# Highly Active Visible-Light Photocatalysts for Curing a Ceramic Precursor[1]

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Three platinum(II) bis($\beta$-diketonate) complexes are highly active for photocatalytic hydrosilation cross-linking of oligo[(methylsilylene)methylene] with tetravinylsilane. Platinum(II) bis(benzoylacetonate), platinum(II) bis(trifluoroacetylacetonate), and platinum(II) bis(benzoyltrifluoroacetonate) are photoactivated by visible light for catalysis, while platinum(II) bis(hexafluoroacetylacetonate) can be used as a thermal catalyst. Kinetic data from FT-IR and UV−visible spectroscopies characterizing Si−H bond conversion and catalyst photolysis are reported.

## Introduction

Silicon carbide ceramic is of interest because of its high strength and hardness, semiconductivity (band gap 2.2 eV ($\beta$), 2.9 eV ($\alpha$)), high-temperature stability, chemical resistance and X-ray resistance.[2,3] Conversion of carbosilane polymers into silicon carbide fibers has been extensively researched[4−10] and reviewed.[11−14] The precursor polymers are polysilanes,[15,16] $(-Si(R)_2-)_n$; polycarbosilanes,[17] $(-Si(R)_2-CH_2-)_n$; or copolymers of the two.[18] During pyrolysis of precursors under inert gas hydrogen is evolved, along with volatile organic compounds in many cases ($CH_4$ is typical), to yield amorphous silicon carbide char.[19,20] At high temperatures (>1200 °C) crystalline polytypes ($\beta$) are formed.

The advantage of polymer precursor routes to silicon carbide is that shapes or patterns may be produced at the polymeric stage when the material is relatively easy to form and subsequently be converted to an extremely hard ceramic. For this advantage to be realized, the precursor must be a thermosetting polymer to prevent loss of structure during the pyrolysis. Highly cross-linked polymers satisfy this requirement.[21]

Our interest is in using laser techniques (stereolithography)[22−26] and photoimaging[27−30] to produce shaped preceramic objects or thin-film patterns that can be converted into ceramic with retention of the photocured shapes and patterns. For this work platinum(II) bis($\beta$-diketonate) complexes $[Pt(L)_2]$ have been employed as hydrosilation photocatalysts.[31,32] The utility of $Pt(L)_2$ for photopolymerization[33] and photocuring[34] of carbosilanes was demonstrated with the UV absorbing homologue platinum(II) bis(acetylacetonate), or $Pt(acac)_2$. Absorption of photons by $Pt(L)_2$ produces ligand cleav-

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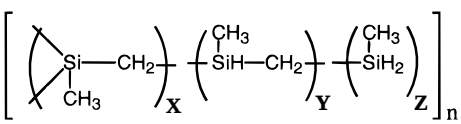
age[35] and, subsequently, an active metal center that functions as a homogeneous hydrosilation catalyst, apparently through a Chalk−Harrod-type mechanism.[36] This report describes the use of visible-light-absorbing $Pt(L)_2$ complexes for photocuring the silicon carbide precursor oligo(methylsilylene)methylene (OMSM) by hydrosilation cross-linking.

## Experimental Section

**Materials.** Potassium tetrachloroplatinate(II) (99.9%), platinum(II) bis(acetylacetonate) [$Pt(acac)_2$], and silver perchlorate monohydrate (99.9%) were purchased from Alfa Aesar. Dibenzoylmethane (Hdbm, 98%), 1-benzoylacetone (Hbac, 99%), 1,1,1-trifluoro-2,4-pentanedione (or trifluoroacetylacetone, Htfac, 98%), 4,4,4-trifluoro-1-phenyl-1,3-butanedione (or benzoyltrifluoroacetone, Hbtfac, 99%), 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (or hexafluoroacetylacetone, Hhfac, 98%), and perchloric acid (70% solution) were purchased from Aldrich. Tetravinylsilane (TVS, 95%) was purchased from Gelest. Mercuric oxide (purified) was from Fisher. All these chemicals were used without further purification.

Oligo[(methylsilylene)methylene] (OMSM) was synthesized by a previously reported procedure.[34,37,38] The liquid oligomer was characterized by GPC and had a bimodal distribution with $M_n = 442$, $M_w/M_n = 1.4$ (60%); and $M_n = 28\,900$, $M_w/M_n = 2.4$ (40%). $^{29}Si$ NMR of the oligomer gave the relative amounts of silicon centers to be $R_4Si = 29\%$, $R_3SiH = 39\%$ and $R_2SiH_2 = 32\%$. The structure is as follows:




OMSM

**General Techniques.** $^1H$ NMR spectra were obtained using a Varian Gemini 200 in deuterated solvents (Aldrich). Chemical shifts were reported using residual solvent peaks at 7.26 ppm for $CDCl_3$ and at 7.19 ppm for $C_6D_6$ downfield from external TMS. A Varian UnityPlus 400 NMR with a switchable probe was used to collect the $^{29}Si$ spectra (79.5 MHz, $C_6D_6$, chemical shift relative to external TMS).

