

Quantitative Photochemistry of Cp'Pt(CH₃)₃ (Cp' = η⁵-C₅H₄CH₃) in Solution: A Highly Efficient Organometallic Photoinitiator for Hydrosilylation

Vladimir Jakubek and Alistair J. Lees*

Department of Chemistry, State University of New York at Binghamton,
Binghamton, New York 13902-6000

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The quantitative photochemistry of the platinum organometallic complex, Cp'Pt(CH₃)₃ (Cp' = η⁵-C₅H₄CH₃), has been investigated in methylcyclohexane and *n*-pentane solutions at 293 K following UV irradiation into the lowest lying absorption bands. Absolute photochemical quantum efficiency (ϕ_{cr}) results obtained for Cp'Pt(CH₃)₃ at 313 and 366 nm reveal that the system very effectively photoreacts with $\phi_{cr} = 0.34$ – 0.41 in these solvents and 0.79 – 0.85 when 53 mM Et₃SiH is incorporated. These photoefficiencies indicate that the quantitative photochemistry is 2 orders of magnitude higher than previously recognized. The application of Cp'Pt(CH₃)₃ as an effective photoinitiator for hydrosilylation reactions involving vinyl/hydride silicone mixtures is demonstrated.

Several transition-metal organometallic compounds are known to be excellent photoinitiators for various photochemical processes, and they have consequently attracted intense scientific and technological interest.^{1–6}

Notable examples of these photoinitiators are iron sandwich complexes,² titanocenes,³ the [CpFe(CO)₂]₂ dimer (Cp = η⁵-C₅H₅),⁴ (benzene)Cr(CO)₃,⁵ and other transition-metal complexes with d⁶-configurations.⁶ On the other hand, platinum organometallic photoinitiators, such as CpPt(CH₃)₃

and Cp'Pt(CH₃)₃ (Cp' = η⁵-C₅H₄CH₃), have been used much less extensively.⁷ These complexes may have been overlooked because previous studies have indicated that this system has a relatively low quantum efficiency for photo-reaction ($\phi_{cr} = 0.0044$ in methylcyclohexane at 350 nm).⁸

Recent investigations in our laboratory have focused on determining photophysical properties of organometallic complexes and the quantitative nature of their photoreactions. During the course of this work, we have developed a kinetic method for measurement of absolute quantum efficiencies.⁹ This method enables measurements to be performed at low concentrations of the starting complex, and it takes into account complicating inner filter absorbances that change throughout the photochemical reaction. We have now applied this procedure to accurately determine the quantitative photoreaction of Cp'Pt(CH₃)₃ and find, surprisingly, that this molecule undergoes an extremely efficient photochemical reaction following UV-light excitation, similar in magnitude to that of the well-known [CpFe(arene)]⁺ photoinitiator ($\phi_{cr} = 0.2$ – 0.8).^{2,10}

Photoproduced catalytic Pt species are understood to be the same as those formed via established thermal decomposition routes.^{7a} It is also recognized that reductive elimination occurs after initial CH₃ dissociation in CpPt(CH₃)₃, involving a hydrido intermediate,^{11,12} and that analogous Pt(IV) complexes give rise to thermal CH bond activation.¹³ The observation of high quantum efficiency for Cp'Pt(CH₃)₃ is significant for industry, as it is now apparent that this organometallic platinum system is a much more effective

* To whom correspondence should be addressed. E-mail: alees@binghamton.edu.

