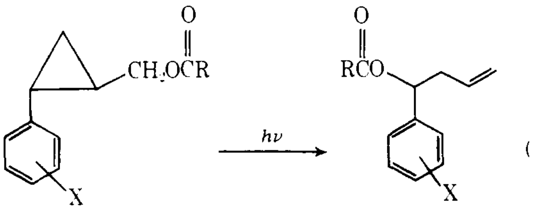
Arylcyclopropane Photochemistry. Substituent Effects on the Photochemical Cyclopropylcarbinyl-Homoallyl Rearrangement of 2-Arylcyclopropylcarbinyl Acetates

Sir:

trans-2-Phenylcyclopropylcarbinyl acetate (**1a**) undergoes a singlet-state photochemical rearrangement to the homoallyl acetate **2a** (eq 1).[1] Other 2-arylcyclopropylcarbinyl acetates

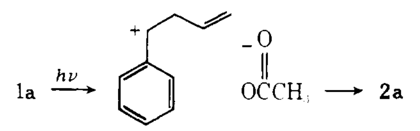


(1)

1a–h, R = CH_3 **3a–h**, R = $C(CH_3)_3$
a, X = H
b, X = *p*-CH_3
c, X = *m*-CH_3
d, X = *p*-OCH_3
e, X = *m*-OCH_3
f, X = *p*-CN
g, X = *m*-CN
h, X = *m*-CF_3

2, R = CH_3
4, R = $C(CH_3)_3$

behave similarly. The evidence obtained strongly suggests that the rearrangement of **1a** is a stepwise process involving ionic intermediates (eq 2).[1,2]

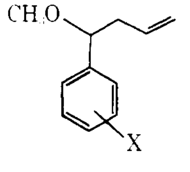


(2)

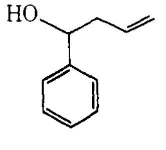
Studies of the effects of polar aromatic substituents on the rate constants for excited-state reactions of compounds with aromatic chromophores are very few in number, in spite of the fact that such studies have much potential for increasing our understanding of the detailed electronic features of these processes.[3] We present here the novel results of an investigation of substituent effects on the rate constant for the reaction shown in eq 1.

Upon irradiation[4] in dry, N_2-purged acetonitrile acetates **1b–d,f–h**, like **1a**, rearranged to the homoallyl acetates **2**;[5] see Table I.[6] The yields of acetates **2** in preparative-scale photolyses were generally low, in part because they are themselves light sensitive. Only the *m*-OCH_3 derivative **1e** failed to undergo the reaction, and control studies showed that our failure to observe rearrangement with **1e** was not due to the fact that **2e** was being formed and subsequently destroyed. Photolysis of the pivaloate esters **3b–h** gave, except in the case of **3e**, the homoallyl pivaloates **4b–h**. The rearrangement of **3a** has been reported previously.[1]

Upon triplet sensitization with acetone as sensitizer (Pyrex filter), **1a–h** and **3a–h** underwent trans-cis isomerization as the only detectable reaction, indicating that the observed cyclopropylcarbinyl-homoallyl rearrangements of **1** and **3** are singlet-state processes.



5a, X = H
d, X = *p*-CH_3
f, X = *p*-CN
g, X = *m*-CN
h, X = *m*-CF_3



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Irradiation of **1d,f–h** in methanol gave, in addition to **2d,f–h**, the homoallyl methyl ethers **5d,f–h**[8]—a reaction that had also been found for **1a**.[1] (We have not studied the photolyses of the other cyclopropylcarbinyl derivatives **1** and **3** in methanol.) Irradiations of **1d** and **1g** in methanol with added sodium bicarbonate gave results similar to those photolyses carried out without added bicarbonate; these methanol substitution reactions are therefore not acid-catalyzed thermal processes.[9] Appropriate controls showed that the methyl ethers **5d,f–h** are primary photoproducts of the cyclopropylcarbinyl acetates **1d,f–h**. Sensitization studies (acetone-methanol) revealed ether formation also to be a singlet reaction. As expected, photolysis of **1a** in 5% water-acetonitrile (containing sodium carbonate) gave both **2a** and 1-phenyl-3-buten-1-ol (**6**).[10]

