Curiously, this coupling reaction is only observed for the amido derivative.[19] There is a hint, here, that ruthenium carbonyl cluster complexes activated by nitrogen bases may be potential synthons for promoting carbon-carbon bond formation between different kinds of olefins. The next challenge will be to render the codimerization process catalytic.

Acknowledgment. This work was supported by the CNRS. We are grateful to Johnson-Matthey for generous loans of ruthenium trichloride, to Dr. Renê Mathieu for helpful discussions, and to Ms. Sylvie Segura for her contribution.

Supplementary Material Available: Details for the preparation and characterization of the complexes [PPN][**1a**,**c**], [PPN][**2a**–**c**], **3a**,**b**, **4a**,**b**, **5a**,**b**, and **6**, details of hydrogenation and codimerization reactions, preliminary crystallographic data for [PPN][**1c**] and [PPN][**2a**], and a listing of full crystallographic data for **5a** including atomic coordinates, thermal parameters, and selected interatomic distances and bond angles (17 pages); listing of observed and calculated structure factor amplitudes for **5a** (27 pages). Ordering information is given on any current masthead page.

(19) While we were in the process for submitting this work, a parallel report on vinyl ethylene combination appeared: Bruce, G. C.; Knox, S. A. R.; Phillips, A. J. *J. Chem. Soc., Chem. Commun.* **1990**, 716-718.

Intramolecular Reactions of Diazocyclobutanes. Synthesis of *trans*-Tricyclo[4.2.0.$0^{1,3}$]octane ([3,5,4]Fenestrane)†,[1]

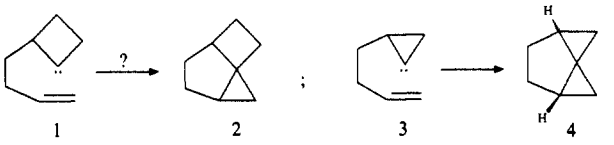
Udo H. Brinker,*,‡ Theodor Schrievers,§ and Linxiao Xu‡

Department of Chemistry
University Center at Binghamton
State University of New York, P.O. Box 6000
Binghamton, New York 13902-6000

Received July 13, 1990

Small-ring carbenes, i.e., divalent carbons in three-[2] and four-membered rings,[3] respectively, have successfully been used for the construction of highly strained,[4] polycyclic compounds. While inter- and intramolecular additions of cyclopropylidenes and/or their corresponding carbenoids[2] are well-known, only *inter*molecular additions of cyclobutyliden(oid)s[5] to carbon double and triple bonds have been reported in the literature.[6]

The addition of 3-butenyl substituted cyclopropyliden(oid)s **3**, generated from the corresponding geminal dibromocyclopropanes on treatment with methyllithium, provides an easy access to *trans*-tricyclo[4.1.0.$0^{1,3}$]heptanes **4**.[7] Since an organometallic route to cyclobutyliden(oid)s **1** containing an additional double bond has not yet been uncovered, we chose to generate **1** via the corresponding diazo precursor.



1 2 3 4

Figure 1.

Tricyclo[4.2.0.$0^{1,3}$]octane (**2**) resulting from the addition of the divalent carbon in **1** to the double bond represents a unique structure, comprising a three-, four-, and five-membered ring. In the literature besides a geminal dichloro-substituted ketone three pentasubstituted compounds with the carbon skeleton of **2** can be found.[8] The connection of the cyclopropane and the cyclobutane ring in **2** by the ethano bridge can be in either a cis or a trans fashion. The strain energy for *trans*-tricyclo[4.1,0.$0^{1,3}$]-heptane (**4**) and the corresponding cis isomer has been calculated to be 80 and 120 kcal/mol, respectively.[9] Of the five possible isomeric, unbridged, tricyclic carbon skeletons containing three-, four-, and five-membered rings sharing one common carbon atom, **2** comprises the highest computed strain energy (70.1 kcal/mol).[10]

For the synthesis of the unknown 2-(but-3-enyl)cyclobutanone, ethyl 3-chloropropanoate was converted to 1-ethoxy-1-(trimethylsiloxy)cyclopropane.[11] Treatment with phosphorus tribromide gave 1-bromo-1-ethoxycyclopropane,[12] which with 4-pentenal yielded 1-ethoxy-1-(1-hydroxy-4-pentenyl)cyclopropane. With HBF_4 (50%) this compound rearranged[13] to the required cyclobutanone. The corresponding cyclobutanone with two methyl groups on the terminal olefinic carbon was also prepared according to this methodology.

