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Preparation and Structure of Pt[C6H9OC2H5][P(C6H5)3]2. An Unusual Compound Formed by Reaction of Ethanol with a Platinum-Olefin Complex

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In a previous paper,[1] we reported the preparation and crystal structure of $\Delta^{1,4}$-bicyclo[2.2.0]hexenebis(triphenylphosphine)platinum (or (*SP*-4-3)(1,4-bicyclo[2.2.0]hexanediyl)bis(triphenylphosphine)platinum), Pt[C6H8][P(C6H5)3]2 (1), a complex in which the coordinated olefin has considerable ring strain. Upon dissolution in ethanol (originally for the purpose of recrystallization), this olefin complex underwent an unusual reaction: ethanol added across the σ bond between the two coordinated carbon atoms in the complex with loss of bonding between them. The two Pt–C interactions were retained. The complex, **2**, has a structure very similar to the bicyclo[2.2.1]heptane (norbornane) ring system. The reaction product has been characterized by X-ray diffraction; the crystal contained water of crystallization, having the composition Pt[C6H9OC2H5][P(C6H5)3]2·$\frac{1}{2}$H2O. A preliminary report of this work has been made.[2]

Experimental Section

Preparation of Pt[C6H9OC2H5][P(C6H5)3]2·$\frac{1}{2}$H2O (2). The olefin complex 1, Pt[C6H8][P(C6H5)3]2, was prepared by the literature method previously described.[1] Pt[C6H8][P(C6H5)3]2 was dissolved in a small amount of methylene chloride, and to this was added enough 100% ethanol to make the solution cloudy. The methylene chloride was allowed to evaporate slowly in a drybox, precipitating white to cream colored crystals. The complex decomposed in the range 152–158 °C (vacuum). IR spectrum (CH2Cl2, 0.1 mm): 3350 (br), 3041 (m), 2966 (m), 1670 (m), 1583 (w), 1566 (w), 1473 (m), 1420 (s), 1250 (s) cm⁻¹.

Anal. Calcd for C44H45O1.5P2Pt: Pt, 22.82; P, 7.25; C, 61.81; H, 5.31; O, 2.81. Found: P, 7.11; C, 50.92; H, 5.01; O, 2.7.[3]

ESCA Spectrum:[4] Pt $4f_{5/2}$, 75.5 eV; Pt $4f_{7/2}$, 72.2 eV.[5]

Collection and Reduction of X-ray Diffraction Data. Crystal data and the experimental conditions for data collection are given in Table I. The crystal was assigned to the monoclinic system on the basis of optical examination and preliminary X-ray photography. The observed systematic absences are hkl, $h + k = 2n + 1$, $h0\,l$, $l = 2n + 1$, and $0k0$, $k = 2n + 1$, which is consistent with space groups C_s^4, Cc, and C_{2h}^6, $C2/c$. The structure was refined with the assumption of the space group to be $C2/c$, and this assumption was confirmed by the structure refinement. The cell constants, obtained by least-squares refinement using the setting angles of 12 reflections centered on a Picker four-circle automatic diffractometer with Mo Kα X-radiation (λ = 0.7107 Å), were (at 20 °C) a = 26.242 (8) Å, b = 12.161 (3) Å, c = 26.744 (8) Å, β = 115.76 (2)°. For eight formula weights of the complex molecule plus four formula weights of water in the unit cell, the calculated density is 1.48 g/cm³; the observed density (by flotation) is 1.52 g/cm³.

The crystal used in data collection was bound by the faces of the form {100}, {11$\bar{2}$}, and {$\bar{1}$12} with distances between parallel faces of 0.09, 0.22, and 0.17 mm, respectively. The crystal was initially aligned about the c axis of the cell and was misset before data collection. The intensity data were collected in the ω–2θ scan mode with graphite crystal monochromated Mo Kα X-radiation. The intensities of the reflections $h,k,\pm l$ were recorded to a 2θ value of 70°. The intensities of three standard reflections were measured at intervals throughout data collection; these intensities varied throughout the experiment with a final average loss of 10%.