Table I. Photolysis of *trans*-2-Arylcyclopropylcarbinyl Acetates **1a–h** in Acetonitrile[a]

compd (X)	mmol	time, h	yield, %[b] *trans*-**1**	*cis*-**1**	**2**	other[c]
1a (H)	3.16	20	46	13	6 (15)	1
1a[d]	1.58	36	77	10		
1b (*p*-CH_3)	1.13	8	46	25	18 (62)	
1c (*m*-CH_3)	1.37	8	37	18	2 (4)	~1
1d (*p*-OCH_3)	2.41	16	27	24	10 (20)	~1
1e (*m*-OCH_3)	0.454	16	13	5	≤0.2%[e]	
1f (*p*-CN)	2.56	16	29	3	1.5 (5)	32
1g (*m*-CN)	0.349	1	50	~2	4 (8)	~2
1h (*m*-CF_3)	0.775	3	56	21	13 (57)	7
1h[d]	0.388	1	49			<1

[a] Irradiations were carried out on 100-mL solutions with a Hanovia 450-W medium-pressure mercury arc equipped with a Corex filter except where noted. [b] Determined by gas chromatography and based on total amount of **1** irradiated; yields in parentheses are based on total cyclopropane (*cis,trans*-**1**) consumed. [c] Approximate yields of other unidentified products; see note 6. [d] Containing 0.079 M *N,N*-dimethylaniline; Pyrex filter used. [e] None detected.

Table II. Reaction Quantum Yields, Singlet Lifetimes, and Reaction Rates for **1a–h** and **3a–h**

compd (R, X)	ϕ_r,[a,b]	τ_s, ns[b]	$10^{-6}k_r$, s^{-1} [c]	k_r (rel)
1a (CH_3, H)	0.039	18.4	2.1	1.0
3a (*t*-Bu, H)				(0.99)[d]
1b (CH_3, *p*-CH_3)	0.026	18.0	1.4	0.67
3b (*t*-Bu, *p*-CH_3)	0.023	14.3	1.6	0.76
1c (CH_3, *m*-CH_3)	0.010	22.8	0.44	0.21
3c (*t*-Bu, *m*-CH_3)	0.0084	20.0	0.42	0.20
1d (CH_3, *p*-OCH_3)	0.012	4.95	2.4	1.1
3d (*t*-Bu, *p*-OCH_3)	0.0095	4.85	2.0	0.95
1e (CH_3, *m*-OCH_3)	≤0.002[e]	7.95	<0.25[e]	<0.12
3e (*t*-Bu, *m*-OCH_3)	≤0.002[e]	7.95	<0.25[e]	<0.12
1f (CH_3, *p*-CN)	0.033	<0.1[f]	>330	>160
3f (*t*-Bu, *p*-CN)	0.26	<0.1[f]	>260	>120
1g (CH_3, *m*-CN)	0.94	<0.1[f]	>940	>450
3g (*t*-Bu, *m*-CN)	0.11	<0.1[f]	>1100	>520
1h (CH_3, *m*-CF_3)	0.088	0.65	140	67
3h (*t*-Bu, *m*-CF_3)	0.11	0.65	170	81

[a] Quantum yield for formation of **2a–h** or **4a–h**; 2537-Å light; potassium ferrioxalate actinometry. [b] Acetonitrile solvent; room temperature. [c] Calculated using $k_r = \phi_r\tau_s^{-1}$. [d] See ref 1; an approximate k_r (rel) when both **1a** and **3a** are irradiated in cyclohexane. [e] No **2e** (**4e**) detected. [f] Lifetime too short to measure.

Quantum yields for the rearrangements of the *trans*-cyclopropylcarbinyl acetates **1** and pivaloates **3** to the homoallyl derivatives **2** and **4** in acetonitrile were determined (Table II). Singlet lifetimes for the esters **1** and **3** were measured by the single photon counting technique; the lifetimes of the cyano derivatives **1f,g** and **3f,g** proved too short to measure. Rate constants for rearrangement were then calculated according to the equation $k_r = \phi_r\tau_s^{-1}$. See Table II.