- (1) (a) Lohse, F.; Zweifel, H. *Adv. Polym. Sci.* **1986**, *78*, 61. (b) Klingert, B.; Reidiker, M.; Roloff, A. *Comments Inorg. Chem.* **1988**, *7*, 109. (c) Dietliker, K. K. In *Chemistry for Coatings, Inks and Paints*; Oldrings, P. K. T., Ed.; SITA Technology Ltd.: London, 1991; Vol. 3, p 228. (d) Cunningham, A. F.; Desorby, A. In *Radiation Curing in Polymer Science and Technology*; Fouassier, J. P., Rabek, J. K., Eds.; Elsevier Applied Science: London, 1993; Vol. 2, p 323.
- (2) (a) Meier, K. *Coord. Chem. Rev.* **1991**, *111*, 97. (b) Jakubek, V.; Lees, A. J. *Inorg. Chem.* **2000**, *39*, 5779 and references therein.
- (3) (a) Pouerrau, D. B.; Geoffroy, G. L. *Adv. Organomet. Chem.* **1985**, *24*, 249. (b) Finter, J.; Riediker, M.; Rohde, O.; Rotzinger, B. *Makromol. Chem., Macromol. Symp.* **1989**, *24*, 177.
- (4) (a) Brown-Wensley, K. A.; DeVoe, R. J.; Palazzotto, M. C. EP Patent 306161, 1987. (b) Palazzotto, M. C.; Brown-Wensley, K. A.; DeVoe, R. J. EP Patent 306162, 1987.
- (5) Wagner, H. M.; Purbrick, M. D. *J. Photogr. Sci.* **1981**, *29*, 230.
- (6) Adair, P. C.; Gottschalk, P. U.S. Patent 494 414, 1988.

- (7) (a) Boardman, L. D. *Organometallics* **1992**, *11*, 4194. (b) Chaiken, J.; Casey, M. J.; Villarica, M. J. *Phys. Chem.* **1992**, *96*, 3183.
- (8) Hackelberg, O.; Wojcicki, A. *Inorg. Chim. Acta* **1980**, *44*, L63.
- (9) Lees, A. J. *Anal. Chem.* **1996**, *68*, 226.
- (10) Lees, A. J. *Coord. Chem. Rev.* **2001**, *211*, 255 and references therein.
- (11) Vedernikov, A. N.; Borisoglebski, S. V.; Solomonov, A. B.; Solomonov, B. N. *Mendeleev Commun.* **2000**, *1*, 20.
- (12) (a) Puddephatt, R. J. *Coord. Chem. Rev.* **2001**, *219*–*221*, 157 and references therein. (b) Reinartz, S.; White, P. S.; Brookhart, M.; Templeton, J. L. *Organometallics* **2000**, *19*, 3748.
- (13) (a) Crumpton-Bregel, D. M.; Goldberg, K. I. *J. Am. Chem. Soc.* **2003**, *125*, 9442. (b) Fekl, U.; Goldberg, K. I. *J. Am. Chem. Soc.* **2002**, *124*, 6804. (c) Reinartz, S.; White, P. S.; Brookhart, M.; Templeton, J. L. *Organometallics* **2000**, *19*, 3854.

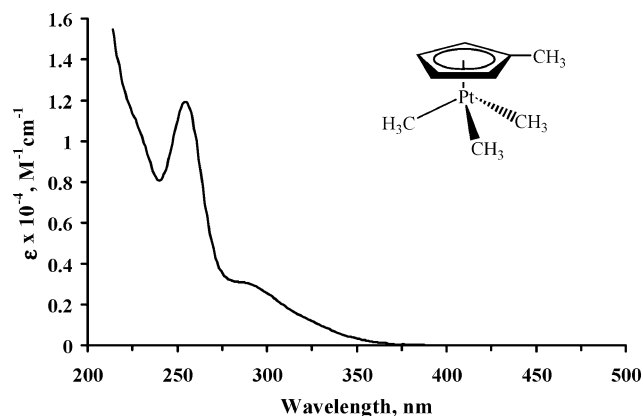
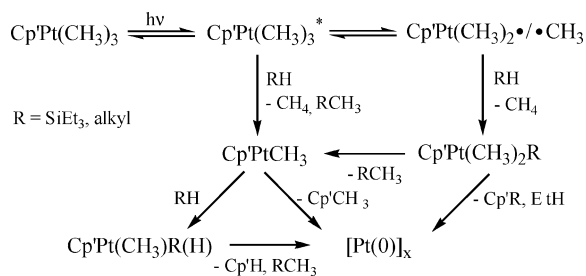


Figure 1. UV-vis absorption spectrum of $\text{Cp}^*\text{Pt}(\text{CH}_3)_3$ in *n*-pentane at 293 K (inset depicts the structure of the complex).