The data were corrected for background and for the changes in the standard reflections. The linear absorption coefficient was 37.7

Table I. Crystal Data and Data Collection Parameters

C44H45O1.5P2Pt	fw = 854.87 daltons
space group $C2/c$	Z = 8
a = 26.242 (8) Å[a]	d(obsd) = 1.52 g cm⁻³
b = 12.161 (3) Å	d(calcd)[b] = 1.48 g cm⁻³
c = 26.744 (8) Å	λ = 0.7107 Å (Mo Kα)
β = 115.76 (2)°	μ = 37.7 cm⁻¹

crystal faces: 100, $\bar{1}$00, 11$\bar{2}$, $\bar{1}\bar{1}$2, 1$\bar{1}$2, $\bar{1}$12
crystal dimens: 0.09, 0.22, 0.27 mm
data collected: $h,k,\pm l$ for 0 < 2θ ⩽ 70°
scan: symmetric scan of 2.0° in 2θ, 1°/min
bkgd: 10-s stationary crystal–stationary counter at scan limits
stds: 3 recorded every 100 reflections
no. of data in final refinement: 1367[c]
R(final): 0.069[c]
R_w(final): 0.055[c]

[a] The numbers in parentheses here and elsewhere in this paper are estimated standard deviations in units of the last digit. [b] By flotation. [c] The final refinement utilized all data for which $F_o > 0$.

cm⁻¹, and corrections were applied,[6] the transmission coefficients ranging between 0.44 and 0.72. Lorentz–polarization corrections were applied to the independent reflections, and standard deviations, $\sigma(F^2)$, were calculated from counting statistics. A total of 1729 reflections were measured and processed. There were 1367 independent reflections with $F^2 > 0$; 953 of these had a measured net intensity greater than three times the estimated standard deviation, calculated from counting statistics, of the background counts. These reflections were classed as observed.

Solution and Refinement of the Structure. Initial values for the fractional coordinates of the platinum atom were obtained from a three-dimensional Patterson function.[6] Succeeding applications of least-squares refinement and difference Fourier calculations yielded the coordinates of all nonhydrogen atoms in the complex molecule. The ether oxygen atom was identified as such by the height of the difference Fourier peak. The carbon atoms of the phenyl rings were refined as groups. The scattering factors were calculated with use of analytical approximations for neutral atoms,[7] and the effects of anomalous dispersion[8] were included in F_c. The function minimized in refinement was $\sum w\|F_o| - |F_c\|^2$, where $w = 4F_o^2/\sigma^2(F_o^2)$. Anisotropic thermal parameters for the platinum and phosphorus atoms, isotropic thermal parameters for the other nongroup atoms, and one overall thermal parameter for each group were refined. The phenyl ring hydrogen atoms were included, with the assumption of an idealized group geometry with a C–H bond length of 0.95 Å and thermal parameters 0.3 Å² higher than the carbon atoms to which they were bound. The R factor (on F) at this stage of refinement was 0.056 for the 953 observed reflections. A difference Fourier in the region of the hydrocarbon ligand was examined for evidence of the positions of the hydrogen atoms. The pairs of hydrogen atoms attached to C(2), C(3), C(5), and C(6) were found and subsequently included in idealized positions with a C–H bond length of 0.95 Å and an H–C–H angle of 109.5°. Electron density appropriate for one other hydrogen atom was observed in the region of C(4), and the position of this atom was refined with use of the limited data set of 953 observed reflections. This hydrogen atom was observed in (and refined to) a position chemically reasonable for it to be bound to C(4); the C–H distance was 1.22 Å.

Individual thermal parameters were refined for the carbon atoms in the groups and a systematic variation was observed.[1,4,9] An overall

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(5) Energies adjusted so that carbon-1s = 285.0 eV.
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Table II. Positional and Thermal Parameters for Nongroup Atoms in $Pt[C_6H_9OC_2H_5][P(C_6H_5)_3]_2$

atom	x	y	z	$\beta_{11}{}^a$	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pt	0.25173 (6)	−0.02388 (11)	0.31509 (5)	0.00199 (4)	0.0110 (4)	0.00204 (3)	−0.00018 (9)	0.0047 (3)	−0.00006 (9)
P(1)	0.3033 (3)	−0.0206 (7)	0.4106 (3)	0.0018 (2)	0.008 (1)	0.0025 (2)	0.00	0.0005 (2)	0.0003 (5)
P(2)	0.1620 (4)	−0.0327 (8)	0.3081 (3)	0.0025 (3)	0.0121 (11)	0.0026 (2)	0.00	0.0014 (3)	−0.0002 (5)