As was the case with **1a**,[1,2] two main pieces of evidence indicate that the observed rearrangements of the esters **1** and **3** are predominantly ionic rather than radical in nature. Thus,

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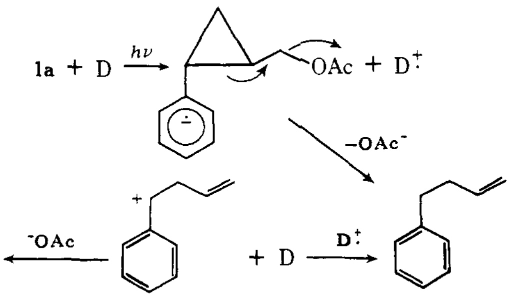
Scheme I.



formation of methyl ethers **5d,f–h** from acetates **1d,f–h** and of alcohol **6** from acetate **1a** is strong evidence for the formation of carbonium ion intermediates in methanol and water–acetonitrile, respectively.[11] In addition, the similarity in rate constants k_r (and quantum yields) for rearrangement of acetates **1** and pivaloates **3** having the same aromatic substituent is highly indicative of an ionic reaction. That is, k_r, as measured, is actually the product of two terms—k_i, the rate constant for formation of the intermediate ion (or radical) pair, and f, the fraction of the intermediate pair which goes on to product: $k_r = k_i f$.[12] Similar k_r's for derivatives **1** and **3** having the same aromatic substituent means that either both the k_i's and f's are similar for both or else the differences in k_i are in every case fortuitously compensated by differences in f. Since the chromophores of cyclopropanes **1** and **3** with the same aromatic group are essentially identical and the ester leaving groups are electronically much the same, it is most reasonable to conclude that the k_i's and therefore the f's are similar. Similar f values in turn strongly indicate the reactions follow an ionic course, for the pivaloyloxy radical is much less stable with respect to loss of CO_2 than the acetoxy radical,[13] and a much lower f value would be anticipated for the pivaloyl derivative than the acetoxy derivative if radical intermediates predominated.

Most striking, then, are the effects of substituents on the rate constant for reaction, for they appear to be almost the opposite to what one might expect if an ionic process were operative. We find (Table II) that electron-withdrawing groups (-CN, $-CF_3$) greatly speed up the reaction while electron-donating groups ($-CH_3$, $-OCH_3$) either have little effect or actually retard rearrangement. Clearly the relative rates of reaction that we have measured are not determined to any great extent by relative carbonium ion stabilities; i.e., carbonium ion formation is not rate determining.

One possibility that we have considered to explain the results is that an electron-transfer process is occurring (Scheme I). The process shown in Scheme I is analogous to that formulated by Ullman[14] to explain the excited-state solvolyses of certain benzyl alcohols and benzoate esters; in the present case D (Scheme I) would be an unspecified electron donor present in the reaction solution.[15] The electron-transfer mechanism is surely consistent with the observed rate acceleration by electron-withdrawing groups on the aromatic ring. However, two factors argue against such a mechanism. (1) The reaction **1a** → **2a** proceeds in cyclohexane and ether as well as in acetonitrile.[1,2] The quantum yield for **1a** → **2a** is only 10% greater in acetonitrile than in cyclohexane, and the (estimated) rate constant for rearrangement of **1a** is only 50% greater in the more polar solvent.[1] It would be highly fortuitous that an electron-transfer process brought about by some adventitious electron donor would proceed with such similar efficiencies and rates in two such different media. (2) As indicated in Table I, no rearrangement was observed when solutions containing **1a** or **1h** plus the added electron donor *N,N*-dimethylaniline were irradiated under conditions where the dimethylaniline absorbed most of the incident light.[14] In the case of **1a** only slow trans–cis isomerization and gradual loss of cyclopropane was noted; with **1h** only loss of starting material and no trans–cis isomerization could be detected.[16] In light of these observations an electron-transfer mechanism seems unlikely.[17]

Instead, an alternative mechanism involving carbonium-ion formation from the initial excited singlet state in two stages is favored.[19] The first and most important of these steps does not involve the creation of charged species and is the weakening and stretching of the C-1–C-2 cyclopropane bond to form a "radical-like" singlet excited state (see Becker et al.[20]). This highly polarizable species then rapidly loses acetate ion to form a ground-state ion pair.[21] The effect of the aromatic substituents is most pronounced on the first cyclopropane bond-stretching step; i.e., electron-withdrawing groups enhanced excited-state three-ring bond weakening[22] and electron-donating groups do not (or retard it).