Scheme 1



photoinitiator than previously recognized and represents an alternative system to thermally based Pt complexes and other photoinitiators. The mechanism of thermal Pt-catalyzed reactions has been recently explored in detail¹⁴ and is identical to these Pt photoinitiated systems (see simplified mechanism, Scheme 1).^{7a,11}

The UV-vis absorption spectrum of $\text{Cp}^*\text{Pt}(\text{CH}_3)_3$ in *n*-pentane is shown in Figure 1. The absorption spectrum is dominated by a band centered at 255 nm ($\epsilon = 12300 \text{ M}^{-1} \text{ cm}^{-1}$) and lower energy shoulder at ~ 289 nm; these are tentatively assigned to $\text{Cp} \rightarrow \text{Pt}$ CT and σ -bond (PtCH_3) \rightarrow Pt CT, respectively, analogous to $\text{Cp}_2\text{Ti}(\text{CH}_3)_2$.¹⁵ The energy positions of these two features were observed not to be solvent dependent. Irradiations have been performed at 313 and 366 nm to explore the photochemical reaction taking place following excitations into the lowest lying absorption band of $\text{Cp}^*\text{Pt}(\text{CH}_3)_3$.

Photolyses of $\text{Cp}^*\text{Pt}(\text{CH}_3)_3$ were carried out in methylcyclohexane and *n*-pentane at room temperature, and in each case the photochemical reaction of the platinum complex was monitored by UV-vis spectroscopy at 255 nm. Figure 2a illustrates the UV-vis absorption spectra recorded at 5-min time intervals during the 366-nm excitation of $\text{Cp}^*\text{Pt}(\text{CH}_3)_3$ in methylcyclohexane; the absorption band, centered at 255 nm, progressively decreases in intensity as

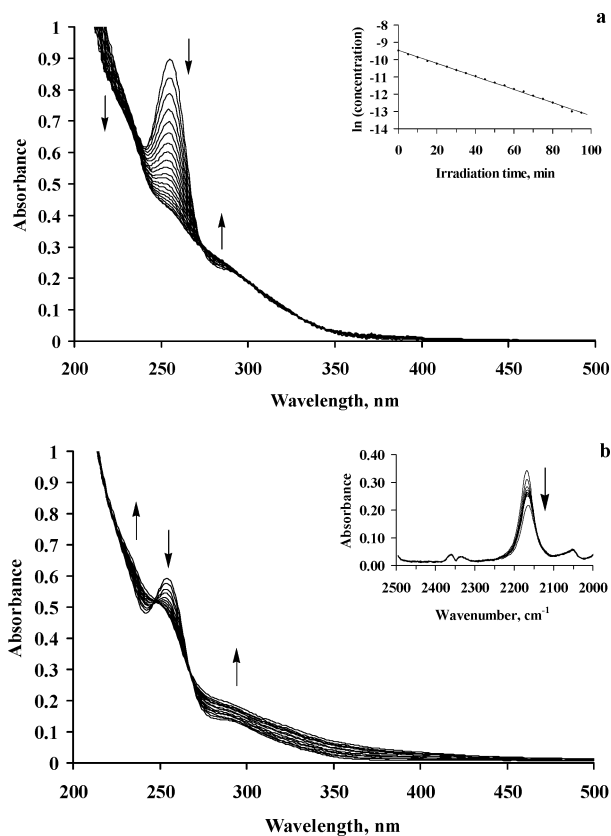


Figure 2. (a) UV-vis absorption spectral changes accompanying the 366-nm photolysis of $7.6 \times 10^{-5} \text{ M}$ $\text{Cp}^*\text{Pt}(\text{CH}_3)_3$ in deoxygenated methylcyclohexane at 293 K (depicted following 5-min irradiation time intervals from 0 to 95 min). Inset depicts photodecomposition of $\text{Cp}^*\text{Pt}(\text{CH}_3)_3$ in methylcyclohexane (absorbance measured at 255 nm). (b) UV-vis absorption spectral changes accompanying the 366-nm photolysis of $5.4 \times 10^{-5} \text{ M}$ $\text{Cp}^*\text{Pt}(\text{CH}_3)_3$ in methylcyclohexane containing 53 mM Et_3SiH at 293 K (depicted following 5-min irradiation time intervals from 0 to 95 min). Inset shows infrared spectral changes of Si-H stretch at 2169 cm^{-1} in a vinyl/hydride silicone mixture containing $\text{Cp}^*\text{Pt}(\text{CH}_3)_3$ (520 ppm of Pt) following an initial 1-min UV irradiation (depicted following 0.5-min time intervals from 0 to 4.5 min, and then a final one after 30 min).