The flash pyrolyses[14] of the tosylhydrazone sodium salts of **5** and **6** each at 250 °C (10^{-5}–10^{-4} Torr) gave totally different results. While it is assumed that from both **5** and **6** the diazocyclobutanes **7** and **8** are formed, their reaction behavior differs strongly. In **7** preferentially a 1,3-dipolar cycloaddition[15] to **14** takes place which isomerizes to the more stable pyrazoline **16**. The loss of nitrogen in **7** and the generation of carbene **1** competes with the intramolecular 1,3-dipolar cycloaddition (ratio 3:7).

In carbene **1** the ring contraction reaction to **10** dominates over the 1,2-hydrogen migration to **12** (ratio 94:6); in addition, 2-(but-3-enyl)methylenecyclopropane, which seems to be a secondary thermal product of **10**, is formed. However, **2**, the product resulting from intramolecular addition of the divalent carbon in **1** to the double bond, is not found. In stark contrast to **7**, **8** liberates predominantly nitrogen to generate carbene **9**, while the 1,3-dipolar cycloaddition to **15** is only of minor significance (ratio 8:2). Not surprisingly, the reaction pattern of carbene **9** is almost identical

† Dedicated to Professor Wolfgang Kirmse on the occasion of his 60th birthday.

‡ State University of New York at Binghamton.

§ Fakultät für Chemie, Ruhr-Universität Bochum, 4630 Bochum, Federal Republic of Germany.

(1) Carbene Rearrangements, Part 36. Part 35: Brinker, U. H.; Erdle, W. Heterocycloalkylidene, In *Houben-Weyl (Methoden der Organischen Chemie)*; Regitz, M., Ed.; Thieme: Stuttgart, 1989; Vol. E19b, pp 623-663.

(2) Backes, J.; Brinker, U. H. In *Houben-Weyl (Methoden der Organischen Chemie)*; Regitz, M., Ed.; Thieme: Stuttgart, 1989; Vol. E19b, pp 391-510.

(3) Backes, J.; Brinker, U. H. In *Houben-Weyl (Methoden der Organischen Chemie)*; Regitz, M., Ed.; Thieme: Stuttgart, 1989; Vol. E19b, pp 511-541.

(4) Strained Organic Compounds, *Chem. Rev.* **1989**, *89*, No. 5. Venepalli, B. R.; Agosta, W. C. *Chem. Rev.* **1987**, *87*, 339. Wiberg, K. B. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 312. *Molecular Structure and Energetics*; Liebman, J. F., Greenberg, A., Eds.; VCH Publishers, Inc.: Deerfield Beach, FL, 1986; Vol. 3. Greenberg, A.; Liebman, J. F. *Strained Organic Molecules*; Academic Press: New York, 1978.

(5) Friedman, L.; Shechter, H. *J. Am. Chem. Soc.* **1960**, *62*, 1002. Brinker, U. H.; Schenker, G. *J. Chem. Soc., Chem. Commun.* **1982**, 679.

(6) Brinker, U. H.; Boxberger, M. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 974. Brinker, U. H.; Weber, J. *Tetrahedron Lett.* **1986**, *27*, 5371.

(7) Skattebøl, L. *Chem. Ind. (London)* **1962**, 2146; *J. Org. Chem.* **1966**, *31*, 2789. Brinker, U. H.; Streu, J. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 631. Brinker, U. H.; Wilk, G.; Gomann, K. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 868; *Angew. Chem. Suppl.* **1983**, 1228. Gleiter, R.; Krennrich, G.; Brinker, U. H. *J. Org. Chem.* **1986**, *51*, 2899. Boese, R.; Bläser, D.; Gomann, K.; Brinker, U. H. *J. Am. Chem. Soc.* **1989**, *111*, 1501. Wiberg, K. B.; Chaves, A. *J. Am. Chem. Soc.* **1989**, *111*, 8052.