This interpretation is in accord with the results of several other investigations of arylcyclopropane substituent effects. For example, UV studies indicate that the conjugative interaction between adjacent aromatic and cyclopropane rings in arylcyclopropanes is strong only when the aromatic ring is substituted with an electron-withdrawing group.[23] Likewise, the interaction between the cyclopropane and aromatic rings is a spectroscopically detectable function of the relative orientation of the two rings only in those cases where the aryl group is electron poor.[24] Certainly, then, the excited-state interaction between the three-ring and the aromatic group will be greater for those derivatives **1** and **3** having the -CN and $-CF_3$ groups than for the others. Cyclopropane bond weakening on excitation will be more substantial (the excited state will have greater σ, π^*, and σ^* character) and relaxation to a "radical-like" singlet will be more rapid.

The nonreactivity of the *m*-OCH_3 derivatives is interesting and may arise as a result of the fact that the *m*-OCH_3 group inhibits both stages of the reaction: The excited-state electron-donating effect of the $-OCH_3$[25] (the excited state is anisole-like) lessens cyclopropane bond weakening and retards bond stretching; the ground-state electron-withdrawing effect inhibits loss of acetate (pivaloate) from the radical-like species (the excitation energy here is concentrated in the stretched cyclopropane bond).

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References and Notes

(1) S. S. Hixson, *J. Chem. Soc., Chem. Commun.*, 681 (1974).
(2) S. S. Hixson and R. E. Factor, *Tetrahedron Lett.*, 3111 (1975).
(3) See, for example, (a) S. S. Hixson, *J. Am. Chem. Soc.*, **84**, 2507 (1972); (b) S. S. Hixson and T. P. Cutler, *ibid.*, **95**, 3032 (1973); (c) H. E. Zimmerman and B. R. Cotter, *ibid.*, **96**, 7445 (1974); (d) H. E. Zimmerman and W. T. Gruenbaum, *J. Org. Chem.*, **43**, 1997 (1978); (e) L. A. Paquette, D. M. Cottrell, and R. A. Snow, *J. Am. Chem. Soc.*, **99**, 3723 (1977).
(4) Photolysis were carried out with Corex-filtered light from a Hanovia 450-W medium-pressure mercury arc.
(5) All new compounds gave satisfactory microanalytical and/or high resolution mass spectral data as well as consistent NMR and IR spectra.
(6) In most cases a compound assigned the cis cyclopropane structure was the major photoproduct. With **1b–d**, the cis cyclopropanes and homoallyl acetates **2b–d** were the only products detected other than very minor amounts of unidentified materials. With **1f–h**, complex mixtures of products were formed in addition to **2**. These other products were not identified; they are presumably analogous to the isomerization products (olefins and indanes) formed on photolysis of 1,2-diphenylcyclopropane.[7]
(7) C. S. Irving, R. C. Petterson, I. Sarkar, H. Kristinsson, C. S. Aaron, G. W. Griffin, and G. J. Boudreaux, *J. Am. Chem. Soc.*, **88**, 5675 (1966).
(8) Low conversion ratios of acetate **2**:ether **5** follow: **1d**, 2.1:1; **1f**, 2.4:1; **1g**, 2.9:1; **1h**, 2.8:1.
(9) Added EDTA had no noticeable effect on the photolysis of **1a** in methanol.
(10) Photolysis[4] for 9 h of 5.21 mmol of **1a** in 200 mL of 5% water–acetonitrile with 0.8 g of added sodium carbonate gave 27% recovered *trans*-**1a**, 10% *cis*-**1a**, 16% (25% based on total cyclopropane consumed) **2a**, 4% (6%) **6**, and 7% (11%) total of two unidentified products. Less than 0.1% 4-

acetamido-4-phenyl-1-butene was formed. (An authentic sample was prepared for comparison.)