The irradiation apparatus consists of an Oriel 66002 illuminator with a 200 W Hg lamp collimated by a lens through a cooled IR water filter and a cutoff filter ($\lambda > 340$ nm or $\lambda > 400$ nm with a $NaNO_2$ solution filter in series with the cutoff filter). The light intensity was 0.30 W/cm$^2$ for $\lambda > 340$ nm and 0.15 W/cm$^2$ for $\lambda > 400$ nm. Incident light intensity was measured with a Scientech 365 power and energy meter by replacing the sample holder with the power meter sending unit.

**Conversion of Photopolymer Films.** NaCl or KBr salt plates (Aldrich) were used for the FT-IR experiments. Liquid mixtures of 0.400 g of OMSM + 0.150 g of TVS + 3.6 $\mu$mol of $Pt(L)_2$ were prepared in dimmed light immediately prior to use.[39] One drop of this mixture was placed between two salt plates and irradiated on the optical bench for certain intervals of time. FT-IR spectra were taken after illumination periods (acquisition time is 0.67 min). Infrared spectroscopy was done with a Mattson Galaxy 6020 spectrophotometer. The degree of $SiH_x$ conversion was determined by calculating the decrease in the integrated area of the 2125 cm$^{-1}$ peak normalized by the area of the $SiCH_3$ deformation peak at 1253 cm$^{-1}$ after photolysis.

**Irradiation of Solutions.** Quartz cuvettes (Spectrocell) capped with septa were used for the catalyst photolysis kinetics experiments. The cell holder was maintained at 25.0 ± 0.1 °C by a Lauda circulating bath, and the solutions were magnetically stirred during irradiation. Stock solutions of catalysts and silane additives in dichloromethane (Aldrich, spectral grade) were prepared in red actinic glassware and mixed to the proper concentration before runs. $Pt(L)_2$ solutions ($6.0 \times 10^{-4}$ M) with silane additives (0.14 M OMSM[40] + 0.022 M TVS) were irradiated on the optical bench. The decrease in $Pt(L)_2$ concentration was measured by the change in optical density at 368 nm for $Pt(acac)_2$, at 400 nm for $Pt(tfac)_2$, at 422 nm for $Pt(hfac)_2$ and $Pt(bac)_2$, and at 464 nm for $Pt(dbm)_2$. UV−vis absorption spectroscopy was carried out with an HP 8452A spectrophotometer. Experiments were performed in duplicate and photolyses carried out only to low conversions (<20%).

No fluorescence could be detected from $Pt(acac)_2$ solutions (in $CH_3CN$ or $CH_2Cl_2$) or from $Pt(acac)_2$ and vinyldimethylsilane solutions (in $CH_2Cl_2$).

**Thin-Film Patterns.** Photopatterning was done with silicon wafers of about 1.5 × 1.5 cm, pretreated by refluxing 5 h with 30% chlorotrimethylsilane in toluene. The wafers were spin coated with a mixture of 0.400 g of OMSM + 0.150 g of TVS + 3.6 $\mu$mol of $Pt(tfac)_2$ + 1.10 g of benzene. Images were formed by placing 200 mesh copper masks onto the film surfaces before irradiation. The coated wafers were irradiated with the illuminator above ($\lambda > 400$ nm) for 5−30 s in an optical bench oven at 40 °C. The light was directed vertically onto the wafers with a mirror; this apparatus has been described elsewhere.[34] Immediately following photocure, the wafers were rinsed several times with benzene to remove the mask and uncured photopolymer.

**Gel Time.** The photocatalyst cure times were estimated by irradiating vials containing OMSM, TVS, and $Pt(L)_2$ (proportioned as above) with a dental lamp (Demetron model VCI 401, $\lambda > 340$ nm, $\lambda_{max} = 516$ nm, 1.2 W/cm$^2$). These mixtures were prepared in vials and irradiated by directing the entire lamp beam (unfocused) into the bottoms of the vials. The minimum irradiation exposure required to solidify the samples (determined by observation) was as follows: 0.13 wt % $Pt(hfac)_2$, 20 s; $Pt(tfac)_2$, 30 s; $Pt(btfac)_2$, 40 s; $Pt(acac)_2$, 60 s; $Pt(bac)_2$, 90 s; 0.5 wt % $Pt(dbm)_2$, 120 s.

The gel times of OMSM, TVS, and $Pt(L)_2$ mixtures in the dark are as follows: $Pt(hfac)_2$, <1 min; $Pt(tfac)_2$, $Pt(btfac)_2$, and $Pt(dbm)_2$, 2−5 h; $Pt(bac)_2$ and $Pt(acac)_2$, >12 h. The temperature during the control experiments was ∼23 °C.