atom	x	y	z	B_{iso}, Å²	atom	x	y	z	B_{iso}, Å²
O	0.3798 (10)	−0.007 (2)	0.3468 (8)	10.2 (7)	H(1)ᶜ	0.1754	−0.0487	0.2056	7.3
x(1)ᵇ	0.0	0.429 (7)	0.25	13.1 (28)	H(2)ᵈ	0.3160	0.1588	0.2949	11.9
x(2)ᵇ	0.0	0.330 (7)	0.25	14.7 (28)	H(3)ᵈ	0.3404	0.1088	0.2563	11.9
C(1)	0.3187 (13)	−0.007 (3)	0.2976 (13)	7.0 (9)	H(4)ᵈ	0.2265	0.1569	0.2200	8.6
C(2)	0.3129 (18)	0.101 (3)	0.2700 (18)	11.6 (14)	H(5)ᵈ	0.2498	0.0942	0.1837	8.6
C(3)	0.2484 (17)	0.096 (3)	0.2187 (15)	8.3 (11)	H(6)ᵈ	0.2419	−0.1681	0.2161	9.3
C(4)	0.2235 (11)	−0.013 (3)	0.2285 (10)	5.1 (8)	H(7)ᵈ	0.2566	−0.0828	0.1809	9.3
C(5)	0.2579 (18)	−0.098 (3)	0.2164 (15)	9.0 (12)	H(8)ᵈ	0.3286	−0.1675	0.2774	8.6
C(6)	0.3187 (16)	−0.099 (3)	0.2590 (16)	8.3 (11)	H(9)ᵈ	0.3433	−0.0824	0.2422	8.6
C(7)	0.4342 (19)	0.029 (4)	0.3353 (18)	16.7 (16)					
C(8)	0.4763 (16)	−0.005 (3)	0.3886 (16)	13.1 (13)					

^{a} The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. ^{b} Refined as half-oxygen atoms. ^{c} Positional parameters refined with a limited data set; esd's at that stage of refinement were 0.011, 0.021, and 0.010, respectively. The thermal parameter is assigned. ^{d} None of the parameters for this atom was varied in the refinement.

thermal parameter for each group was defined and subsequently varied. The differences from this overall parameter for each of the positions around the ring were averaged for all of the rings and then not subsequently varied. The mean differences were as follows: C(1), −1.6; C(2) and C(6), 0.7; C(3) and C(5), 1.7; C(4), 1.5 Å². The R factor at this stage of refinement was 0.079 for the 953 observed reflections. The refinement was not satisfactory at this stage, because not only was the R factor comparatively high but many of the thermal parameters were very high (e.g., B_{iso} for C(4) is 40.2 Å²).

Another difference Fourier was calculated and two significant electron density maxima were observed; they had also been present in earlier difference Fourier maps but had not been included in refinement as they were clearly not part of the complex molecule. The maxima were located precisely on the twofold axes of the unit cell (with the assumption of the space group to be $C2/c$). The maxima were both of height appropriate to a carbon atom and were separated by 1.20 Å. It was judged highly unlikely that a two-carbon compound such as ethylene would be present as a molecule of crystallization. Instead, each pair of peaks could be assigned to one disordered oxygen atom (presumably of a water molecule originating from not-quite-anhydrous ethanol used as part of the recrystallizing solvent). The oxygen content of the sample was determined by neutron activation analysis, and the result (vida supra) proved the strongest evidence that the molecule of crystallization might indeed be water. The two maxima were included as half-oxygen atoms in least-squares refinement. Further evidence supporting the identity of the molecule of crystallization was that a subsequent difference Fourier showed no maxima appropriate for the hydrogen atoms of a hydrocarbon. It did indicate electron density in a region appropriate for a hydrogen atom (there would be only one independent hydrogen atom) bound to either half-oxygen, raising the possibility that the hydrogen atoms might be ordered and the oxygen atoms disordered. This atom was not included in subsequent refinement.

