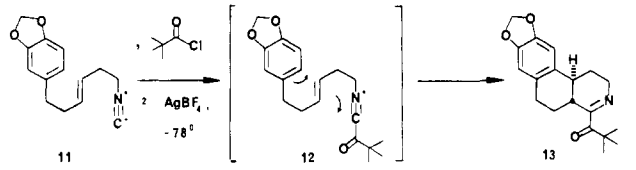
pyridine (1 equiv) over 1-3 h. The cyclization of the unpurified α-keto imidoyl chlorides **7a-f** to the pyrrolines **8a-f** was readily accomplished in the presence of $AgBF_4$ (1.1 equiv) under high dilution in CH_2Cl_2-$ClCH_2CH_2Cl$ at -78 °C.[12,13] It is noteworthy that the removal of the pyridine buffer prior to the cyclization of the intermediates **7a-f** was determined to be unnecessary. A summary of results obtained from a comprehensive series of $AgBF_4$-promoted acylnitrilium ion-silylenol ether cyclizations appears in Table I.

We have previously noted that acylnitrilium ions are sufficiently electrophilic to undergo facile cyclization with nonactivated arenes at -20 °C.[8] The use of *simple* alkenes as nucleophilic addends in acylnitrilium ion initiated heteroannulations would be of considerable synthetic interest. To explore this possibility, the unsaturated isonitrile **11** was sequentially acylated ($(CH_3)_3CCOCl$, 25 °C, 6 h) and then subjected to $AgBF_4$-mediated cyclization (CH_2Cl_2-CH_3NO_2, -78 °C). As had been desired, the tetrahydropyridine **13** was obtained as the major cyclized product in 53% isolated yield.[14] The extension of this methodology to the synthesis of naturally occurring ring systems is under current pursuit.

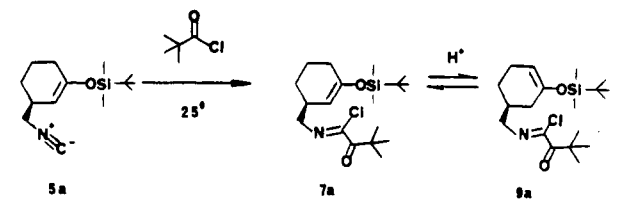


The examples presented above clearly indicate the utility of acylnitrilium ion initiated cyclizations for the synthesis of polyfunctional azacycles. The use of these cations in hetero-[4 + 2] cycloaddition reactions as well as the application of the present methodology to the synthesis of the *Orchidaceae* alkaloids will be reported in due course.

Acknowledgment. Support for this research by a grant from the National Institutes of Health is gratefully acknowledged. This communication is dedicated to the memory of Professor Robert V. Stevens.

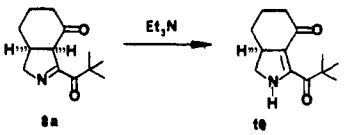
Supplementary Material Available: Representative experimental procedure for the synthesis of a 2-acylpyrroline (1 page). Ordering information is given on any current masthead page.

(11) Prolonged exposure of the substrate **5a** to trimethylacetyl chloride (e.g., 4-7 h, 25 °C) in the absence of pyridine led to the formation of the anticipated adduct **7a** along with its positional isomer **9a** (**7a**/**9a** = 1/1). The formation of **7a** and its subsequent conversion to **9a** was conveniently monitored by 300-MHz NMR spectroscopy. The isomerization of the silylenol ether function under these conditions is attributable to trace amounts of HCl present in the reaction medium.



(12) Several alternative procedures intended to bring about the cyclization of the adducts **7a-f** [e.g.: $Bu_4N^+F^-$ (THF, -78 °C), AgF (CH_3CN, -30 → 25 °C), and $SnCl_4$ (CH_2Cl_2, -78 → 0 °C)] gave lower yields of the desired pyrrolines.