(8) Carpino, L. A.; Gund, P.; Springer, J. P.; Gund, T. *Tetrahedron Lett.* **1981**, *22*, 371. Ishii, K.; Lyle, T. A.; Schweizer, W. B.; Frei, B. *Helv. Chim. Acta* **1982**, *65*, 595.

(9) Wiberg, K. B. *J. Org. Chem.* **1985**, *50*, 5285. Wiberg, K. B.; Bader, R. F. W.; Lau, C. D. H. *J. Am. Chem. Soc.* **1987**, *109*, 985.

(10) Gund, P.; Gund, T. *J. Am. Chem. Soc.* **1981**, *103*, 4458. It is assumed that the calculations were performed with the trans isomer of **2**, though the authors do not specify this.

(11) Rühlmann, K. *Synthesis* **1971**, 236. Salaün, J.; Marguerite, J. *Org. Synth.* **1985**, *63*, 147.

(12) Miller, S. A.; Gadwood, R. C. *Org. Synth.* **1988**, *67*, 210.

(13) Trost, B. M.; Keeley, D. E.; Arndt, H. C.; Rigby, J. H.; Bogdanowicz, M. J. *J. Am. Chem. Soc.* **1977**, *99*, 3080, 3088.

(14) Brinker, U. H.; König, L. *Chem. Ber.* **1983**, *116*, 882.

(15) Huisgen, R. In *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed.; Wiley: New York, 1983; Vol. 1, pp 1-176.

0002-7863/90/1512-8609$02.50/0

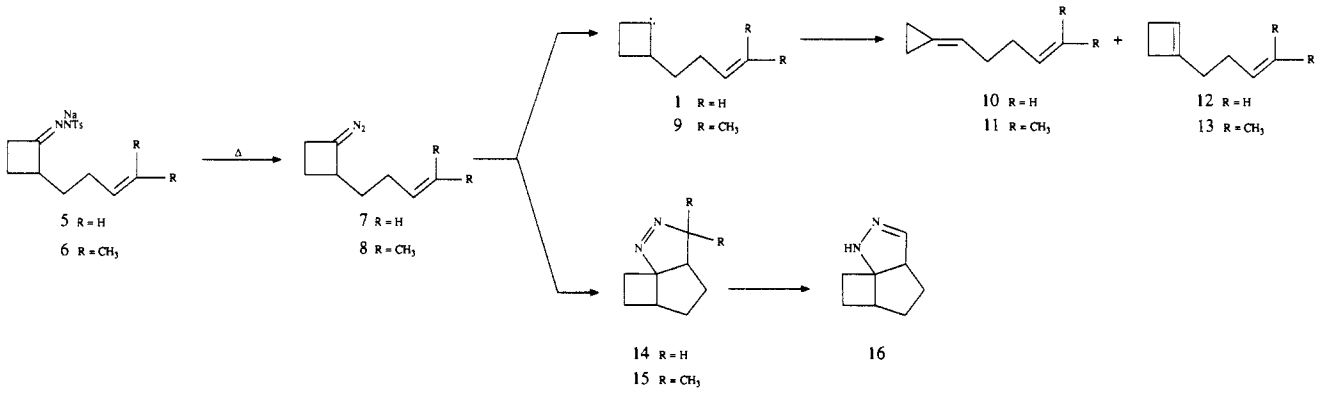


Figure 2.

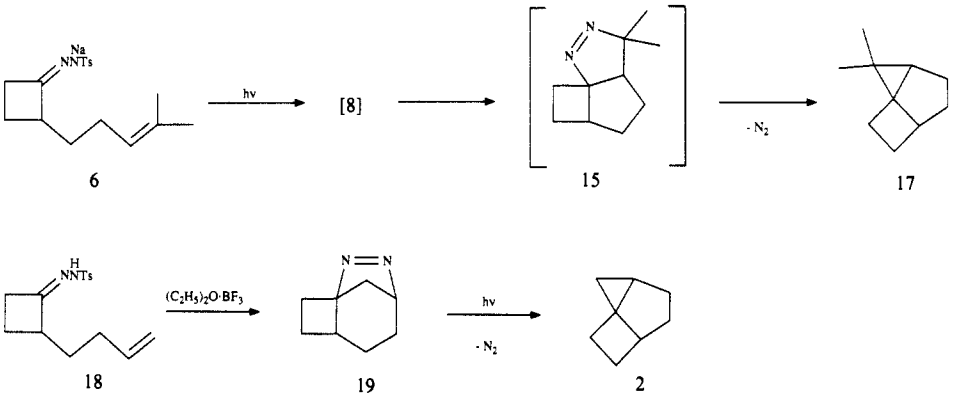


Figure 3.

with that of **1** (ratio of **11** and **13**, 93:7). As in the case of **1**, an intramolecular addition did not take place.

