Table III. Fraction of ONCN Decomposed by the First Mechanism, Calculated in Two Different Ways

	Run 1	Run 2	Run 3	Run 4
$f(\mathrm{NN})/f(\mathrm{N^*NO})$	0.80	0.67	0.91	0.62
$[f(\mathrm{N^*NO}) - f(\mathrm{N^*CCN})]/f(\mathrm{N^*NO})$	0.86	0.94	0.90	0.91

whole can be quantitatively accounted for in terms of two concurrent mechanisms. We propose the principal mechanism

$$\mathrm{2ONCN \rightarrow 2NO + (CN)_2} \tag{1}$$

$$\mathrm{NO + ONCN \rightarrow N_2O + OCN} \tag{2}$$

$$\mathrm{NO + OCN \rightarrow CO_2 + N_2} \tag{3}$$

Reaction 1 is quite reasonable as the initiation step in view of the very low C–N bond dissociation energy of nitrosyl cyanide. Reaction 2 can be envisaged as taking place in either of two ways. In the first way, the NO molecule essentially plucks off the terminal nitrogen atom from the ONCN molecule to form the fulminate radical, ONC

$$\mathrm{ONCN + NO \rightarrow ONC\cdots N\cdots NO \rightarrow ONC + NNO}$$

This radical has been observed as a short-lived product of the photolysis of ozone–cyanogen mixtures.[7] We assume that it rapidly rearranges to the more stable cyanate radical, OCN.[8] When labeled ONCN is used, this first way leads to labeled N_2O and unlabeled OCN. In the second way, the NO and ONCN molecules react by a four-center process

$$\mathrm{ONCN + NO \rightarrow \begin{array}{c} ON\cdots CN \\ \vdots\quad\;\vdots \\ N\cdots O \end{array} \rightarrow ONN + OCN}$$

When labeled ONCN is used, the second way yields unlabeled N_2O and labeled OCN. Reaction 3 is probably a four-center process. The fact that NO does not abstract the nitrogen atom from OCN, giving CO and N_2O, is probably related to the fact that the latter products are less stable by 87 kcal/mol than the observed products CO_2 and N_2.[9]

According to the first mechanism, the use of terminally labeled ONCN should yield only doubly labeled cyanogen, and the amount of labeled N_2 should equal the amount of unlabeled N_2O. To account for the fact that the observed data deviate from these predictions, we propose that the following mechanism occurs concurrently with, but to a lesser extent than, the first mechanism

$$\mathrm{NO + ONCN \rightarrow N_2O + OCN} \tag{2}$$

$$\mathrm{OCN + ONCN \rightarrow NO_2 + (CN)_2} \tag{4}$$

$$\mathrm{NO_2 + ONCN \rightarrow CO_2 + N_2 + NO} \tag{5}$$

This mechanism consists of three chain-propagating steps, involving the chain carriers NO, OCN, and NO_2. Reactions 1 and 3 can serve as the chain-initiating and -terminating steps, respectively, of this mechanism. It should be noted that the first step of the second mechanism (reaction 2) is the same as the second step of the first mechanism. The second step (reaction 4) is probably a four-center process; it yields singly labeled $(CN)_2$ when the OCN is unlabeled and the ONCN is labeled. The third step (reaction 5) may occur directly as a complicated multicenter process or may actually be a two-step process, involving nitryl cyanide as an intermediate.

The fraction of the nitrous oxide which is formed in reaction 2 by the abstraction by nitric oxide of the terminal nitrogen atom of nitrosyl cyanide is equal to the fraction of labeled N_2O formed in the experiments with labeled nitrosyl cyanide, $f(\mathrm{N^*NO})$. The average value of this quantity in runs 1–4 was 0.82 ± 0.03. The fraction of the nitrosyl cyanide which decomposed by the first mechanism, f_1, can be calculated from two independent sets of data

$$f_1 = f(\mathrm{NN})/f(\mathrm{N^*NO})$$

$$f_1 = [f(\mathrm{N^*NO}) - f(\mathrm{N^*CCN})]/f(\mathrm{N^*NO})$$

The values of f_1 calculated in these ways for each of the four ^{15}N-labeled runs are given in Table III. The values calculated by the two different ways are in good agreement except in the case of runs 2 and 4. In spite of these discrepancies, all the data clearly indicate that the first mechanism (reactions 1–3) predominates in the thermal decomposition.