**Synthesis of Platinum Complexes.** The synthesis of $Pt(L)_2$ involves two major steps, a first step preparing the $[Pt(H_2O)_4]^{2+}$ ion from the $[PtCl_4]^{2-}$ anion in a $HClO_4$ solution, assisted by both $Hg^{2+}$ and $Ag^+$, and a second step forming the chelate between platinum and the ligands through ligand exchange (eqs 1 and 2).

$$[PtCl_4]^{2-} + Hg^{2+}\,(Ag^+) + \text{excess } H_2O \rightarrow [Pt(H_2O)_4]^{2+} + HgCl_2\,(AgCl) \quad (1)$$

$$[Pt(H_2O)_4]^{2+} + 2L + 2OH^- \rightarrow Pt(L)_2 + 6H_2O \quad (2)$$

The acidity of the $HClO_4$ solution of the $[Pt(H_2O)_4]^{2+}$ has to be *properly adjusted* in order for reaction 2 to take place. Various authors have reported that the pH of the solution is adjusted, by addition of a strong alkali solution (KOH or NaOH), to pH = 2−3 before the addition of the ligand, and afterward adjusted a second time to pH = 3−4.[41−44] In our hands, numerous attempts to follow these procedures resulted in low yields of the products $Pt(L)_2$. We observed irreversible formation of platinum colloid from $Pt(OH)_x$ species during the acidity adjustment due to either abrupt changes in localized pH values arising from the use of a strong base, or overall pH values raised above 2.0. We therefore incorporated low concentrations (e.g., 3%) of a mild base $K_2CO_3$ in place of KOH/

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(39) The wt % of catalyst is 0.25% for $Pt(acac)_2$.

(40) Concentration based on $-SiH(CH_3)CH_2-$ segmers.

**Table 1. $^1$H NMR Data for the Platinum Complexes**

| complexes | chemical shifts (ppm)[a] |
|---|---|
| $Pt(bac)_2$ | 7.94 (m, 2H, *o*-Ph), 7.54 (m, 1H, *p*-Ph), 7.45 (m, 2H, *m*-Ph), 6.21 (s, *cis*-CH), 6.19 (s, *trans*-CH), *cis*-CH/*trans*-CH = 1:1, 2.11 (s, 3H, $CH_3$) |
| $Pt(dbm)_2$ | 8.06 (d, 4H, *o*-Ph), 7.59 (dd, 2H, *p*-Ph), 7.46 (dd, 4H, *m*-Ph), 6.88 (s, 1H, CH) |
| $Pt(btfac)_2$ | 8.01 (m, 2H, *o*-Ph), 7.66 (dd, 1H, *p*-Ph), 7.49 (dd, 2H, *m*-Ph), 6.68 (s, 1H, CH) |
| $Pt(tfac)_2$ | 6.01 (s, 1H, CH), 2.08 (s, 3H, $CH_3$) |
| $Pt(tfac)_2$[b] | 5.44 (s, 1H, CH), 2.08 (s, *cis*-$CH_3$), 2.08 (s, *trans*−$CH_3$), *cis*-$CH_3$/*trans*−$CH_3$ = 2:3 |
| $Pt(hfac)_2$ | 6.51 (s, 1H, CH) |

[a] Measured in $CDCl_3$. [b] Measured in $C_6D_6$.

**Table 2. UV−Vis Data for the Platinum Complexes[a]**

| complex | $\lambda_{max}$ ($\epsilon \times 10^{-3}$) |
|---|---|
| $Pt(bac)_2$ | 232 (sh, 12), 254 (18), 282 (21), 310 (sh, 16), 344 (sh, 9.1), 386 (3.2) |
| $Pt(dbm)_2$ | 238 (27), 310 (43), 342 (sh, 31), 368 (sh, 20), 414 (7.3) |
| $Pt(btfac)_2$ | 234 (11), 296 (27), 328 (sh, 18), 352 (17), 366 (sh, 16), 418 (3.4) |
| $Pt(tfac)_2$ | 232 (sh, 7.7), 254 (10), 308 (6.5), 326 (sh, 5.2), 386 (2.3) |
| $Pt(hfac)_2$ | 242 (sh, 5.7), 260 (9.3), 326 (4.5), 344 (sh, 4.0), 424 (1.8) |

[a] sh = shoulder.