The reactions **7** → **14** and **8** → **15** are the first examples of *intra*molecular 1,3-dipolar cycloadditions of diazocyclobutanes. The different reaction behavior of **7** and **8** can be rationalized with the frontier orbital model which has successfully been applied for *inter*molecular 1,3-dipolar reactions.[16] According to this model, the terminal methyl groups in **8** slow down the 1,3-dipolar cycloaddition to **15**, and the competing cleavage of nitrogen with concomitant generation of carbene **9** becomes the dominant reaction. Steric hindrance in the transition state may also be responsible for the lower yield of **15**. In contrast, in **7** the 1,3-dipolar cycloaddition to **14** proceeds at a faster rate than the generation of carbene **1**.

On *photolysis* of **6**, 2,2-dimethyltricyclo[4.2.0.0^{1,3}]octane (**17**) was isolated in 63% yield. **11** and **13**, deriving from carbene **9**, could not be detected. Furthermore, when **15**, which had been *isolated* from the flash pyrolysis of **6**, was subjected to the photolysis conditions of **6**, the tricyclus **17** was obtained as the single product. These results suggest that **17** is not formed by intramolecular addition of carbene **9** but via the reaction sequence **6** → **8** → **15** → **17**.

In contrast, when **5** was photolyzed, no nitrogen evolution took place and neither tricyclus **2** nor **10** and **12** were formed. In addition, pyrazole **14** could not be detected. Obviously, under the conditions applied, the 1,3-hydrogen shift **14** → **16** proceeds faster than cleavage of nitrogen in **14** to give tricyclus **2** via the corresponding 1,3-diradical. **16** seems to polymerize under the photolysis conditions.

Our efforts to synthesize the parent tricyclus **2** were met with success when a method was found which allowed the formation of a potential precursor, e.g., 8,9-diazatricyclo[5.2.1.0^{1,4}]dec-8-ene (**19**). Thus, on treatment of 2-(3-butenyl)cyclobutanone tosylhydrazone (**18**) with boron trifluoride etherate, **19** could be isolated.[17] Under the acidic conditions applied, the intramolecular cyclization leading to **19** seems to proceed via carbocations as intermediates.[18] The observed regioselective formation of **19** in the BF_3-catalyzed reaction of **18** is remarkable.

When **19** was irradiated (Philips, HPK 125) in acetone, tricyclo[4.2.0.0^{1,3}]octane ([3,5,4]Fenestrane) (**2**) could be isolated in 45% yield (purity 91%). Preparative GC yielded pure **2**.[17] From the 2D NMR COSY and H,C correlation spectra obtained for **2**,[17] it was not possible to decide whether the three- and the four-membered rings in **2** are connected by the ethano bridge in a trans or a cis fashion. Attempts to obtain an X-ray analysis of **2** at low temperatures failed.[19] However, the NOE difference experiment unambiguously showed that irradiation at H2 syn resulted in a clear positive NOE at the C6 hydrogen atom. Thus, the ethano bridge in **2** connects the cyclopropane and the cyclobutane ring in a trans fashion. Semiempirical AM-1 calculations show the trans isomer of **2** ($H_f°$ = 34 kcal/mol) to be about 28

(16) Sustmann, R. *Tetrahedron Lett.* **1971**, 2717; *Pure Appl. Chem.* **1974**, *40*, 569.