the reaction proceeds. Irradiation at 366 nm of a $7.6 \times 10^{-5} \text{ M}$ solution of $\text{Cp}^*\text{Pt}(\text{CH}_3)_3$ in methylcyclohexane resulted in clean first-order disappearance of the platinum complex as seen in the inset in Figure 2a. The photochemistry was determined to be the same at 313 and 366 nm and uncomplicated by any thermal processes or secondary photoreactions under these experimental conditions. Figure 2b depicts the UV-vis absorption spectra recorded at 5-min time intervals during the 366-nm excitation of a $5.4 \times 10^{-5} \text{ M}$ solution of $\text{Cp}^*\text{Pt}(\text{CH}_3)_3$ in methylcyclohexane containing 53 mM triethylsilane (Et_3SiH). The absorption band at 255 nm decreases in intensity, and new absorption bands arise at both lower and higher energies as the reaction proceeds.

Absolute photochemical quantum efficiencies for chemical reaction (ϕ_{cr}) have been obtained for the disappearance of $\text{Cp}^*\text{Pt}(\text{CH}_3)_3$ following excitation at 313 and 366 nm. These values were determined by our previously reported procedure, which accounts for the substantial increasing inner filter absorbances due to the photoproducts,⁹ as applied recently to a wide range of organometallic photoreactions.^{2b,10} The obtained photochemical quantum efficiencies for $\text{Cp}^*\text{Pt}(\text{CH}_3)_3$ are shown in Table 1, revealing that the photochemistry

(14) (a) Roy, A. K.; Taylor, R. B. *J. Am. Chem. Soc.* **2002**, *124*, 9510. (b) Marciniec, B. *Silicon Chem.* **2002**, *1*, 155. (c) Sakaki, S.; Mizoe, N.; Sugimoto, M.; Musashi, Y. *Coord. Chem. Rev.* **1999**, *190–192*, 933. (d) Sakaki, S.; Sumimoto, M.; Fukuhara, M.; Sugimoto, M.; Fujimoto, H.; Matsuzaki, S. *Organometallics* **2002**, *21*, 3788.
(15) (a) Bruce, M. R. M.; Kenter, A.; Tyler, D. R. *J. Am. Chem. Soc.* **1984**, *106*, 639. (b) Kenney, J. W., III; Boone, D. R.; Striplin, D. R.; Cheng, Y.-H.; Hamar, K. B. *Organometallics* **1993**, *12*, 3671.

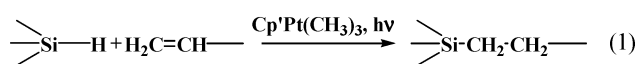
Table 1. Absolute Photochemical Quantum Efficiencies (ϕ_{cr}) for Decomposition of $Cp^*Pt(CH_3)_3$ in Various Solvents at 293 K Following Excitation at 313 and 366 nm^a

solvent	ϕ_{cr}	
	313 nm	366 nm
methylcyclohexane		0.34
<i>n</i> -pentane	0.41	0.41
<i>n</i> -pentane/ Et_3SiH^b	0.79	0.85

^a Errors estimated at $\pm 10\%$. ^b 53 mM Et_3SiH .

proceeds extremely efficiently. Clearly, the photoreaction of $Cp^*Pt(CH_3)_3$ is a much more effective process than currently thought ($\phi_{cr} = 0.34$ in methylcyclohexane at 366 nm) as previously the ϕ_{cr} value was determined to be 0.0044 following 350-nm irradiation of $CpPt(CH_3)_3$ in methylcyclohexane.^{8,16} It can be seen that the ϕ_{cr} values are not particularly dependent on the irradiation wavelength, although they are even higher in the presence of 53 mM triethylsilane ($\phi_{cr} = 0.79$ – 0.85) than in the neat solvents. The mechanism of the photoreaction involves initial cleavage of one of the Pt–CH₃ bonds,^{7a,8,11} and the high ϕ_{cr} values are consistent with the σ -bond (PtCH₃) \rightarrow Pt CT assignment.¹⁵ Moreover, the higher ϕ_{cr} values in Et_3SiH solution reveal a substantial recombination reaction in neat solvent, with an added amount of scavenging reactant resulting in the back reaction becoming less influential.¹⁷