(11) (a) Shono et al.[11b] reported that hydrolysis of the 3,5-dinitrobenzoate analogous to **1a** (**7**) in 75% aqueous dioxane at 130 °C gave 85-88% **6** and 12-15% 2-phenylcyclopropylcarbinyl alcohol (**8**). Under the same conditions, the 3,5-DNB of **6** gave only **6**. Methanolysis of **7** gave **5a** and a trace of **8**. (b) T. Shono, I. Nishiguchi, and R. Oda, *J. Org. Chem.*, **35**, 42 (1970). (c) Deamination of *trans*-2-phenylcyclopropylcarbinyl amine afforded 82% **6**, 14% *trans*-**8**, 3% phenylcyclopropylcarbinyl alcohol, 1% 4-phenyl-3-buten-1-ol, and <1% *cis*-**8**.[11d] (d) C. Dupin and R. Fraisse-Jullien, *Bull. Soc. Chim. Fr.*, 1993 (1964).

(12) For a discussion, see P. J. Wagner in "Creation and Detection of the Excited State", Vol. 1, A. A. Lamola, Ed., Marcel Dekker, New York, 1971, p 173.

(13) (a) J. K. Kochi in "Free Radicals", Vol. 2, J. K. Kochi, Ed., Wiley-Interscience, New York, 1973, p 698; (b) T. Koenig, ref 13a, Vol. 1, p 113; (c) T. Koenig and H. Fischer, ref 13a, Vol. 1, p 157.

(14) C.-I. Lin, P. Singh, and E. F. Ullman, *J. Am. Chem. Soc.*, **98**, 6711 (1976); **98**, 7848 (1976).

(15) For example, D could be water. It is very difficult to prepare and maintain absolutely dry acetonitrile.

(16) In yet another experiment a solution of **1a** (0.1 M) and *N,N*-dimethylaniline (0.05 M) in 10 mL of methanol was irradiated through Pyrex with the 300-nm lamps of a Rayonet photochemical reactor. After 32 h there remained 33% *trans*-**1a**, 20% *cis*-**1a**, and a small amount of an unidentified product similar in GC retention time to *trans*-**1a**. No **2a** or **5a** could be detected.

(17) The trifluoroacetate **9** analogous to **1a** had a measured τ_s of 1.5 ns.[18] Photolysis[4] of 1.56 mmol of **9** in acetonitrile for 4 h provided 31% *trans*-**9**, 25% *cis*-**9**, and at least six unidentified higher boiling products. No product analogous to **5** could be detected. (In a previous experiment,[18] it had been found that extended irradiation of **9** resulted only in cis-trans isomerization and little loss of cyclopropane.) Attempts to study the photolysis of **9** in methanol were frustrated by its rapid methanolysis (hydrolysis?) to *trans*-2-phenylcyclopropylcarbinyl alcohol; see R. A. Sneen, K. M. Lewandowski, I. A. I. Taha, and B. R. Smith, *J. Am. Chem. Soc.*, **83**, 4843 (1961).

(18) J. A. Gere, Ph.D. Thesis, University of Massachusetts, 1977.

(19) It is convenient to view the ionization as occurring in two steps, though the "radical-like" singlet postulated may not lie at an energy minimum.

(20) R. S. Becker, L. Edwards, R. Bost, M. Elan, and G. Griffin, *J. Am. Chem. Soc.*, **94**, 6584 (1974).

(21) This mechanism is in many ways similar to that discussed by Walling for the decomposition of diacyl peroxides: C. Walling, H. P. Waits, J. Milanovic, and C. G. Pappiaonnou, *J. Am. Chem. Soc.*, **92**, 4927 (1970).

(22) It is the inductive effect of the $-CF_3$ (and $-CN$) group which is considered to enhance excited-state interaction between the cyclopropane and aromatic rings and thus promote cyclopropane bond weakening. The effect of the aromatic $-CF_3$ group on benzylic radical stability is of lesser importance.

(23) L. A. Strait, R. Ketcham, D. Jambotkar, and V. P. Shah, *J. Am. Chem. Soc.*, **86**, 4628 (1964).

(24) (a) A. L. Goodman and R. H. Eastman, *J. Am. Chem. Soc.*, **86**, 908 (1964); (b) R. C. Hahn, P. M. Howard, S. M. Kong, G. A. Lorenzo, and N. L. Miller, *ibid.*, **91**, 3558 (1969); (c) R. M. Kellogg and J. Butler, *J. Org. Chem.*, **36**, 2236 (1971).

(25) J. Cornelisse, *Pure Appl. Chem.*, **41**, 433 (1975), and references therein.

