

on the analytical data, as well as on modeling studies.

Another interesting result is the stabilization by the surface of a tris(neopentyl)zirconium(IV) complex. This tetracoordinated (siloxy)tris(neopentyl)zirconium complex is a highly electron-deficient d^0 complex; stabilization is probably related to steric crowding at the Zr center, even if one considers that some $p\pi-d\pi$ donation by siloxy oxygens could eventually participate in this stabilization. Studies on stoichiometric or catalytic reactions of such systems are now under investigation.

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**The Product of the Reaction of
trans-Diamminedichloroplatinum(II) with Diamines Is
Dependent on Chain Length. Example of a Bridging
Ethylenediamine and Formation of a Novel Trans-Chelated
Structure with 1,5-Pentanediamine**

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Bis(platinum) complexes containing two platinum-amine coordination spheres linked by a variable length diamine chain are of interest for their chemical and biological properties.¹⁻³ The most general formula for bis(platinum) complexes with chloride and amine ligands is $[\{PtCl_m(NH_3)_{3-m}\}_2(\text{diamine})]^{2(2-m)+}$ ($m = 0-3$, and the diamine is usually $H_2N(CH_2)_nNH_2$), and our studies include the design of synthetic pathways to all possible isomers of these complexes. Recently we reported the properties of a complex containing monodentate coordination spheres ($m = 1$, above) of specific formula $[\{trans-PtCl(NH_3)_2\}_2(NH_2(CH_2)_4NH_2)]Cl_2$.⁴ This complex is of particular interest for its DNA interstrand cross-linking ability and antitumor activity in cell lines resistant to cisplatin. We wished to examine this series of complexes further to study how these properties are affected by varying diamine chain length. The synthesis involves reaction of 1 equiv of diamine with 2 equiv of *trans*- $[PtCl_2(NH_3)_2]$.^{1,5}

$$2 \text{ trans-}[PtCl_2(NH_3)_2] + H_2N(CH_2)_nNH_2 \rightarrow [\{trans-PtCl(NH_3)_2\}_2H_2N(CH_2)_nNH_2]Cl_2$$

The starting material (0.3 g, 0.001 mol) is suspended in H_2O (40 mL) with stirring at 60 °C. A half-equivalent of the appropriate diamine is slowly added dropwise, and stirring is maintained at 60 °C for 3 h, during which time all the *trans*- $[PtCl_2(NH_3)_2]$ dissolves. Upon cooling, the solution is filtered and evaporated in volume to approximately 2 mL and MeOH (50 mL) added. The white precipitate is then filtered off and recrystallized consecutively in $H_2O/MeOH$ until pure. In this contribution we show that the products obtained are dependent on diamine chain length, and with 1,5-pentanediamine we describe the characterization of a novel trans-chelated monomeric species where the amine groups of the pentanediamine bind in mutually trans positions to the same platinum center.

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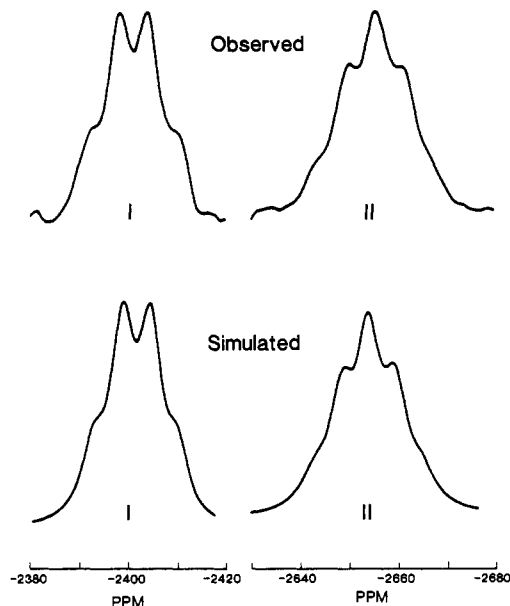
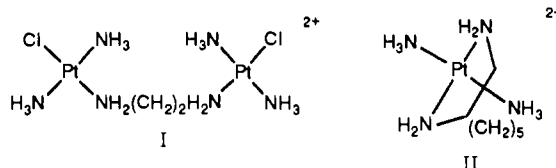


Figure 1. Observed and simulated ^{195}Pt NMR spectra of $[\{trans-PtCl-(^{15}NH_3)_2\}_2H_2^{15}N(CH_2)_2^{15}NH_2]Cl_2$ (I) containing bridging ethylenediamine and *trans*- $[Pt(^{15}NH_3)_2(H_2^{15}N(CH_2)_3^{15}NH_2)]Cl_2$ (II) with trans-chelating 1,5-pentanediamine. See the text for structures.