(13) The Δ^1-pyrroline **8a** was found to undergo facile tautomerization to its Δ^2-isomer upon exposure to amine bases or silica gel. Accordingly, treatment of the crude pyrroline **8a** with triethylamine (1 equiv) immediately following cyclization provided the Δ^2-pyrroline **10** in 71% chromatographed yield.



(14) Evidence for the existence of a trans-fused B, C ring junction in **13** was provided by 300-MHz COSY experiments. A definitive assignment awaits single crystal X-ray structure determination.

Intrastrand Bis(guanine) Chelation of d(CpGpG) to *cis*-Platinum: An X-ray Single-Crystal Structure Analysis

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The antitumor drug *cis*-diamminedichloroplatinum(II) (*cis*-$PtCl_2(NH_3)_2$, abbreviated as *cis*-Pt) is known to bind preferentially to neighboring guanines in the DNA, both in vitro and in vivo.[1-7] This has initiated studies-mainly by NMR-on *cis*-Pt interactions with CG-containing oligonucleotides.[8-15] Recently, Lippard et al.[16] succeeded in solving the crystal structure of *cis*-$Pt(NH_3)_2$-[d(pGpG)-*N*7(1), *N*7(2)], which appears to be hardly different from the predicted structure in solution.[17] Since the stacking properties of the neighboring bases on the GG chelate could be important, we started studies on the precise structure of platinated trinucleotides that contain a d(GpG) sequence.

In this paper, the preliminary results of an X-ray structure determination of *cis*-$Pt(NH_3)_2$[d(CpGpG)-*N*7(2),*N*7(3)] are reported. The synthesis of the trinucleosidediphosphate[18] d(CpGpG) and the stoichiometric reaction of this DNA fragment with *cis*-Pt[19] have been described elsewhere. Two types of single crystals[20] were obtained.[21] Because the crystal form II showed

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(20) The crystals were grown by vapor diffusion from aqueous solutions containing 12.5% 2-methyl-2,4-pentanediol (2-MPD) and 10 mM of the compound at pH 8.1, which are in equilibrium with a reservoir which contains a 0.1 M HAc/KAc buffer solution and 25% 2-MPD (+H 5.7).

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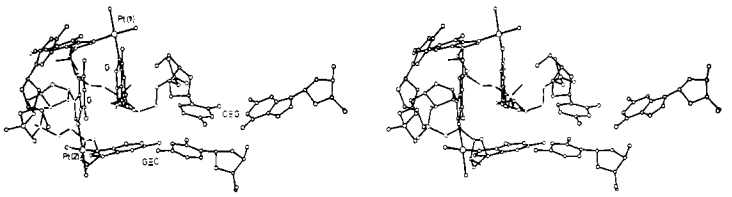

Figure 1. ORTEP stereodrawing of the dimer (1,2). Part of the other dimer (2,1) is indicated as well.

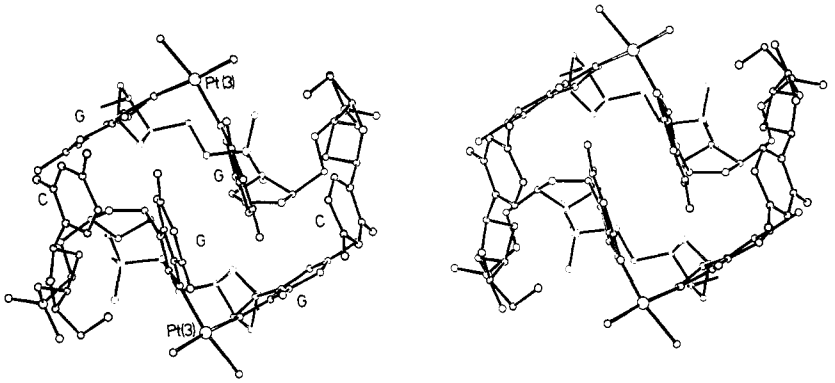

Figure 2. ORTEP stereodrawing of the dimer (3,3).