NaOH and limited the acidity adjustment of the $HClO_4$ solution to pH = 2.0 before the ligands were added. The use of ethanol appeared to have facilitated the chelation between the metal and ligands due to solubilization of the ligands.[42,43] Our modifications to this synthesis resulted in much improved yields of $Pt(L)_2$. All of the platinum complexes prepared by this modified procedure have been characterized by NMR, mass spectral, and UV−vis spectroscopies, and the data were found consistent with literature values.[41,44]

The following platinum complexes were synthesized by literature procedures with the modifications detailed herein.[41−44]

**Platinum(II) Bis(trifluoroacetylacetonate).** Red, solid $K_2PtCl_4$ (2.41 mmol) was dissolved in 50 mL of 1 N $HClO_4$ by stirring at 50 °C for 1.0 h, resulting in a red solution and a white precipitate of $KClO_4$. After the solution was cooled to room temperature, HgO (7.23 mmol) dissolved in 20 mL of 1 N $HClO_4$ was added with vigorous stirring over a period of 15 min. The stirring at ambient temperature was continued for an additional 2.0 h, at which stage $AgClO_4 \cdot H_2O$ (2.41 mmol) in 10 mL of 1 N $HClO_4$ was added dropwise. The brown precipitates were filtered off promptly, and the greenish yellow filtrate was titrated with 3.5% $K_2CO_3$ to pH = 1.7, giving rise to a white precipitate of $KClO_4$ which was filtered off leaving a greenish-yellow solution of $Pt(H_2O)_4^{2+}$.

A solution of Htfac (11.7 mmol) in 50 mL of ethanol was added to the vigorously stirred solution of $Pt(H_2O)_4^{2+}$ at 40−50 °C. The stirring was continued overnight at this temperature. Copious amounts of yellow precipitate were formed. The precipitate was filtered and redissolved into ∼200 mL $CHCl_3$. The solution was dried over anhydrous $MgSO_4$, and the solvent was removed by rotary evaporation. The yellow powder was redissolved into 20 mL of $CHCl_3$ and passed through a silica gel column (200 mesh, 5 × 30 cm) with 1:1 $CHCl_3$ and a mixture of hexanes. The yellow band was collected, and the solution dried on a rotary evaporator. A yellow powder of $Pt(tfac)_2$, was obtained in a yield of 0.81 g (67%). Mass spectral (*m*/*e*): 348 ($P^+$, tfac), 69 ($CF_3$), 43 ($CH_3C$-(O)).

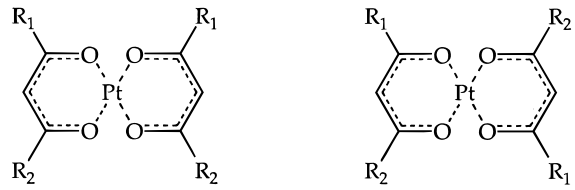
**Platinum(II) Bis(benzoyltrifluoroacetonate).** An orange-yellow powder of $Pt(btfac)_2$ was obtained in 82% yield by following a similar procedure starting from $K_2PtCl_4$ and Hbtfac. Mass spectral (*m*/*e*): 625 ($P^+$), 410 (Pt(btfac)), 215 (btfac).

**Platinum(II) Bis(hexafluoroacetylacetonate).** Red crystals of $Pt(hfac)_2$ were obtained in 85% yield by following the same procedure starting from $K_2PtCl_4$ and Hhfac. Mass spectral (*m*/*e*): 69 ($CF_3$).

**Platinum(II) Bis(benzoylacetonate).** A yellow powder of $Pt(bac)_2$ was obtained in 59% yield by following the same procedure starting from $K_2PtCl_4$ and Hbac. Mass spectral (*m*/*e*): 356 ($P^+$, bac), 105 ($C_6H_5C(O)$), 77 ($C_6H_5$), 43 ($CH_3C(O)$).

**Platinum(II) Bis(dibenzoylmethanate).** A bright yellow powder of $Pt(dbm)_2$ was obtained in 10% average yield by following the literature procedure starting from $K_2PtCl_4$ and Hdbm. This procedure was similar to that described above except that KOH was used in place of $K_2CO_3$ and the pH of the $Pt(H_2O)_4^{2+}$ solution was further adjusted to pH = 3.0 after addition of the ligand dibenzoylmethane. Mass spectral (*m*/*e*): 641 ($P^+$), 418 (Pt(dbm)), 223 (dbm).

**Spectral Data.** The structures for all five platinum complexes are shown below. The spectroscopic characterization data ($^1$H NMR and UV−vis) are compiled in Tables 1 and 2.[45] The cis and trans isomers were not separated.