(17) Satisfactory combustion analyses or high-resolution mass spectra were obtained for all new, stable compounds. Selected spectral data are as follows: **2**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.28 ("t", A part of the ABX system, 1 H, H2syn, $J_{H2syn,H2anti}$ = −5.5 Hz, $J_{H2syn,H3}$ = 5.0 Hz), 0.80 ("dd", B part of the ABX system, 1 H, H2anti, $J_{H2anti,H3}$ = 8.5 Hz), 1.08 (X part of the ABX system, 1 H, C3), 1.49–1.81 (m, 5 H, C4, C5, C7, C8), 2.01–2.08 (m, 1 H, C7), 2.08–2.19 (m, 1 H, C4), 2.30–2.40 (m, 1 H, C8), 2.51 (dq, 1 H, C6); ^{13}C NMR (90.6 MHz, $CDCl_3$) δ 17.1 (t, C2, $J_{^{13}C,H}$ = 157 Hz), 24.8 (d, C3, $J_{^{13}C,H}$ = 163 Hz), 26.6 (t, C7, C8), 29.7 (t, C4), 32.7 (t, C5), 38.3 (s, C1), 45.4 (d, C6). **17**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.82 (s, 3 H, CH_3), 0.89 (br d, 1 H, C3), 0.91 (s, 3 H, CH_3), 1.50–1.60 (m, 1 H, C8), 1.60–1.82 (m, 4 H, C4, C5, C7), 2.02–2.15 (m, 2 H, C5, C8), 2.15–2.24 (m, 1 H, C4), 2.45 (dq, 1 H, C6); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 16.1 (q, C9 or C10), 22.6 (q, C10 or C9), 23.0 (t, C4), 25.1 (s, C1 or C2), 25.5 (t, C5), 27.0 (t, C8), 37.0 (d, C3), 37.7 (t, C7), 42.5 (d, C6), 48.8 (s, C2 or C1). **19**: ^{1}H NMR (400 MHz; $CDCl_3$) δ 1.12–1.27 (m, 1 H, C6), 1.39–1.53 (m, 4 H, C3, C5, C6, C10), 1.61–1.72 (m, 1 H, C5), 1.96–2.13 (m, 4 H, C2, C3, C4, C10), 2.98–3.10 (m, 1 H, C2), 4.58 (dd, 1 H, C7); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 16.3 (t, C6), 24.8 (t, C5), 25.6 (t, C2), 25.8 (t, C3), 29.4 (t, C10), 32.7 (d, C4), 74.3 (d, C7), 82.2 (s, C1); IR (film) ν 1505 (−N=N−) cm^{-1}.

(18) Wilson, R. M.; Rekers, J. W.; Packard, A. B.; Elder, R. C. *J. Am. Chem. Soc.* **1980**, *102*, 1633. Padwa, A.; Ku, H. *J. Org. Chem.* **1980**, *45*, 3756.

(19) We thank Dr. R. Boese and T. Miebach, University of Essen, for their attempts to determine the structure of **2**.

kcal/mol more stable than the cis isomer.[20] Thus, in the cis and trans isomers of **4** and **2**, approximately the same magnitude in the difference and the same order of strain energies seem to be present,

Acknowledgment. Partial support from the donors to the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. We are indebted to Dr. H. Wüster and Dipl. Chem. T. Miebach, for having investigated alternative routes to **2**. We thank especially Prof. W. B. Smith, Texas Christian University, Fort Worth, Texas, for having performed the crucial NOE experiments with **2**.

(20) T. Miebach, unpublished results.

Stability of Platinated Oligonucleotide Duplexes Containing a Base Pair Mismatch at the Site Complementary to the Platination Site

Hidehito Urata, Katsushi Fujikawa, Masahiro Tamura, and Masao Akagi*

Osaka University of Pharmaceutical Sciences
2-10-65 Kawai, Matsubara, Osaka 580, Japan