The characterization and analytical data for the $n = 2-4$ diamines are consistent with the formation of the proposed bis(platinum) product.⁶ In contrast the $n = 5$ derivative showed a ^{195}Pt NMR chemical shift at -2679 ppm (relative to $PtCl_6^{2-}$) more characteristic of a PtN_4 core, no $\nu(Pt-Cl)$ in the IR spectrum, and an elemental analysis indicating the presence of only 1 Pt per diamine.⁶ These results are consistent with a platinum-tetraamine complex $[Pt(NH_3)_2(H_2N(CH_2)_5NH_2)]Cl_2$, but in this case the 1,5-pentanediamine must chelate trans positions. Diamines with longer chain lengths ($n = 6-8$) gave a mixture of products as indicated by two peaks in the ^{195}Pt NMR spectrum corresponding to PtN_3Cl and PtN_4 coordination spheres.⁷

To confirm the structural assignments, we prepared ^{15}N -substituted complexes for $n = 2$ (complex I) and $n = 5$ (complex II).



For both complexes, a plot of conductivity versus equivalent concentration^{8,9} showed that both complexes behave as 1:2 electrolytes in comparison to standards such as $[Pt(NH_3)_4]^{2+}$, $[Pt(NH_3)_2(en)]^{2+}$ (complex III), $[Co(NH_3)_6]^{3+}$, and $[\{Pt(NH_3)_3-(H_2N(CH_2)_nNH_2)\}_2]^{4+}$ ($n = 4, 5$).¹⁰ Table I summarizes the spectral data. The ^{15}N NMR spectrum of the ethylenediamine

- (6) Analytical data for $n = 2$ are as follows. Anal. Calcd for $C_8H_{20}N_6Cl_4Pt_2$: C, 3.64; H, 3.05; N, 12.73; Cl, 21.48. Found: C, 3.62; H, 3.04; N, 12.63; Cl, 21.16. $\delta(^{195}Pt) = -2415$ ppm, $\delta(^1H) = 3.07$ ppm. $\nu(NH) = 3300, 3190, 3120$ cm^{-1} , $\nu(Pt-Cl) = 344$ cm^{-1} . Analytical data for $n = 3$ are as follows. Anal. Calcd for $C_9H_{22}N_6Cl_4Pt_2$: C, 5.34; H, 3.29; N, 12.46; Cl, 21.03. Found: C, 5.50; H, 3.28; N, 12.46; Cl, 20.53. $\delta(^{195}Pt) = -2421$ ppm, $\delta(^1H) = 2.78, 2.11$ ppm. $\nu(NH) = 3100$ (br), 3170 cm^{-1} , $\nu(Pt-Cl) = 330$ cm^{-1} . The properties of the $n = 4$ complex were as reported.^{4,5} Analytical data for $n = 5$ are as follows. Anal. Calcd for $C_{12}H_{20}N_4Cl_2Pt$: C, 14.93; H, 5.01; N, 13.93; Cl, 17.63. Found: C, 14.99; H, 5.25; N, 13.79; Cl, 17.94. $\delta(^{195}Pt) = -2679$ ppm, $\delta(^1H) = 2.68, 1.66, 1.38$ ppm. $\nu(NH) = 3160, 3080$ cm^{-1} . Spectral conditions are as per Table I.
- (7) For $n = 6$, -2425 and -2678 ppm, for $n = 7$, -2418 and -2673 ppm, and for $n = 8$, -2431 and -2682 ppm. Spectral conditions are as per Table I.
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Table I. NMR Parameters for $[[trans\text{-PtCl}(\text{}^{15}\text{NH}_3)_2\text{H}_2\text{}^{15}\text{N}(\text{CH}_2)_2\text{}^{15}\text{NH}_2]\text{Cl}_2$ (I), $trans\text{-[Pt}(\text{}^{15}\text{NH}_3)_2(\text{H}_2\text{}^{15}\text{N}(\text{CH}_2)_5\text{}^{15}\text{NH}_2)]\text{Cl}_2$ (II), and $cis\text{-[Pt}(\text{}^{15}\text{NH}_3)_2(\text{H}_2\text{}^{15}\text{N}(\text{CH}_2)_2\text{}^{15}\text{NH}_2)]\text{Cl}_2$ (III)^a