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Registry No. ONCN, 4343-68-4; nitrosyl chloride, 2696-92-6; silver cyanide, 506-64-9; $ONC^{15}N$, 63089-51-0.

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Crystal and Molecular Structure of Allyl(bromo)bis(triethylphosphine)platinum(II). An Example of σ Bonding of an η^1-Allyl Group

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Interest in transition metal σ-allyl complexes stems from their postulation as intermediates in the rearrangement reactions of fluxional π-allyl complexes.[1] Although much work has been devoted to the study of such fluxional π-allyl complexes of the platinum triad, until recently only a few stable σ-allyl derivatives of these metals had been isolated or even detected.[1-3] In the past year, a surprising number of reports have described various Pt(σ-allyl) complexes in solution or in the solid state.[4-10] Presently, we wish to report the crystallographic structure of *trans*-$Pt(\eta^1\text{-}C_3H_5)Br(PEt_3)_2$. An important feature of this x-ray structural study is the refinement of all the atoms in the molecule allowed by the excellent diffraction data obtained at −160 °C.

Experimental Section

The complex *trans*-η^1-allylbromobis(triethylphosphine)platinum(II) was synthesized from tetrakis(triethylphosphine)platinum(0) and allyl bromide as described elsewhere.[10] Crystals suitable for crystallographic examination were obtained by evaporation of a hexane solution of the complex at room temperature.

Structure Determination. A small fragment cleaved from a larger crystal was used for characterization and data collection. Precession photographs and a diffractometer search of reciprocal space revealed a monoclinic cell, space group $P2_1/c$. The crystal was mounted on an ultrastable goniometer head of local design using silicone grease and cooled to −160 °C on the goniostat using a nitrogen vapor cooling system.[11] The diffractometer used was locally designed and