*cis*-$Pt(L)_2$ *trans*-$Pt(L)_2$

| $Pt(L)_2$ | $R_1$ | $R_2$ |
|---|---|---|
| $Pt(dbm)_2$ | $C_6H_5$ | $C_6H_5$ |
| $Pt(bac)_2$ | $C_6H_5$ | $CH_3$ |
| $Pt(btfac)_2$ | $C_6H_5$ | $CF_3$ |
| $Pt(tfac)_2$ | $CH_3$ | $CF_3$ |
| $Pt(hfac)_2$ | $CF_3$ | $CF_3$ |

## Results and Discussion

**OMSM/TVS Cross-Linking.** We have reported $Pt(acac)_2$ near-UV-light-activated cross-linking of OMSM with TVS.[34] An important feature of this oligomer is the presence of a large proportion of dihydridosilicon groups. Attempts to cure carbosilane oligomers con-

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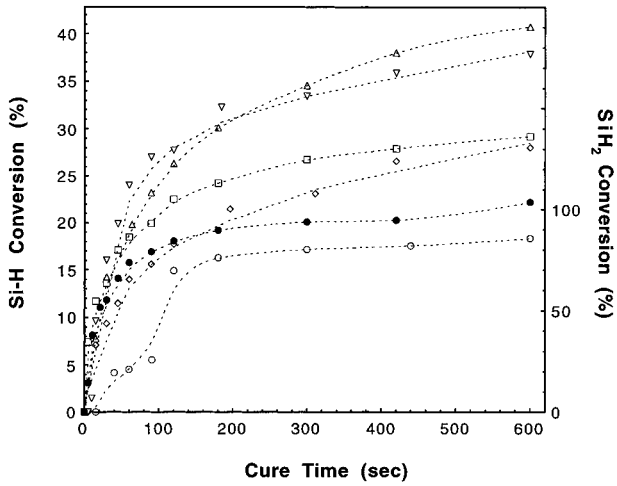



**Figure 1.** FT-IR silicon hydride conversion curves for platinum catalysts under UV irradiation ($\lambda$ > 340 nm) with OMSM and TVS: (△) Pt(bac)$_2$; (○) Pt(dbm)$_2$; (□) Pt(hfac)$_2$; (◇) Pt(tfac)$_2$; (▽) Pt(acac)$_2$; (●) Pt(btfac)$_2$. Incident light intensity is 0.30 W/cm$^2$. SiH$_2$ is fully consumed after ~21% conversion of total SiH$_x$ peak area assuming that SiH$_2$ groups are the most reactive.

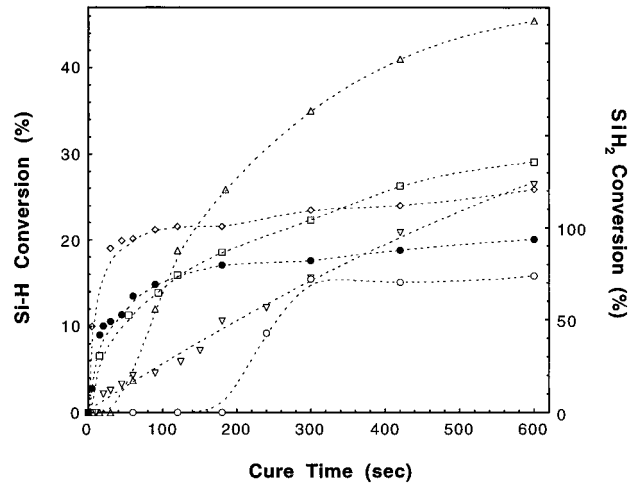



**Figure 2.** FT-IR silicon hydride conversion curves for platinum catalysts under visible irradiation ($\lambda$ > 400 nm) with OMSM and TVS: (△) Pt(bac)$_2$; (○) Pt(dbm)$_2$; (□) Pt(hfac)$_2$; (◇) Pt(tfac)$_2$; (▽) Pt(acac)$_2$; (●) Pt(btfac)$_2$. Incident light intensity is 0.15 W/cm$^2$. SiH$_2$ is fully consumed after ~21% conversion of total SiH$_x$ peak area assuming that SiH$_2$ groups are the most reactive.

taining only monohydridosilicons [−SiH(CH$_3$)−] or containing large proportions of trihydridosilicon groups (−SiH$_3$) in the presence of TVS and Pt(L)$_2$ were not successful. The dihydridosilicon moieties of OMSM are necessary for rapid hydrosilation to occur in this system. Oligomers containing vinylsilane [SiH$_x$(C$_2$H$_3$), $x = 1$ or 2] were cured by the photocatalyst (without TVS) at a slower rate when monohydridosilicon groups ($x = 1$) were predominant compared to the case where SiH$_2$ was abundant ($x = 2$).[46]

Results from dental lamp curing (see Experimental Section) indicated that Pt(tfac)$_2$, Pt(hfac)$_2$, and Pt(btfac)$_2$ cross-link OMSM faster than Pt(acac)$_2$, whereas Pt(bac)$_2$ and Pt(dbm)$_2$ cause polymerization at a slower rate. To substantiate and further quantify these observations, we utilized FT-IR to monitor the changes in the extent of cross-linking, and significantly different results were thus obtained (see Figures1 and 2). With UV irradiation (Figure 1), except for Pt(dbm)$_2$, all the catalysts promoted rapid initial conversion of Si−H, and the highest overall conversion was achieved with Pt(acac)$_2$ and Pt(bac)$_2$. Under visible irradiation (Figure 2), Pt(tfac)$_2$, Pt(hfac)$_2$, and Pt(btfac)$_2$ exhibited rapid initial conversion rates, while Pt(bac)$_2$, after a delay, yielded the highest final conversion. Pt(acac)$_2$ does not absorb appreciably in the visible region. The dental lamp gel times best match the cure rates of the visible-light FT-IR experiment.

