity, the catalytic system **I**, described here, combines more than one important feature. In addition to its very high selectivity to hydrosilylation, it is a commercially inexpensive catalyst. The activity of the supported catalyst is comparable to that of the homogeneous counterparts, as shown in entries (1–4) of Table 4. The support did not inhibit the activity of the catalyst. In this way, the supported catalyst **I** is better than other reported supported catalysts, where loss of activity has been observed as a result of the supporting process [19–26].

The fact that the supported catalyst partly retained its catalytic activity on reuse indicates that both of the two Mn atoms in the dimer are anchored to the surface in a close proximity manner. The partial loss of activity of the catalyst after reuse could be due to either or both of two reasons, namely: the leaching out of the manganese complex and the decomposition of the complex. The leaching out of the complex was excluded by the fact that the solution phase of the reaction mixture isolated by filtration failed to catalyze the hydrosilylation reaction. This indicates that no significant amounts of the Mn compound leach out in its complex form. The loss of catalytic activity of **I** after use is presumably due to partial decomposition of the manganese complex to metallic Mn. Slight darkening of the supported complex was observed under the reaction conditions, especially at higher reaction temperatures. Solid state FT-IR spectra for the catalyst **I** was measured after use. No significant changes in the positions of characteristic IR bands were observed, as shown in entries (2) and (9) of Table 6. This is another indication that any loss in the supported catalyst will be due to decomposition into metallic Mn. Decomposition of supported organometallic catalysts during chemical reactions is often encountered and is one shortcoming of supported

catalysts. However, the fact that supported catalyst **I** retained at least 50% of its catalytic activity after the third recovery makes it worth of further development and study.

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