Table I. Fractional Coordinates and Isotropic Thermal Parameters

Atom	$10^5 x^a$	$10^5 y$	$10^5 z$	$10B_{iso}$, Å^2
Pt(1)	85114 (2)	18704 (2)	7225 (2)	19
Br(1)	82794 (7)	31328 (5)	18691 (6)	31
P(1)	105817 (16)	16572 (11)	23918 (14)	21
P(2)	65103 (15)	22849 (13)	−9233 (15)	24
C(1)	86662 (69)	7571 (48)	98384 (60)	25
C(2)	83786 (75)	−1531 (48)	1720 (66)	33
C(3)	73943 (81)	−7099 (58)	−4716 (75)	40
C(4)	115424 (63)	7526 (48)	23593 (58)	26
C(5)	129163 (71)	6345 (61)	34822 (71)	34
C(6)	114723 (73)	27722 (50)	27171 (68)	30
C(7)	115019 (91)	30919 (67)	17225 (86)	44
C(8)	107385 (78)	14077 (57)	37302 (63)	31
C(9)	101581 (93)	4538 (66)	36794 (83)	42
C(10)	52833 (75)	21343 (62)	−7197 (75)	35
C(11)	51482 (108)	11155 (71)	−4603 (115)	48
C(12)	58707 (72)	16743 (59)	−23207 (66)	33
C(13)	45755 (88)	20147 (102)	−34141 (76)	54
C(14)	63956 (81)	35602 (58)	87286 (76)	37
C(15)	72971 (112)	38772 (82)	−15297 (111)	55
H(1)	944 (9)	70 (6)	5 (8)	61 (23)
H(2)	806 (6)	89 (4)	−95 (6)	22 (13)
H(3)	923 (6)	−41 (5)	121 (6)	34 (15)
H(4)	733 (7)	−142 (5)	−14 (6)	34 (15)
H(5)	667 (9)	−47 (7)	−137 (8)	75 (25)
H(6)	1156 (6)	91 (4)	175 (6)	23 (14)
H(7)	1106 (6)	18 (4)	215 (5)	16 (12)
H(8)	1341 (5)	121 (5)	376 (5)	14 (12)
H(9)	1337 (8)	25 (6)	334 (8)	58 (23)
H(10)	1294 (7)	43 (5)	410 (6)	32 (16)
H(11)	1089 (6)	334 (4)	282 (6)	29 (14)
H(12)	1217 (6)	270 (4)	338 (5)	13 (12)
H(13)	1195 (6)	357 (5)	197 (6)	23 (14)
H(14)	1063 (6)	316 (4)	105 (5)	13 (12)
H(15)	1202 (11)	267 (9)	150 (10)	104 (36)
H(16)	1155 (5)	135 (4)	434 (4)	2 (10)
H(17)	1037 (7)	193 (5)	383 (6)	30 (16)
H(18)	1023 (7)	36 (5)	447 (7)	40 (17)
H(19)	43 (7)	982 (5)	349 (6)	34 (16)
H(20)	938 (7)	44 (5)	307 (7)	34 (18)
H(21)	453 (9)	237 (6)	−137 (8)	61 (23)
H(22)	563 (7)	256 (6)	−0 (7)	43 (18)
H(23)	473 (8)	79 (6)	−107 (8)	44 (24)
H(24)	463 (7)	110 (5)	−18 (6)	39 (17)
H(25)	592 (9)	89 (6)	15 (8)	53 (24)
H(26)	579 (7)	96 (6)	−217 (7)	48 (19)
H(27)	640 (7)	176 (5)	−245 (6)	27 (16)
H(28)	467 (13)	276 (12)	−353 (12)	123 (48)
H(29)	405 (8)	201 (6)	−332 (7)	38 (21)
H(30)	436 (10)	168 (7)	−419 (10)	80 (28)
H(31)	556 (8)	363 (6)	−190 (7)	47 (19)
H(32)	663 (8)	385 (7)	956 (8)	69 (25)
H(33)	709 (12)	353 (9)	−214 (11)	99 (41)
H(34)	820 (10)	356 (8)	−80 (10)	77 (27)
H(35)	720 (9)	452 (7)	−174 (8)	63 (24)

[a] Hydrogen fractional coordinates are $\times 10^3$.

constructed[12] using a Picker four-circle goniostat equipped with a highly oriented graphite monochromator and controlled by a Texas Instruments TI980 minicomputer. Cell dimensions at −160 °C are $a = 13.216\ (4)$ Å, $b = 13.975\ (5)$ Å, $c = 14.207\ (4)$ Å, and $\beta = 127.53\ (2)°$, based on a least-squares fit of angular data from nine reflections centered in $\pm 2\theta$. The calculated density for $Z = 4$ is 1.763 g cm^{-3}. The linear absorption coefficient for the monochromatized molybdenum radiation (λ 0.71069 Å) is 88.58 cm^{-1}.

Integrated intensities were measured using θ–2θ scan techniques, with a speed of 4.0°/min over a range symmetrically disposed 1° on either side of the calculated $K\alpha_1$ and $K\alpha_2$ positions. Ten-second background counts were recorded at the extreme of each scan.

The data were corrected for Lorentz and polarization terms,[13] corrected for absorption (maximum and minimum transmission coefficients were 0.313 and 0.410), and reduced to 3670 unique structure amplitudes. Of these, 3469 had $I > 0.00$, 3231 had $I > \sigma(I)$, and 2927 had $I > 2.33\sigma(I)$, where I is the corrected intensity and $\sigma(I)$ is the estimated σ based on counting statistics and an "ignorance factor" of 0.05.