too much disorder and/or microtwinning, the data set for crystal I, even though of relatively low resolution due to the small crystal volume, was used for refinement. The positions of the platinum atoms were readily obtained from a Patterson synthesis, after which a series of subsequent weighted $2F_o - F_c$ Fourier maps resulted into the location of three independent molecules plus 26 water molecules. Least-squares refinement was carried out with bond angles and bond distances constrained to values derived from the literature.[22,23] Only the platinum atoms were refined anisotropically while the other atoms were refined with isotropic thermal parameters.[24]

The packing in the crystal consists of three crystallographically independent molecules (1, 2, and 3). Molecules 1 and 2 form a tetramer (dimer of dimers (1,2)), whereas two molecules of 3—which are related by a crystallographic twofold rotation axis—form another dimer (3,3) (Figures 1 and 2). The molecules within the dimers are held together by stacking interactions of the central guanines as well as hydrogen bonding between the nucleobases. Dimer (1,2) has also strong hydrogen-bonding contacts of the Watson–Crick type with a second dimer (2,1), forming a tetrameric unit; i.e., the cytosine of molecule 1 and the 3′-guanine base of molecule 2 show Watson–Crick-type hydrogen bonding with the other dimer (1,2). Furthermore, stacking interactions of the cytosine and the 3′-guanine of molecule 2 with two other molecules 2 occur. Dimer (3,3) on the other hand has only contacts with other molecules via its N4 of the cytosines and there is no interdimer base–base stacking. As a result of this loose packing, molecule 3 displays a relatively large thermal motion. Figure 3 describes schematically the intermolecular interactions.

The torsion angles of the sugar–phosphate backbone and the glycosyl bond have been listed as supplementary material. The sugar ring conformation of molecules 1 and 2 are similar: cytosine,

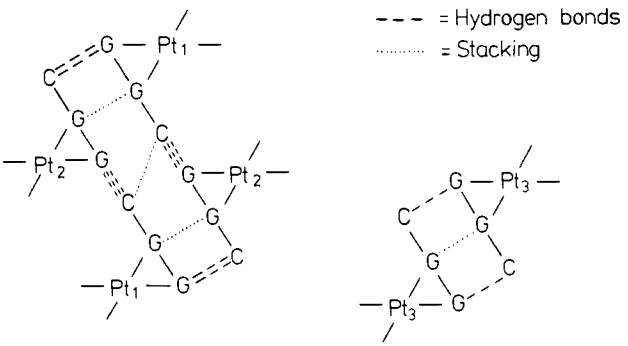

Figure 3. Schematic structures of the tetramer (1,2:2,1) and dimer (3,3) with special indication of stacking and hydrogen-bond interactions between the bases.

C2′-endo(S); central guanine, C3′-endo(N); and the terminal guanine, C2′-endo/C1′-exo(S). For the GpG part, this appears to agree well with the published structure[16] of the *cis*-Pt adduct with d(pGpG) as well as with NMR studies of d(CpGpG).[19] Due to the large thermal motion of the sugar–phosphate backbone of molecule 3, the detailed conformation of this molecule could not yet be determined accurately, although it is clear that the central guanine has its sugar ring in the N-conformation.

The geometry of the Pt atoms[24] and the coordinated N-atoms and guanine bases agree well with the structure of *cis*-Pt-$(NH_3)_2$[d(pGpG)-N((1),*N*7(2)].[16] Thus, head-to-head orientation of the guanine bases is present, and the dihedral angle[21] between these bases ranges from 80° to 84°. There is a weak intramolecular hydrogen bond between an NH_3 ligand and a guanine O6 in each of the three molecules (O···N = 295 (10) pm). The O6 atoms of the central guanine are only intramolecularly hydrogen bonded to an NH_3 group. Such intramolecular O6···NH_3 interactions may play an important role in stabilizing the conformation of the platinum-coordinated guanine bases. The short intramolecular phosphate···NH_3 ligand hydrogen bond observed[16] in the structure of the pGpG adduct appears to be somewhat longer (the shortest PO···NH_3 contact being 331 (8) pm).