The R factor at this stage of refinement was 0.044 for the 953 observed reflections, with a weighted R factor, $R_w = (w(F_o - F_c)^2/wF_o^2)^{1/2}$, of 0.047. This lower R factor was accompanied by thermal parameters which, though still high, were more reasonable than earlier. Clearly this diffraction experiment has not provided a precise result: factors contributing to the low quality can be identified as the descriptions of the water of crystallization and the ethoxy group. C(7) and C(8) could well be disordered; the contributions of these atoms were removed from a structure factor calculation, but a subsequent difference Fourier showed only one maximum for each of these atoms, even though the electron density was diffuse. The possibility that refinement was being conducted in the wrong space group was considered; the systematic absences are also consistent with space group Cc, but the derived crystal structure indicates Cc is unlikely to be the correct space group.

A further two cycles of the refinement were calculated with use of all 1367 independent reflections for which $F_o^2 > 0$. The final values of the R factor and weighted R factor were 0.069 and 0.055, and the error in an observation of unit weight was 0.81. The final values of the positional and thermal parameters and their standard deviations
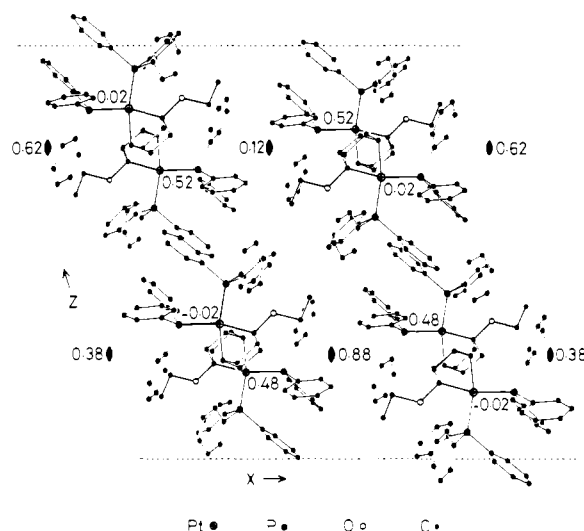

Figure 1. $Pt[C_6H_9OC_2H_5][P(C_6H_5)_3]_2$ (**2**). Contents of a unit cell viewed down the b axis. The outline of the unit cell is shown by broken lines. Adjacent to each platinum atom is given the y coordinate of that atom. The oxygen atoms of the water of crystallization are disordered and lie on the crystallographic twofold axes; the y coordinate adjacent to each axis is that of the midpoint of a pair of half-oxygen atoms.

calculated from the inverse matrix are given in Table II. The phenyl ring atoms were refined as groups, and the parameters are given in Table III.[10] Table IV[10] lists the fractional coordinates (derived from the group parameters) and the thermal parameters for the carbon atoms in the groups. Table V[10] gives the root-mean-square amplitudes of vibration for those atoms refined with anisotropic thermal parameters. A list of $10|F_o|$ vs. $10|F_c|$ is found in Table VI.[10]

Description of the Structure

The crystal belongs to the monoclinic system with eight molecules of the platinum complex and four molecules of water in the unit cell. The packing of these molecules is illustrated in Figure 1; the view direction is parallel to the b axis of the cell, and the outline of a unit cell is indicated by broken lines. The y coordinate of each platinum atom is given alongside that atom. The positions of the twofold axes are indicated by the conventional symbol and the adjacent number is the y coordinate of the point midway between two half-oxygen atoms; the half-oxygen atoms are 0.60 Å above and below this point. It can be seen that the 200 planes in the crystal have a low
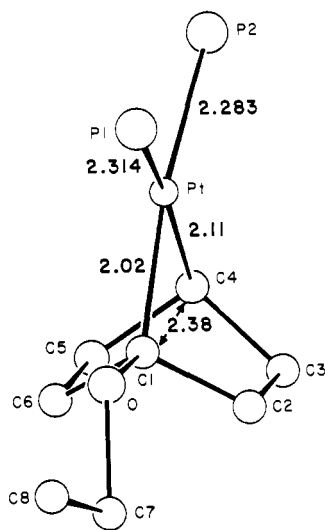
(10) Supplementary material.