Received May 30, 1990

cis-Diamminedichloroplatinum(II) (cDDP) is a very clinically useful antitumor agent.[1] It is also mutagenic[2] and carcinogenic.[3] These interesting biological activities of cDDP are said to be due to preferential bifunctional chelation to two adjascent guanine residues in DNA.[4-6] This chelation induces significant decrease in the melting temperature (T_m) of the platinated oligonucleotide duplexes.[7,8] This effect is attributed to a kinked cDDP-DNA structure by NMR experiments[9] and molecular mechanics calculations.[10] Although the imino resonances of the platinated guanine residues in oligonucleotides can be observed at low temperature, these are the first to be disrupted at higher temperature[8] and there is no proof that imino resonances observed at low temperature in oligonucleotide duplexes participate in the same sort of hydrogen bonding as exists under normal conditions. Moreover, molecular mechanics calculations indicated possible unusual base pairing in platinated oligonucleotides.[10] A recent report suggests that the kinked structure does not occur in the monofunctional-platinated nonanuclotide although the double-helical structure is significantly destabilized.[11] Thus, the platination of N(7) of guanine residues in DNA may reduce their ability and selectivity for G-C base pairing. In fact, cDDP coordination at N(7) of guanines facilitates the deprotonation at N(1) of guanine ligands (pK = 8.2 compared to 9.8 for free guanine).[12,13] This causes the formation of significant amounts of both protonated and deprotonated guanine at pH 7. The deprotonated guanine forms hydrogen bonding with G or T rather than C.[14] It is still uncertain to what extent the binding of cDDP affects base pairing in an oligonucleotide,

Table I. Melting Temperatures and Hypochromicity of Four Decanucleotide Duplexes Modified and Unmodified with cDDP[a]

		T_m, °C (hypochromicity)					
		0.5 M NaCl				0.1 M NaCl	
		-Pt		+Pt		-Pt	+Pt
	X	pH 7	pH 9	pH 7	pH 9	pH 7	pH 7
duplex 1	C	54.7 (24.1%)	53.4 (23.9%)	33.5 (18.5%)	31.5 (19.2%)	49.2 (25.1%)	29.6 (19.5%)
duplex 2	T	40.6 (22.9%)	38.4 (25.2%)	11.5 (13.9%)	10.0 (13.6%)	33.5 (25.5%)	8.0 (16.1%)
duplex 3	A	37.0 (21.2%)	36.3 (22.4%)	10.0 (13.1%)	9.3 (13.6%)	30.5 (21.5%)	6.5 (13.5%)
duplex 4	G	31.4 (20.4%)	31.0 (21.2%)	N.D.[b] (8.7%)	N.D.[b] (8.9%)	23.4 (20.8%)	N.D.[b] (8.7%)

[a] T_m values were determined[20] by measuring change in absorbance at 274 nm as a function of temperature at 5.7 μM duplex concentration in 10 mM sodium phosphate buffer containing 0.5 M NaCl. When a base line at low temperature was observed, the T_m was calculated by using sloping base lines. For duplexes with T_m < 20 °C, such a base line could not be observed, and T_m values were calculated by using a flat base line. Hypochromicity is indicated in parentheses. [b] In these cases, helix-to-coil transition was not observed.

We investigated pH dependence and the effects of base substitution at the site complementary to the platination site for the stability of platinated decanuclotide duplexes so as to assess base pairing ability and the selectivity of the platinated guanine residue in oligonucleotides.

The decamers were synthesized by β-cyanoethylphosphoramidite methodology,[15] *cis*-Pt(NH$_3$)$_2$ [d(ACTCGGCTCA)-N7-G(5),-N7-G(6)] was prepared by an equimolar reaction of cDDP with d(ACTCGGCTCA). Purification was performed on a C-18 column. Finally, the product was converted to the sodium salt.[16] The synthesized decamers and Pt complex were more than 95% pure with reversed phase HPLC and identified by enzymatic digestion with nuclease P1.[17] We investigated the stability of the duplexes containing the base pair mismatches at the complementary site of the coordinated 5'-guanosine for two reasons. First, the theoretical models derived from molecular mechanics calculations suggested there was only one hydrogen bond between the 5'-guanosine and complementary cytosine on the opposite strand,[10] Second, in a preliminary study, we introduced the G-T mismatch at the site of the coordinated 3'-guanosine. The results indicated that the extent of the T_m lowering of this duplex by platination was comparable[19] with that of Duplex 2, and the T_m of Duplex 1 was decreased by this mismatch in a similar tendency