nucleus	complex I		complex II		complex III	
	δ	J	δ	J	δ	J
^1H	3.06 (m)		1.40 (m) 1.68 (m) 2.67 (m)		2.6	$^3J(\text{Pt-H}) = 40.5$
^{13}C	49.27	$^1J(\text{C-N}) = 5.1$ $^2J(\text{Pt-C}) = 64.7$	25.87 33.04 48.99	$^3J(\text{Pt-C}) = 37.35$ $^2J(\text{Pt-C}) = 39.55$	49.87	
$^{15}\text{N}_d$	-49.0	$^1J(\text{Pt-N}) = 344$	-41.5	$^1J(\text{Pt-N}) = 291$	-28.2	$^1J(\text{Pt-N}) = 278$
$^{15}\text{N}_a$	-61.2	$^1J(\text{Pt-N}) = 287$	-60.5	$^1J(\text{Pt-N}) = 304$	-64.3	$^1J(\text{Pt-N}) = 320$
^{195}Pt	-2401		-2655		-2795	

^a All spectra were run on a Bruker 250-MHz spectrometer. Derived coupling constants in Hz are given when resolved. Solvent D_2O for ^1H and ^{13}C , H_2O for ^{15}N and ^{195}Pt . ^1H , ^{13}C relative to TMS, ^{195}Pt relative to PtCl_6^{2-} , ^{15}N relative to $^{15}\text{NH}_4\text{NO}_3$. m = multiplet. N_a refers to N of NH_3 , N_d refers to N of $\text{H}_2\text{N}(\text{CH}_2)_n\text{NH}_2$ ($n = 2$ or 5). Free ethylenediamine has $\delta(^1\text{H}) = 3.42$ ppm and $\delta(^{13}\text{C}) = 39.20$ ppm. Free 1,5-pentanediamine dihydrochloride has $\delta(^1\text{H}) = 1.45$ (C3), 1.72 (C2,4), and 3.02 (C1,5) ppm and $\delta(^{13}\text{C}) = 25.08$ (C3), 28.61 (C2,4), and 41.95 (C1,5) ppm.

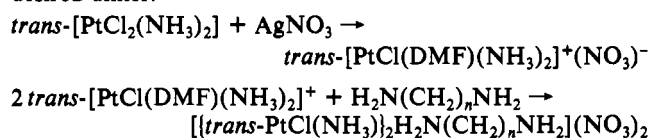
complex I showed the expected two principal resonances with satellites from which $^1J(\text{Pt-N}_d) = 344$ Hz (N trans Cl) and $^1J(\text{Pt-N}_a) = 287$ Hz (N trans N) were derived, consistent with previously reported values.¹¹ Complex II also showed the two expected ^{15}N resonances with satellites with $^1J(\text{Pt-N}_d) = 291$ Hz and $^1J(\text{Pt-N}_a) = 304$ Hz (both N trans N). The assignment of N_d was confirmed by preparing the partially substituted complex $trans\text{-[Pt}(\text{NH}_3)_2(\text{H}_2\text{}^{15}\text{N}(\text{CH}_2)_5\text{}^{15}\text{NH}_2)]\text{Cl}_2$ (using only labeled diamine in the reaction), which displayed only one triplet at -41.4 ppm ($^1J(\text{Pt-N}_d) = 292$ Hz) in the ^{15}N NMR spectrum. The ^{195}Pt NMR spectrum of I consisted of a broad quartet due to overlap of the doublet splitting (coupling to the unique N of the diamine) and the triplet (coupling to the two equivalent NH_3 groups). In contrast, the ^{195}Pt NMR spectrum of II now shows a more complicated five-line pattern from overlap of the two expected triplets.¹² Figure 1 shows the observed and simulated spectra.¹³ The fully ^{15}N -substituted complex $cis\text{-[Pt}(\text{}^{15}\text{N-en})(\text{}^{15}\text{NH}_3)_2]^{2+}$ prepared from $[\text{PtCl}_2(\text{}^{15}\text{N-en})]$ and $^{15}\text{NH}_4\text{Cl}$ also gave the expected five-line pattern from overlap of two triplets centered at -2795 ppm.