Figure 2. General view of a molecule of Pt[C₆H₉OC₂H₅][P(C₆H₅)₃]₂ (2). All atoms have been assigned artificial thermal parameters for the purpose of clarity. Distances are in angstroms.

density of atoms from the complex molecule; the oxygen atoms of the water molecules of crystallization lie in these planes. The water molecules also have a crystallographically imposed twofold axis of symmetry. There are no unusually short intermolecular contacts in this crystal structure, not even when the hydrogen atoms of the water of crystallization are considered in reasonably postulated positions. Thus, hydrogen bonding is probably not a significant feature of this crystal structure.

The complex molecule has no symmetry crystallographically imposed upon it. An overall view of the molecule (excluding phenyl rings) is given in Figure 2. Selected parameters describing the molecular structure are given in Table VII; the relatively low precision of this structure determination is manifested in the high esd's of these parameters. The hydrocarbon ligand can be considered a substituted cyclohexane constrained to the boat conformation by σ bonds from C(1) and C(4) to the platinum atom. The cyclohexane–platinum fragment is a bicyclo[2.2.1]heptane ring system, and its structure is similar to that of norbornane.[11] There is no bonding interaction between C(1) and C(4), and their separation is 2.38 (4) Å (cf. 2.32 (2) Å in norbornane).[11] The six C–C bond lengths around the cyclohexane ring average 1.52 Å, and none are significantly different from that expected for carbon atoms linked by a single σ bond. The carbon atoms C(1) and C(4) do not have inverted geometry; indeed, there seems to be little ring strain in the cyclohexane moiety. The C–C–C angles around the cyclohexane ring range from 101 (3) to 112 (3)° and average 105°. The Pt–C–C angles range from 104 (2) to 110 (2)° and average 107°. While these angles, along with the Pt–C(1)–O angle of 119 (2)°, vary from the ideal tetrahedral angle, the variations are not very great and are much less than in the parent olefin complex,[1] Pt-[C₆H₈][P(C₆H₅)₃]₂ (1). The dihedral angle between the planes C(1), C(2), C(3), C(4) and C(1), C(6), C(5), C(4) is 112 (3)°, much less than the 124 (2)° found in 1 and closer to the 108 (1.5)° observed for the corresponding angle in norbornane.

The cyclohexane group is bound to platinum by two σ bonds, Pt–C(1) and Pt–C(4), and the coordination sphere of platinum is close to square planar. The dihedral angle between the planes Pt, C(1), C(4) and Pt, P(1), P(2) is 4.5 (8)°; P(1) and P(2) are displaced from the Pt, C(1), C(4) plane by 0.14 (4) and 0.09 (5) Å in the same direction. The main distortion is

Table VII. Parameters Describing the Structure of Pt[C₆H₉OC₂H₅][P(C₆H₅)₃]₂

(i) Bond Lengths (Å)

Pt–P(1)	2.314 (8)	Pt–P(2)	2.283 (8)
Pt–C(1)	2.02 (3)	Pt–C(4)	2.11 (2)
C(1)–C(2)	1.48 (4)	C(1)–C(6)	1.52 (4)
C(2)–C(3)	1.66 (5)	C(5)–C(6)	1.51 (4)
C(3)–C(4)	1.54 (4)	C(4)–C(5)	1.50 (4)
C(1)–O	1.57 (3)	O–C(7)	1.65 (4)
C(7)–C(8)	1.43 (5)		

(ii) Bond Angles (Deg)

P(1)–Pt–C(1)	95.9 (9)	P(2)–Pt–C(4)	93.2 (7)
Pt–C(1)–C(4)	56.5 (10)	Pt–C(4)–C(1)	53.0 (9)
Pt–C(1)–C(6)	110 (2)	Pt–C(1)–C(2)	107 (3)
Pt–C(4)–C(3)	106 (2)	Pt–C(4)–C(5)	104 (2)
Pt–C(1)–O	119 (2)	C(1)–O–C(7)	120 (2)
O–C(1)–C(6)	106 (3)	O–C(1)–C(2)	105 (3)
C(1)–C(2)–C(3)	103 (3)	C(1)–C(6)–C(5)	101 (3)
C(2)–C(3)–C(4)	104 (3)	C(6)–C(5)–C(4)	112 (3)
C(3)–C(4)–C(5)	102 (2)	C(6)–C(1)–C(2)	110 (3)