Having established that $Cp^*Pt(CH_3)_3$ is exceptionally efficient photochemically, we set out to explore whether it is also able to act effectively as a photoinitiator. Photolysis of the Pt complex was performed in a vinyl/hydride silicone mixture, and effective, photoinduced hydrosilylation was observed.¹⁸ The monitored hydrosilylation process is an addition reaction of Si–H compounds to unsaturated organic molecules with the aid of Pt complex catalyst (normally this is a thermal catalyst) and has been widely used for Si–C formation (see eq 1). Infrared spectral changes of the Si–H



stretch at 2169 cm^{-1} were followed via real time FTIR monitoring after an initial 1-min UV irradiation; these results are shown in the inset of Figure 2b. The spectra confirm

(16) Discrepancies of almost 2 orders of magnitude in ϕ_{cr} cannot be attributed to inner filter effects alone or, indeed, normal experimental measurement and may be related to errors in the actinometry calculations.

(17) Dunwoody, N.; Lees, A. J. *Inorg. Chem.* **1997**, *16*, 5770.

(18) Lewis, L. N.; Lewis, N. *J. Am. Chem. Soc.* **1986**, *108*, 7228.

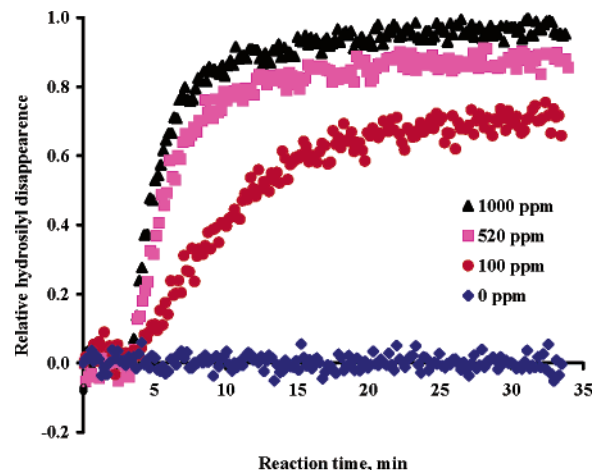


Figure 3. Effect of various Pt amounts during 20 min of UV irradiation time on the photohydrosilylation reaction of a vinyl/hydride silicone mixture at 293 K. Infrared measurements were recorded for 20 min UV irradiation with initial 3 min and subsequent 10 min periods in the dark. The relative hydrosilyl disappearance is determined by the changes in the integrated infrared absorbance at 2169 cm^{-1} from initial to final readings (based on data at 1000 ppm).

that the photohydrosilylation reaction proceeds very effectively following UV irradiation of the platinum complex. Similar results were also obtained with varying amounts of added photoinitiator (see Figure 3), and these illustrate the reaction of the hydrosilyl groups with vinyl groups to form the cross-linked polymer,¹⁸ even at low concentrations of Pt complex (100 ppm of Pt). In a control study without Pt complex present, no reaction was observed upon irradiation. Also, when the Pt complex was incorporated (520 ppm of Pt) and in the absence of light, no reaction occurred. However, it is noted in the data at 100 ppm Pt that the reaction proceeds thermally to completion after the initial period of light irradiation; this is consistent with the complex acting as a photoinitiator, which subsequently forms a catalytic species. This catalytic behavior was confirmed for shorter irradiation times.

The recognition of highly efficient photochemistry of $Cp^*Pt(CH_3)_3$ opens up many more possibilities for industrial applications. These may involve usage as a photoinitiator in various free-radical polymerization processes, such as acrylate polymerization, photohydrosilylation, and photohydrosilylation, which can be applied in solvent-free adhesives, coatings, dental materials, and gaskets.¹⁹

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(19) (a) Boardman, L. D.; Oxman, J. D. JP Patent 2873022, 1999. (b) Oxman, J. D.; Boardman, L. D. EP Patent 561893, 1996. (c) Drahnak, T. J. JP Patent 2500250, 1996. (d) Boardman, L. D. U.S. Patent 5 169 727, 1992.