In favorable cases, further information for the structural assignments may be obtained from ^1H and ^{13}C NMR spectral data. Detailed ^1H and ^{13}C NMR analysis of weak Pt-H-C interactions in the series $trans\text{-[PtCl}_2(\text{L})(\text{substituted quinoline})]$ (L is for example PR_3 and AsR_3) showed that the proton chemical shifts of nonbonded protons in axial positions are deshielded.¹⁴ Weak Pt-H and Pt-C coupling can be observed, the magnitude of which is dependent on the strength of the Pt-H-C interaction. While these observations may not necessarily extend to the present case, we considered it worthwhile to examine the spectra (Table I). The ^1H NMR chemical shifts of both bridging (complex I) and chelated ethylenediamine (complex III) are in fact shielded with respect to the free ligand (3.06 and 2.69 ppm, respectively, compared to 3.42 ppm). The ^{13}C NMR chemical shifts show little difference although there is now an approximate 10 ppm deshielding compared to the free ligand. Both $^1J(^{13}\text{C-N})$, 5.1 Hz, and $^2J(^{195}\text{Pt-}^{13}\text{C})$, 64.7 Hz, couplings could be observed for complex I. The ^1H NMR spectrum of II at 30 °C gives broad peaks for all sets of $-\text{CH}_2-$ protons, indicating that despite the relatively constrained nature of the chelate no major barriers to rotation are observed. As with en, no major chemical shift differences are noted between chelated (complex II) and bridging diamine.⁸ In the ^{13}C NMR spectrum, the amine-bound carbon is deshielded by 7.13 ppm, while the C2 and C4 carbon atoms are also deshielded by 4.45 ppm. At the field strength employed, poorly resolved Pt-C coupling was observed for both signals. The presence of $^3J(\text{Pt-C})$ could support a close contact between these

two atoms, but clearly the factors affecting NMR parameters in bridging diamines are not as clearly defined as the quinoline case.¹⁴

The combined NMR data nevertheless strongly support the novel structures for both complexes. Finally, comparison of the IR spectra of both I and II with standard complexes containing either chelating or bridging diamine agrees with the assignments presented here.^{10,15} In the case of I the complex represents a unique example of bridging ethylenediamine in platinum chemistry. A complex¹⁶ reported as $[[trans\text{-PtCl}_2(\text{C}_2\text{H}_4)_2(\text{en})]$ (en = ethylenediamine) has been reassigned as the salt $[\text{PtCl}(\text{en})(\text{C}_2\text{H}_4)][\text{PtCl}_3(\text{C}_2\text{H}_4)]$.¹⁷ Complex II is the first example of trans chelation using a straight chain alkanediamine. In this case $n = 5$ is the minimal chain length necessary for trans chelation, giving an eight-membered ring. The formation of the complex may be easily understood by considering that the first end of the diamine binds to the Pt center to produce a species such as $trans\text{-[PtCl}(\text{NH}_3)_2\text{H}_2\text{N}(\text{CH}_2)_n\text{NH}_2]^+$ with a "dangling" diamine ligand. Dependent on diamine chain length, this species may react with a further 1 mol of $trans\text{-[PtCl}_2(\text{NH}_3)_2]$ to give the dinuclear species, form a trans chelate, or react with itself to initiate formation of polymeric tetraamines. For $n = 5$, attack of the free amine end on the remaining chloride is favored over attack on a second Pt.