(iii) Dihedral Angles (Deg)

Pt, C(1), C(4)	Pt, P(1), P(2)	4.5 (8)
Pt, C(1), C(4)	C(1), C(2), C(3), C(4)	58 (2)
Pt, C(1), C(4)	C(1), C(4), C(5), C(6)	54 (2)
C(1), C(2), C(3), C(4)	C(1), C(4), C(5), C(6)	112 (3)
C(2), C(1), C(6)	C(3), C(4), C(5)	52 (3)

(iv) Torsion Angles (Deg)

C(1)–C(2)–C(3)–C(4)	6 (4)	C(1)–C(6)–C(5)–C(4)	0 (4)
C(4)–C(1)–C(2)–C(3)	4 (3)	C(4)–C(1)–C(6)–C(5)	0 (3)

caused by the steric restriction imposed by the cyclohexane ring system; the C(1)–Pt–C(4) angle is 20° less than a right angle because the positions of these carbon atoms are constrained by the ring of which they are a part. The platinum atom can be considered equidistant from C(1) and C(4), since the difference between these two bond lengths, 0.09 (4) Å, is not statistically significant. The Pt–P bond lengths average 2.298 Å, and the difference between the two observed values is 0.031 (11) Å, not statistically significant.

The geometry of the triphenylphosphine ligands is normal. The P–C bond lengths range from 1.78 to 1.84 Å and average 1.82 Å. The Pt–P–C angles range from 110.1 to 122.5° and average 115.7°. The only significantly short intramolecular contact is 2.29 Å, between the assumed positions of a hydrogen atom bound to C(6) and a hydrogen atom on ring 1B.

Reaction of Platinum–Olefin Complexes

Much attention has been focused on the reactions of olefins and acetylenes coordinated to platinum, owing in part to their use as industrial catalysts.[12] These complexes have been found to undergo oxidative insertion, oxidation, dissociation, ligand exchange, and the addition of both electrophiles and nucleophiles.[13,14] Only in the last class of reactions, the additions of electrophiles and nucleophiles to the bound olefin or acetylene, is the ligand first attacked by another substance. The formation of the complex 1 must fall within this class.

Nucleophilic attack on platinum(0) complexes are quite rare. However, the addition of strong bases such as amines and alcoholates to platinum(II)–olefin complexes are common and have been used extensively in industry.[15–18] The nucleophile attacks one of the carbon atoms of the olefin to give

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an amine or ether with a Pt–C σ bond trans to the C–N or C–O bond.[17,18]

Few electrophilic additions to either platinum(0)– or platinum(II)–olefin complexes have been observed, as indicated in the review by Hartley.[14] However, the addition of a strong acid such as hydrochloric or trifluoromethanesulfonic acid, to a platinum(0)–acetylene complex results in a σ-bonded alkenylplatinum complex.[19,20]

Hartley and others have pointed to the fact that the stability of platinum(0)–olefin complexes increases as the substituents on the olefin become more highly electron withdrawing.[14] The indication is that back-donation through the *b*-symmetry orbitals, as drawn by McGinnety,[21] is more important than in similar platinum(II) complexes. Thus electron density is built up on the olefinic ligand in strong Pt(0)–olefin bonds. To the extent that this statement follows from the substituent effects on Pt(0)–olefin bond strengths, one would expect these complexes to exhibit enhanced reactivity toward electrophiles and diminished reactivity to nucleophiles.

The reaction of $\Delta^{1,4}$-bicyclo[2.2.0]hexenebis(triphenylphosphine)platinum(0) to give the title compound can thus be envisioned as the protonation of one of the olefinic carbons leaving a cation of structure **3**, which reacts with the solvent
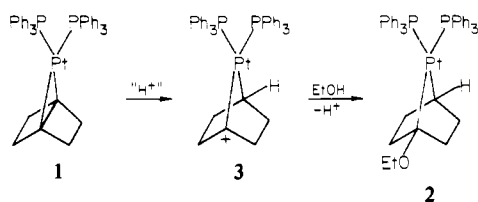
to give the ether complex. This reaction has a direct analogy in the addition of acids to many propellanes.[22–24] Propellanes are subject to reaction with both electrophiles and radicals at one of the bridgehead carbons with simultaneous cleavage of the central bond. It is interesting to note that as a class of compounds they are stable to bases and nucleophiles.