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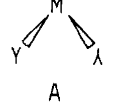
Evidence for Diastereomers of the [Platinum (*N,N,N′,N′*-tetramethylethylenediamine)(guanosine)$_2$]$^{2+}$ Cation[1]

Sir:

In the course of our investigation of the square-planar platinum(II) complex *cis*-$[Pt(NH_3)_2(guanosine)_2]^{2+}$,[1] I, it occurred to us that, as a result of the arrangement of the guanosine ligands, the platinum center of this compound was chiral (Figure 1).

A square-planar metal complex, with two ligands of C_s local symmetry in cis positions, can exist in three possible configurations: A-C. Isomers A and B are nonsuperimposible mirror images and are therefore enantiomers in which the metal atom is the chiral center. Isomer C, corresponding to the meso form, contains an improper symmetry operation and the metal center is not chiral.



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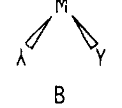

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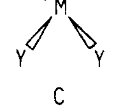

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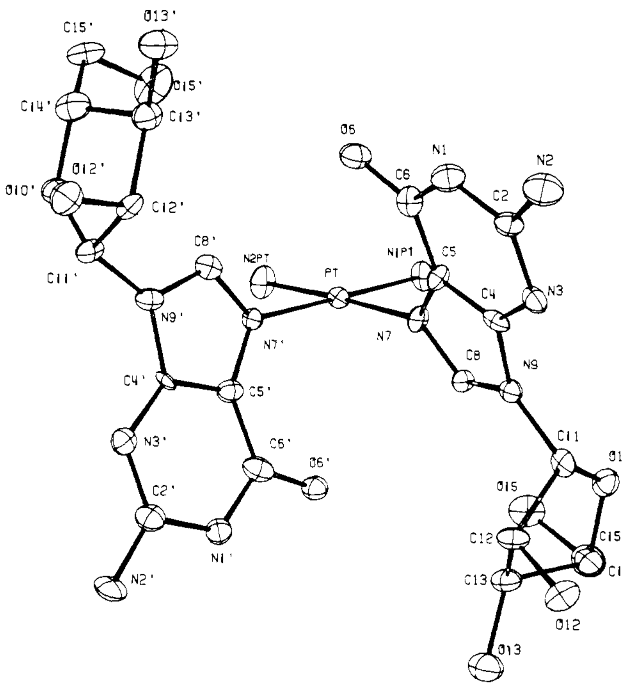


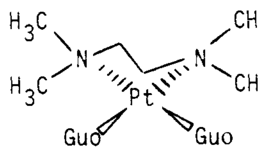
Figure 1. A view of the *cis*-$[Pt(NH_3)_2(guanosine)_2]^{+2}$ cation.

In the case of compound I, the ribose moiety of the guanosine ligands is a source of additional chirality. Since the absolute configuration of the ribose moiety in both guanosine ligands is the same, the mirror symmetry between the enantiomers A and B is broken and these isomers become diastereomers. Since diastereomers are chemically nonequivalent they may be differentiated by various physical techniques in a nonchiral medium.

The crystal structure of compound I shows the presence of only one of the possible diastereomers.[2] However, investigation disclosed only those optical effects due to the guanosines. The ^1H and ^{13}C NMR showed only resonances due to a single isomer, or a mixture of isomers rapidly exchanging on the NMR time scale (Figure 2). We propose that interconversion between the diastereomers occurs and is rapid on the NMR time scale.

A dissociative mechanism for the interconversion of the isomers of I which is rapid enough to be fast on the NMR time scale can be ruled out because platinum(II) is substitution inert. However, rapid exchange of these isomers can occur by simple rotation of both guanosines about the platinum guanosine bond. The bulk of the purine rings will provide some barrier to rotation about this bond, but rotation of a guanosine past an ammonia is easy. However, replacement of the ammonia ligands of I with bulky ligands could sterically inhibit this rotation. We therefore prepared the analogue of I in which the ammonia ligands have been replaced by *N,N,N′,N′*-tetramethylethylenediamine.

(Dichloro)(*N,N,N′,N′*-tetramethylethylenediamine)platinum(II) was prepared by the method of Mann and Watson[3]



II

by the addition of a threefold excess of free amine to an aqueous solution of H_2PtCl_6. The colorless diaquo complex was