Variation of conditions (pH, stoichiometry, order of addition) shows evidence (^{195}Pt NMR) for formation of the $n = 5$ bis-(platinum) complex, but in no case was a unique preparation of this species observed and the major species in all cases is II. Diamines with longer chain length give mixtures corresponding to both I and II. Use of the salt $\text{H}_3\text{N}(\text{CH}_2)_5\text{NH}_3^{2+}(\text{Cl})_2$ in the presence of base (Et_3N) did give improved yields of the bis-(platinum) complex. The bridging complexes for $n > 5$ are in fact best obtained by preparing in situ the cation $trans\text{-[PtCl}(\text{DMF})(\text{NH}_3)_2]^+$.¹⁸ The DMF is selectively displaced, giving the desired dimer:¹⁹



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 (19) Upon filtration and evaporation to dryness, the complexes were dissolved in H_2O , filtered to remove any unreacted starting material, and recrystallized from H_2O /acetone. Analytical data for $n = 5$ are as follows. Anal. Calcd for $\text{C}_5\text{H}_{26}\text{N}_8\text{Cl}_2\text{O}_2\text{Pt}_2$, 0.5 acetone: C, 9.95; H, 3.73; N, 14.29; Cl, 9.04. Found: C, 10.61; H, 3.98; N, 14.63; Cl, 9.26. $\delta(^{195}\text{Pt})$ -2434 ppm, $\delta(^1\text{H})$ 2.68, 1.70, 1.40 ppm. $\delta(^1\text{H})$ (acetone) 2.2 ppm. Analytical data for $n = 6$ are as follows. Anal. Calcd for $\text{C}_6\text{H}_{28}\text{N}_8\text{Cl}_2\text{O}_2\text{Pt}_2$, 0.5 acetone: C, 11.22; H, 3.51; N, 14.04; Cl, 8.90. Found: C, 10.91; H, 3.83; N, 14.50; Cl, 8.82. $\delta(^{195}\text{Pt})$ -2416 ppm, $\delta(^1\text{H})$ 2.68, 1.69, 1.38 ppm. $\delta(^1\text{H})$ (acetone) 2.2 ppm.

Examples of trans-chelating ligands in platinum complexes are rare. Use of diethylenetriamine (dien) with the central N methylated allowed isolation of a complex containing trans-chelating dien (thus also an eight-membered ring) by a complicated procedure involving reduction from Pt(IV) to Pt(II).²⁰ Similarly, phosphines with bulky substituents have been used to produce complexes such as *trans*-[PtCl₂(*t*-Bu₂P(CH₂)_nP-*t*-Bu₂)] (*n* = 9, 10).²¹ Systems such as *trans*-[PtCl₂(L)] and *trans*-[PtHCl(L)], where L is a bidentate ligand with the phosphine or arsine donor atoms bridged by the rigid benzo[*c*]phenanthrene skeleton have also been examined in detail.^{22,23} Complex II thus represents the simplest reported example of a trans-chelating ligand. The mechanism of substitution and the generality of the reaction are being studied further.

Acknowledgment. This work is supported by a grant from the American Cancer Society (ACS CH-463). We thank Prof. T. G. Appleton for helpful comments.

Registry No. I, 138666-63-4; II, 138666-64-5; III, 138666-70-3; *trans*-[PtCl₂(NH₃)₂], 14913-33-8; [[*trans*-PtCl(NH₃)₂]₂H₂N-(CH₂)₃NH₂]₂Cl₂, 129370-25-8; [[*trans*-PtCl(NH₃)₂]₂H₂N(CH₂)₂NH₂]₂Cl₂, 129370-24-7; [Pt(NH₃)₂(H₂N(CH₂)₆NH₂)]Cl₂, 138666-65-6; [Pt(NH₃)₂(H₂N(CH₂)₇NH₂)]Cl₂, 138666-66-7; [Pt(NH₃)₂(H₂N(CH₂)₈NH₂)]Cl₂, 138666-67-8; [[*trans*-PtCl(NH₃)₂]₂H₂N(CH₂)₆NH₂]₂Cl₂, 125408-81-3; [[*trans*-PtCl(NH₃)₂]₂H₂N(CH₂)₇NH₂]₂Cl₂, 138666-68-9; [[*trans*-PtCl(NH₃)₂]₂H₂N(CH₂)₈NH₂]₂Cl₂, 138666-69-0.