The fluorinated photocatalysts appear to cross-link primarily the dihydridosilane (SiH$_2$) end groups in the OMSM, evidenced by the plateaus in the FT-IR curves. Pt(bac)$_2$ and Pt(acac)$_2$ catalyze hydrosilation of both dihydrido- and monohydrido-silicon groups since after about 21% conversion only R$_3$Si−H remains.[47] Photoactivated catalysis with Pt(acac)$_2$ exhibits preferential hydrosilation by SiH$_2$; a similar observation was made with platinum colloids, as well.[34,48] Pt(dbm)$_2$ promotes slow cross-linking rates despite its high extinction coefficient in the entire UV−visible region (Table 2). This is likely caused by the low solubility of Pt(dbm)$_2$ in OMSM/TVS since solids could be observed in irradiated vials containing this mixture. Pt(hfac)$_2$ catalyzes hydrosilation in the dark and is therefore not useful for photoimaging purposes.

**Table 3. Rate Constant ($k_1$) and Half-Life Time ($t_{1/2}$) of the Platinum Catalysts**

| Pt(L)$_2$ | $k_1$ (s$^{-1}$) | $t_{1/2}$ (min) |
|---|---|---|
| | $\lambda$ > 340 nm | |
| Pt(bac)$_2$ | $1.49 \times 10^{-2}$ | 0.8 |
| Pt(dbm)$_2$ | $2.21 \times 10^{-3}$ | 5.2 |
| Pt(hfac)$_2$ | $1.28 \times 10^{-3}$ | 9.0 |
| Pt(btfac)$_2$ | $1.08 \times 10^{-3}$ | 10.7 |
| Pt(tfac)$_2$ | $5.69 \times 10^{-4}$ | 20.3 |
| Pt(acac)$_2$ | $2.00 \times 10^{-4}$ | 57.7 |
| | $\lambda$ > 400 nm | |
| Pt(bac)$_2$ | $4.17 \times 10^{-3}$ | 2.8 |
| Pt(dbm)$_2$ | $8.22 \times 10^{-4}$ | 14.0 |
| Pt(btfac)$_2$ | $3.94 \times 10^{-4}$ | 29.4 |
| Pt(hfac)$_2$ | $3.82 \times 10^{-4}$ | 30.3 |
| Pt(tfac)$_2$ | $1.19 \times 10^{-4}$ | 96.9 |
| Pt(acac)$_2$ | $1.03 \times 10^{-5}$ | 1120 |

**Photolysis of the Platinum Catalysts, Pt(L)$_2$.** Results from absorption spectral measurements with irradiation at $\lambda$ > 340 nm and $\lambda$ > 400 nm are compiled in Table 3 and Figure 3. Figure 3 displays the relative rates of photodecomposition of the catalysts with visible light, whereas Table 3 lists the pseudo-first-order rate constants and the half-lives of the six platinum catalysts at both wavelengths. Regardless of the incident light wavelengths used, the relative photodecomposition rates are in the order Pt(bac)$_2$ > Pt(dbm)$_2$ > Pt(btfac)$_2$ ≈ Pt-

(46) Fry, B. E. Ph.D. Dissertation, Bowling Green State University, 1996, Chapter 4.

(47) From $^{29}$Si NMR, of the silicon groups having SiH$_x$, 57% are monohydridosilane (SiH) and 43% are dihydridosilane (SiH$_2$) groups. Since dihydride reacts preferentially, half of the dihydride in SiH$_2$ will become monohydride early in the hydrosilation. Therefore, after about 21−22% of the total Si−H peak area in the infrared spectrum decays during hydrosilation cross-linking, all remaining Si−H is thought to be monohydridosilicon.

(48) Lewis, L. N.; Uriarte, R. J. *Organometallics* **1990,** *9,* 621.