(1) Loehrer, P. J.; Einhorn, L. H. *Ann. Intern. Med.* **1984**, *100*, 704-713.
(2) (a) Beck, D. J.; Brubaker, R. R. *Mutat. Res.* **1975**, *27*, 181-189. (b) Lecointe, P.; Macquet, J. P.; Butour, J. L. *Biochem. Biophys. Res. Commun.* **1979**, *90*, 209-213. (c) Wiencke, J. K.; Cervenka, J.; Paulus, H. *Mutat. Res.* **1980**, *68*, 69-77.
(3) Leopold, W. R.; Miller, E. C.; Miller, J. A. *Cancer Res.* **1979**, *39*, 913-918.
(4) (a) Eastman, A. *Biochemistry* **1983**, *22*, 3927-3933. (b) Eastman, A. *Biochemistry* **1986**, *25*, 3912-3915.
(5) (a) Pinto, A. L.; Lippard, S. J. *Biochim. Biophys. Acta* **1985**, *780*, 167-180. (b) Sherman, S. E.; Gibson, D.; Wang, A. H.-J.; Lippard, S. J. *J. Am. Chem. Soc.* **1988**, *110*, 7368-7381.
(6) Fichtinger-Schepman, A. M. J.; van der Veer, J. L.; den Hartog, J. H. J.; Lohman, P. H. M.; Reedijk, J. *Biochemistry* **1985**, *24*, 707-713.
(7) den Hartog, J. H. J.; Altona, C.; van Boom, J. H.; van der Marel, G. A.; Haasnoot, C. A. G; Reedijk, J. *J. Am. Chem. Soc.* **1984**, *106*, 1528-1530.
(8) (a) van Hemelryck, B.; Guittet, E.; Chottard, G.; Girault, J.-P.; Huynh-Dinh, T.; Lallemand, J.-Y.; Igolen, J.; Chottard, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 3037-3039. (b) van Hemelryck, B.; Guittet, E.; Chottard, G.; Girault, J.-P.; Herman, F.; Huynh-Dinh, T.; Lallemand, J.-Y.; Igolen, J.; Chottard, J.-C. *Biochem. Biophys. Res. Commun.* **1986**, *138*, 758-763.
(9) den Hartog, J. H. J.; Altona, C.; van Boom, J. H.; van der Marel, G. A.; Haasnoot, C. A. G.; Reedijk, J. *J. Biomol. Struct. Dyn.* **1985**, *2*, 1137-1185.
(10) Kozelka, J.; Archer, S.; Petsko, G. A.; Lippard, S. J.; Quigley, G. J. *Biopolymers* **1987**, *26*, 1245-1271.
(11) van Garderen, C. J.; Altona, C.; Reedijk, J. *Inorg. Chem.* **1990**, *29*, 1481-1487.
(12) Chu, G. Y. H.; Mansy, S.; Duncan, R. E.; Tobias, R. S. *J. Am. Chem. Soc.* **1978**, *100*, 591-606.
(13) Inagaki, K.; Kasuya, K.; Kidani, Y. *Chem. Lett.* **1984**, 171-174.
(14) (a) Lippert, B. *J. Am. Chem. Soc.* **1981**, *103*, 5691-5697. (b) Lippert, B. *Gazz. Chim. Ital.* **1988**, *118*, 153-165.
(15) Sinha, N. D.; Biernat, J.; Köster, H. *Tetrahedron Lett.* **1983**, *24*, 5843-5846.
(16) A solution of the platinated decamer was analyzed for Pt by carbon rod atomic absorption spectroscopy. From the UV absorption at 260 nm, a calculated molar extinction coefficient is approximately 83 000/(mol of Pt), indicating 1 Pt atom per strand.
(17) The digestion mixtures were analyzed by HPLC, which showed the expected nucleotides and 5'-end nucleoside in their expected ratios. In particular, the digestion mixture of the platinated decamer contained not 5'-dGMP but a new peak which was cochromatographed with *cis*-Pt(NH$_3$)$_2$[d(pGpG)-*N7,N7*] prepared by the literature procedure.[18] This result indicates the intrastrand bifunctional chelation of cDDP at the GG site.
(18) Girault, J.-P.; Chottard, G.; Lallemand, J.-Y.; Chottard, J.-C. *Biochemistry* **1982**, *21*, 1352-1356.
(19) The T_m of this duplex with and without platination is 14.4 and 42.3 °C, respectively, in 10 mM sodium phosphate (pH 7) containing 0.5 M NaCl.
(20) Borer, P. N.; Dengler, B.; Tinoco, I., Jr. *J. Mol. Biol.* **1974**, *86*, 843-853.

0002-7863/90/1512-8611$02.50/0