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Photochemical Formation of Oxochromium(IV) Tetraphenylporphyrin from Nitrochromium(III) Tetraphenylporphyrin in Benzene

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It has been well recognized that synthetic metalloporphyrins with central metals Fe, Co, Rh, and Mn react with simple diatomic molecules O₂, CO, and NO to yield their adducts. Laser photolysis studies have revealed that these adducts readily liberate the diatomic molecules to give metalloporphyrins upon photoexcitation.¹⁻⁸ The photoreaction is simply interpreted in terms of the photoinduced dissociation of the axial diatomic molecules from the central metal.

In the present work, we have carried out photochemical studies of nitrochromium(III) tetraphenylporphyrin, ONO-Cr^{III}TPP, which is considered to be an adduct of a triatomic molecule NO₂ of chromium(II) tetraphenylporphyrin, Cr^{II}TPP.

Experimental Section

Chlorochromium(III) tetraphenylporphyrin, ClCr^{III}TPP, was synthesized and purified according to the literature.⁹ Further purification

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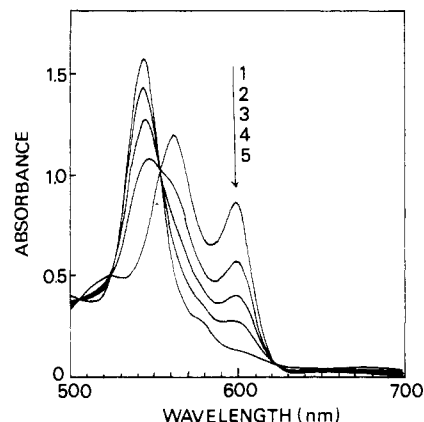
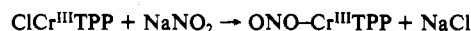


Figure 1. Absorption spectral changes observed for a benzene solution of 1.12×10^{-4} M ONO-Cr^{III}TPP upon irradiation with the mercury lamp with a cutoff filter ($\lambda > 420$ nm): 1, before irradiation; 2, after 10 min; 3, after 30 min; 4, after 70 min; 5, after 150 min.

of ClCr^{III}TPP was carried out by column chromatography with the use of Sephadex LH 20 resin and acid methanol containing 0.1 M HCl as an eluent.

ONO-Cr^{III}TPP was prepared by the anion-exchange method:



A dichloromethane solution of ClCr^{III}TPP and an aqueous solution of NaNO₂ were mixed and stirred for 3 h at room temperature. After removal of the aqueous phase by a funnel, the dichloromethane solution was washed several times with distilled water. The solvent, dichloromethane, was evaporated under reduced pressure, and the resulting solid was dissolved in benzene. After filtration, the solvent, benzene, was evaporated from the filtrate under reduced pressure. The dark solids obtained were dissolved again in boiling diethyl ether. Solids insoluble in diethyl ether were filtered off, and the filtrate was kept in the dark for 2 days to give black needle crystals. Anal. Calcd for ONO-Cr^{III}TPP·(C₂H₅)₂O·H₂O: C, 71.8; H, 4.98; N, 8.73. Found: C, 71.51; H, 4.78; N, 8.64. The absorption spectrum of ONO-Cr^{III}TPP is similar to that of ClCr^{III}TPP. The molar absorption coefficients in benzene are obtained as 2.1×10^5 and 1.12×10^4 M⁻¹ cm⁻¹ at 447 and 560 nm. IR spectrum of ONO-Cr^{III}TPP in KBr pellet, in comparison with that of ClCr^{III}TPP, is found to show characteristic absorption at 727, 1010, and 1622 cm⁻¹.

Laser photolysis was performed with a Nd-YAG laser (HY 500 from JK Lasers, Ltd.) equipped with second, third, and fourth harmonic generators. The detection system of transient spectra was described elsewhere.¹⁰

Quantum yield measurements by the steady light photolysis method were made with the use of monochromatic light from a xenon lamp incorporated in a Hitachi MPF 4 spectrofluorometer. The relative light intensity distribution of the xenon lamp in the region 290-600 nm was determined by measuring the excitation spectrum or rhodamine B in ethylene glycol (8 g/L). The photon flux at 313 nm was measured by actinometry with an aerated cyclohexane solution of *N*-methyl-diphenylamine: the quantum yield for the formation of *N*-methylcarbazole from *N*-methyl-diphenylamine has been determined as 0.45.¹¹ From the light intensity distribution and the photon flux at 313 nm, a photon flux at a given wavelength was obtained.

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