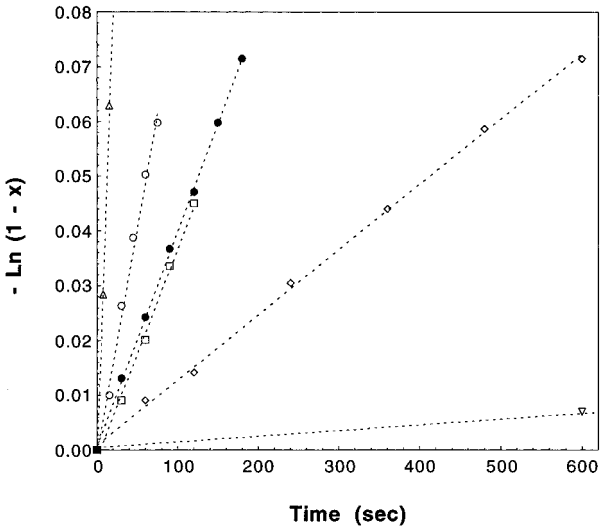



**Figure 3.** First-order photolysis of platinum catalysts in visible light ($\lambda$ > 400 nm) with OMSM and TVS ($6.0 \times 10^{-4}$ M $Pt(L)_2$ in $CH_2Cl_2$): (△) $Pt(bac)_2$; (○) $Pt(dbm)_2$; (□) $Pt(hfac)_2$; (◇) $Pt(tfac)_2$; (▽) $Pt(acac)_2$; (●) $Pt(btfac)_2$. Incident light intensity is 0.15 W/cm$^2$. $Pt(hfac)_2$ starts to show nonlinear behavior after ~5% conversion due to competing dark reaction. The rate constants are listed in Table 3. $X$ = fraction of $Pt(L)_2$ remaining based on optical density of the lowest energy band.

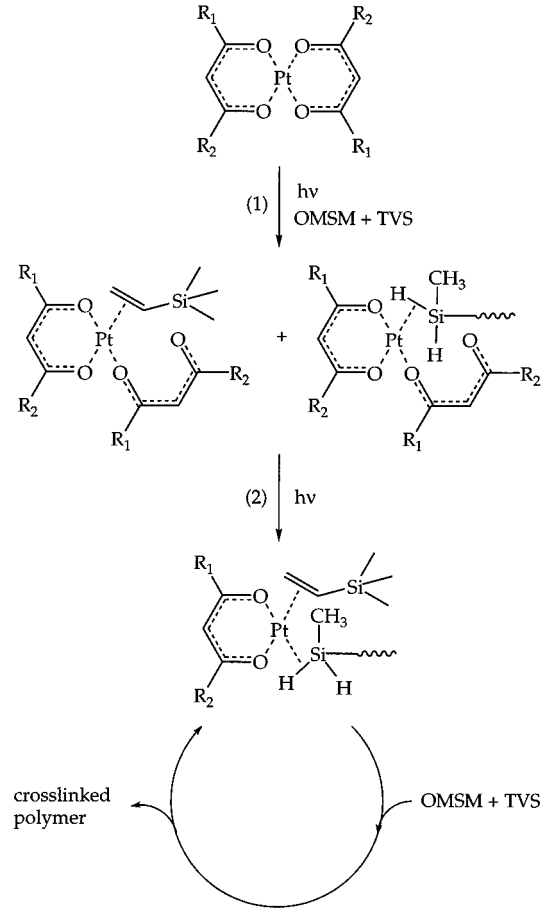
$(hfac)_2$ > $Pt(tfac)_2$ > $Pt(acac)_2$. This reflects the order of extinction coefficients (in the incident light wavelength range) except that $Pt(bac)_2$ and $Pt(dbm)_2$ are reversed. $Pt(hfac)_2$ displayed a significant dark reaction contribution as previously observed.

The photo-cross-linking process of OMSM/TVS using $Pt(L)_2$ as the hydrosilation catalyst is thought to proceed in two major steps (Scheme 1).[32,33,35] Namely $Pt(L)_2$ undergoes Pt−O bond cleavage leading to a ring-opened photoproduct complexed with Si−H or olefin groups, followed by a second Pt−O bond cleavage to remove one of the $\beta$-diketonate ligands, thus generating the active homogeneous catalyst. Step 1 acts in competition with thermal ring closure to regenerate starting material. The secondary photoproduct mediates hydrosilation to yield the cross-linked products. A similar process was recently postulated for photoactivated hydrosilation of silicone polymers with trialkyl($\beta$-dicarbonyl) platinum(IV) complexes.[49,50]

Photolysis of the $Pt(L)_2$ complexes results in bleaching of the lowest energy absorption band and is a measure of step 1 in the activation process. Lewis et al. conducted photolysis studies that correlated the disappearance of this band with the appearance of NMR signals for the primary photoproduct.[35] Thus photolysis (step 1) is a good predictor of the photochemical reactivity of the $Pt(L)_2$ catalysts but is not a direct measure of their relative activities in cross-linking OMSM/TVS.