In none of the three molecules do the cysteine bases stack upon the adjacent central guanine base. In fact the orientation of these nucleobases does not allow stacking, i.e., they are not parallel, and the position of the cytosine appears mostly governed by intermolecular hydrogen bonding. In molecules 2 and 3, the cytosine O2 is strongly intramolecularly hydrogen bonded to the N1 and the N2 of the 3′-guanine of the other molecule in the dimers. In

(21) Two crystal forms were obtained. Type I crystals were large but very thin (<0.02 mm) plates. Type II crystals had a prismatic shape (0.5 mm × 0.3 mm × 0.3 mm). Cell dimensions as obtained from X-ray diffraction are as follows: space group, trigonal $P3_121$, $Z = 48$, $a = b = 30.852$ (2) Å, $c = 73.262$ (6) Å, $\gamma = 120°$, $V = 60\,404$ Å^3; number of reflections, 8431; resolution, 1.0 Å. Because of severe disorder in crystal type II, this structure could not be solved. Crystals of type I showed poor scattering power. Crystal data are as follows: space group, orthorhombic $C222_1$, $Z = 24$, $a = 25.632$ (4) Å, $b = 53.848$ (9) Å, $c = 27.465$ (7) Å, $V = 37\,907$ Å^3; number of reflections, 2479; resolution, 1.8 Å; current R factor, 14.3%. Final atomic coordinates are given in the supplementary material, Table S2.

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(24) At the present stage of the refinement, all angles and distances appear to be normal, i.e., Pt–N = 200 (5) pm, N–Pt–N = 90°.

molecule 1, the cytosine is involved in Watson–Crick base pairing with a second dimer (1,2) (see Figure 1). In addition the cytosine bases of molecule 2 are strongly stacked, as schematically depicted in Figure 3. Finally, stacking occurs between the cytidine base of molecule 2 and the G(1) of a neighbouring molecule 2 (not shown).

In summary, it is concluded that the GG part of the described structure appears to be similar to the structure found in the crystal structure[16] of *cis*-$Pt(NH_3)_2$-(pGpG). As a result of intermolecular interactions of the cytosines, the conformation of this nucleobase in the structure—especially with respect to its stacking on the central guanine—does not reflect the conformation of the compound in solution.

Acknowledgment. This study was supported in part by the Netherlands Foundation of Chemical research (S.O.N.) with financial aid from the Netherlands Organization for the Advancement of pure Research (Z.W.O.), through Grant 11-28-17. Stimulating discussions with the group of Prof. Dr. J. C. Chottard (Paris), made possible through the sponsorship of the French-Dutch cultural agreement, are gratefully acknowledged. Financial aid for the synthesis of d(CpGpG) was supplied by the Netherlands Organization for the Fight against Cancer. We are indebted to Dr. G. Bosshard (EMBL, Heidelberg) for assistance with the graphics system, to Johnson Matthey Chemicals Ltd. (Reading, U.K.) for their generous loan of K_2PtCl_4, and to Prof. S. J. Lippard (MIT) for providing us with the coordinates obtained from the structure determination of the compound *cis*-$Pt(NH_3)_2$[d-(pGpG)-*N*((1),*N*7(2)].

Registry No. *cis*-$Pt(NH_3)_2$[d(CpGpG)-*N*7(2),*N*7(3)], 105834-59-1.

Supplementary Material Available: Tables with conformational parameters of the CpGpG units in each of the three molecules in solid *cis*-$Pt(NH_3)_2$[(CpGpG)-*N*7(2),*N*7(2),*N*7(3)] and atomic coordinates with *B* values (5 pages). Ordering information is given on any current masthead page.