Sensitivity of Pt(0)–olefin complexes to ethanol is in no way a common property. In fact cyclopropene[25] and strained allene complexes are commonly recrystallized from ethanol. It is hoped that this report will create interest in the relationship between the reactivity of metal–ligand complexes and the strain inherent in the ligand.

Registry No. **1**, 54071-60-2; **2**, 54071-61-3.

Supplementary Material Available: Tables of group parameters (Table III) and thermal parameters and derived fractional coordinates of phenyl group carbon atoms (Table IV) in Pt[C₆H₉OC₂H₅][P-(C₆H₅)₃]₂, root-mean-square components of thermal displacement along principal axis R (Table V), and observed and calculated structure factors (Table VI) (11 pages). Ordering information is given on any current masthead page.

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Melting Profiles of *cis*- and *trans*-Dichlorodiammineplatinum(II) Poly(dA-dT) Complexes in Solution

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Numerous spectroscopic studies have investigated the interaction of dichlorodiammineplatinum(II) (DDP) with DNA[1] since the discovery that *cis*-DDP (but not *trans*-DDP) is an active antitumor agent.[2] Both DDP isomers bind strongly to DNA, and the antitumor activity of *cis*-DDP has been related to its ability to inhibit DNA synthesis. Recent extended X-ray absorption fine structure (EXAFS) studies from our laboratory suggest that the local structure of the complexes formed by *cis*- and *trans*-DDP with calf thymus DNA contains no distinct metal–metal bonds.[3] We report here our optical and ¹H NMR studies of the thermal melting (duplex to strand transition) profiles of the complexes formed by *cis*- and *trans*-DDP with the synthetic DNA poly(dA-dT) in an attempt to understand the differences in the binding of these complexes to DNA.

Experimental Section

Optical Melting Studies. The lyophilized sodium salt of poly(dA-dT) was purchased from Collaborative Research and dialyzed against two changes of 5 mM cacodylate buffer (pH 7.0). Cacodylate buffer was used to avoid coordination to the platinum complexes or interference in the ¹H NMR studies (vide infra) by the buffer material. No other salts were added in the buffer in order to avoid raising the melting temperature(s) of the resulting complexes too close to the boiling point (vide infra). The polynucleotide concentration was based on an extinction coefficient, ϵ_{260} = 6.7 × 10³ in phosphates. Solutions of *cis*- or *trans*-DDP and poly(dA-dT) were mixed in 5 mM buffer (final synthetic DNA concentration of 0.15 mM in phosphates) and allowed to react in the dark at 25 °C with constant agitation for 2–3 days. It should be mentioned that at the BP/M ratios employed, the concentrations appropriate for optical measurements, and the reaction times allowed in the present study, all solubilized DDP complexes would have reacted. Control reactions run for a longer period of time (5 days) or dialyzed against the buffer at the end produced essentially the same optical melting data reported here. The thermal melting of the complex with base pair/metal (BP/M) ratios of 64, 32, 24, 16, 8, 4, and 2 was measured as the relative changes in absorbance at 260 nm (ΔA_{260}) with the use of a Gilford 2400-2 spectrometer equipped with a thermoelectric device for heating the sample cell, a thermoprogrammer, and a reference compensator. The samples were held in separate 5-mm quartz cells and were heated at a constant rate of 1 °C/min from 25 to 80 °C. Each set included a poly(dA-dT) control along with the *cis*- and *trans*-DDP·poly(dA-dT) complexes at the same BP/M ratio.

¹H NMR Studies. The DDP·poly(dA-dT) samples for the NMR studies were prepared by reacting *cis*- and *trans*-DDP with poly(dA-dT) at BP/M ratios of 8 and 4 in 5 mM cacodylate buffer in the dark at 25 °C with constant agitation for 2–3 days. The samples (volume 8 mL) were subsequently dialyzed against 5 mM NaCl, 0.5

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