On the basis of photolysis measurements alone, hydrosilation reactivity might be expected to approximately reflect the magnitude of the $Pt(L)_2$ extinction coefficients. That this is not the case is evidence of solubility effects and a rate-determining step (2). Since the bond conversion study was performed with neat

**Scheme 1. Photoactivation of $Pt(L)_2$ Complexes in the Presence of the OMSM and TVS for Hydrosilation Cross-Linking**




photopolymer, whereas the photolysis study was conducted using dichloromethane solutions (in which $Pt(L)_2$ is highly soluble), the former is most affected by photocatalyst solubility in silane compounds. The relatively fast photolysis of $Pt(dbm)_2$ in contrast to its relatively poor bond conversion rate is probably caused by poor solubility in the photopolymer.

In the UV bond conversion plot (Figure 1) $Pt(acac)_2$ has an unexpectedly fast rate of conversion and in the visible-light bond conversion plot (Figure 2), $Pt(tfac)_2$ and $Pt(bac)_2$ have anomalous initial rates compared to their photolysis rates in $CH_2Cl_2$. These differences in relative rates are probably caused by the photoreactivities and absorption spectra of the primary photoproducts. Step 2 of the mechanism may be thermally activated with certain ligands (particularly fluorinated ones) and photochemically activated with others. To the degree that a second photon is required to produce the secondary photoproduct (active catalyst), the absorption of light by the primary photoproduct can be expected to effect the rates of activation (no data to prove this have been collected to date). If a visible-light-absorbing photocatalyst forms a UV absorbing primary photoproduct, long-wavelength-band bleaching may occur rapidly in visible light while hydrosilation is activated reluctantly. Salvi reported the formation of an intermediate with absorption bands of 318, 276, and 254 nm in the first few minutes of 420 nm photolysis of $Pt(bac)_2$ and triethylsilane.[51] If this is the primary photoproduct of $Pt(bac)_2$, then the hydrosilation delay observed with this

(49) Mayer, T.; Burget, D.; Mignani, G.; Fouassier, J. P. *J. Polym. Sci., Part A: Polym. Chem.* **1996,** *34,* 3141.
(50) Burget, D.; Mayer, T.; Mignani, G.; Fouassier, J. P. *J. Photochem. Photobiol. A: Chem.* **1996,** *97,* 163.

photocatalyst in visible light may be caused by low absorption in the step 2 photoreaction. The absence of such a delay with the fluorinated complexes suggests that either their primary photoproducts absorb in the visible or step 2 in these cases is thermally activated.

**Photopatterning Using the Visible-Light Photocatalysts.** Spin-coated photopolymerizable carbosilane films of approximately 1 $\mu$m thickness were produced on chemically treated (see Experimental Section) silicon wafers for imaging purposes. A pattern was solidified on the wafers by irradiating with visible light ($\lambda$ > 400 nm) through a mask (Figure 4). Flat squares of the preceramic polymer were deposited by this technique. Such patterns are able to undergo pyrolytic conversion to silicon-carbide-containing ceramic (characterization reported) with retention of shape and good adherence to the silicon wafers.[34]

## Conclusion

The visible-light-activated photocatalysts $Pt(bac)_2$, $Pt(tfac)_2$, and $Pt(btfac)_2$ were demonstrated to be useful for rapidly cross-linking a polymer precursor to silicon carbide ceramic. A liquid-to-solid transformation of the polymer can be achieved within minutes using these complexes, thus providing a method for rapid deposition of preceramic patterns formed by light.

(51) Salvi, G. D. Ph.D. Dissertation, Northwestern University, 1993; Chapter 3.

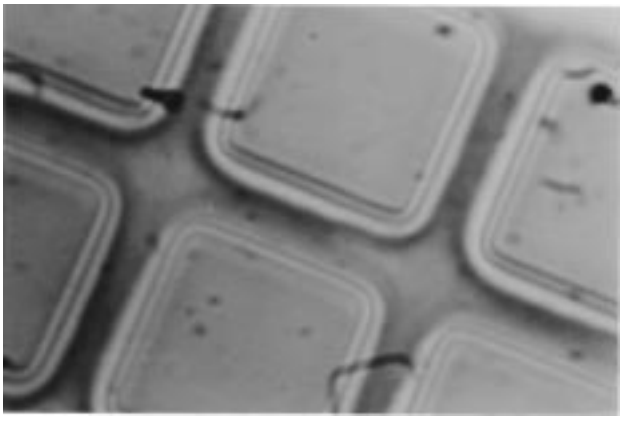


**Figure 4.** Visible-light-cured preceramic polymer images (90 $\mu$m squares) on a silicon wafer made with $Pt(tfac)_2$ as the photocatalyst ($\lambda$ > 400 nm). A spin-coated film of the photopolymer was irradiated for 5 s through a copper mask and rinsed with benzene afterward.

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