How Does Prereduction Affect Electronically the Catalytic Properties of MoO_3 toward Olefin Oxidation

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The recent observation[1] that the (100) face of MoO_3 can catalytically convert propylene into acrolein is of much interest and may be used as a model to understand the catalytic properties of bismuth molybdates.[2] To explain the olefin adsorption, the existence of an "open" Mo atom on the surface, hence prereduction, was suggested. Consequently, not all the Mo atoms[3] can be d^0 (in a +6 oxidation state), a fact in sharp contrast with the assumption[4] of an empty d band in bismuth molybdate catalysts.

To probe the electronic implications of this prereduction step, band structure calculations[5] were carried out on both naked MoO_3 and the whole surface/olefin system. The analysis shows that (i) the surface acquires a metallic character which enhances its ability to chemisorb the olefin and (ii) the extra electron density is *not* localized on the open metallic site but in bulk like states. This "reservoir" is emptied upon adsorption, thereby filling a new set of surface/adsorbate bonding states which fall *below* the Fermi level. A stronger chemisorption results.

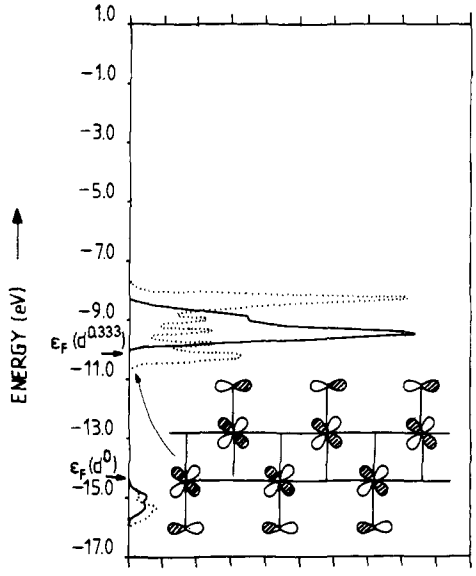
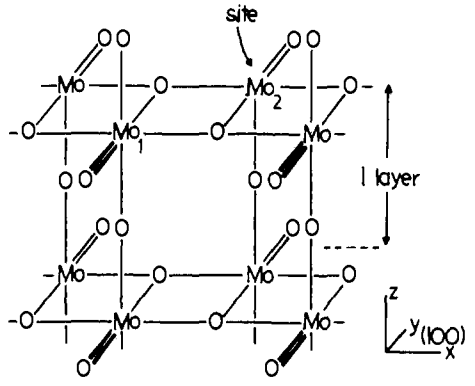


Figure 1. Projected density of states (DOS) of *xy* (dotted line) and *yz*/*xz* (solid line) of the Mo atoms in the surface **1**; the labels ϵ_F (d^0) and ϵ_F ($d^{0+0.333}$) refer to the Fermi level for various electron counts. The topology of the *xy* band at the Γ point is also indicated, from a top view.

The (100) face of MoO_3, perpendicular to the natural cleavage plane of layered[7] MoO_3, has never been structurally characterized. The calculations were performed on a three-layer ribbon with two Mo atoms in the outermost layer belonging to the unit cell;[8] in this model,[12] one (Mo_1) retains the apical oxygen away from the bulk while the other (Mo_2)—the site—is opened, as shown in **1**.



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(5) The Hamiltonian is of the extended Hückel type implemented on a tight-binding framework: Whangbo, M.-H.; Hoffmann, R.; Woodward, R. B. *Proc. R. Soc. London, Ser. A* **1979**, *366*, 23. The Mo and O, C, and H parameters are extracted from the literature.[6ab]

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(8) With each Mo in a local O_h geometry and all Mo–O distances set at 1.98 Å, the band gap and overlap populations obtained[9] for bulk MoO_3 agree well with the experimental[10] and theoretical[11] data.

(9) Silvestre, J., manuscript in preparation.

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(12) Most of the mechanisms suggested[1b,2a,4] for this reaction feature the olefin adsorbed on a Mo site.

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