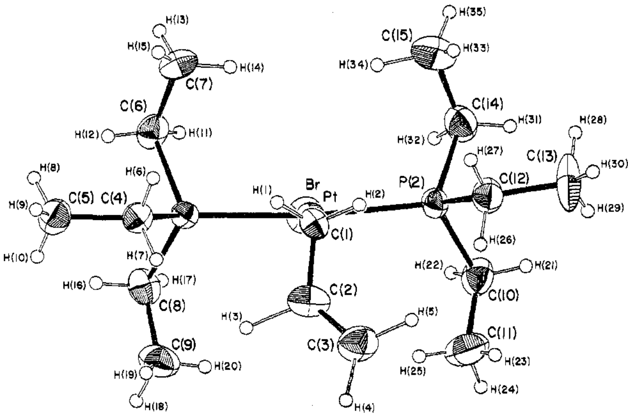

Figure 1. ORTEP drawing of the molecule with the Pt–Br–P(1)–P(2)–C(1) plane perpendicular to the paper. All thermal ellipsoids are drawn at the 50% probability level, and hydrogens have been given an artificial $B_{iso} = 0.5$ Å^2 for artistic purposes.

Table II. Bond Distances (Å)

Pt(1)	Br(1)	2.543 (1)	C(5)	H(9)	0.92 (9)
Pt(1)	P(1)	2.301 (2)	C(5)	H(10)	0.90 (7)
Pt(1)	P(2)	2.294 (2)	C(6)	H(11)	1.17 (6)
Pt(1)	C(1)	2.086 (7)	C(6)	H(12)	0.83 (6)
P(1)	C(4)	1.812 (7)	C(7)	H(13)	0.81 (7)
P(1)	C(6)	1.834 (7)	C(7)	H(14)	0.95 (6)
P(1)	C(8)	1.817 (7)	C(7)	H(15)	1.09 (11)
P(2)	C(10)	1.825 (7)	C(8)	H(16)	0.88 (5)
P(2)	C(12)	1.827 (8)	C(8)	H(17)	0.93 (7)
P(2)	C(14)	1.831 (8)	C(9)	H(18)	1.07 (7)
C(1)	C(2)	1.486 (9)	C(9)	H(19)	1.05 (7)
C(1)	C(3)	2.514 (10)	C(9)	H(20)	0.85 (7)
C(2)	C(3)	1.298 (10)	C(10)	H(21)	0.91 (9)
C(4)	C(5)	1.530 (10)	C(10)	H(22)	1.01 (8)
C(6)	C(7)	1.505 (11)	C(11)	H(23)	0.83 (8)
C(8)	C(9)	1.518 (11)	C(11)	H(24)	0.97 (8)
C(10)	C(11)	1.508 (12)	C(11)	H(25)	0.90 (9)
C(12)	C(13)	1.526 (11)	C(12)	H(26)	1.04 (8)
C(14)	C(15)	1.511 (13)	C(12)	H(27)	0.85 (7)
C(1)	H(1)	0.87 (9)	C(13)	H(28)	1.08 (16)
C(1)	H(2)	0.93 (6)	C(13)	H(29)	0.77 (8)
C(2)	H(3)	1.25 (7)	C(13)	H(30)	1.08 (11)
C(3)	H(4)	1.12 (7)	C(14)	H(31)	0.91 (8)
C(3)	H(5)	1.09 (9)	C(14)	H(32)	1.11 (9)
C(4)	H(6)	0.91 (6)	C(15)	H(33)	0.88 (12)
C(4)	H(7)	0.95 (6)	C(15)	H(34)	1.08 (11)
C(5)	H(8)	0.95 (6)	C(15)	H(35)	0.94 (10)

The platinum and bromine atoms were located by direct methods and their positions confirmed by Patterson techniques.[14] Successive Fourier syntheses were used to locate all remaining nonhydrogen atoms. Isotropic refinement based on all data with $I > 2.33\sigma(I)$ converged to $R(F) = 0.082$ and $R_w(F) = 0.065$, where $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w(F) = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$. A difference Fourier synthesis at this stage, in addition to a peak of 2.8 e/Å^3 at the metal site, clearly located all hydrogen atoms, which were included in further refinements. A full-matrix refinement, in which all nonhydrogen atoms were refined anisotropically and hydrogen atoms isotropically, converged to $R(F) = 0.035$ and $R_w(F) = 0.032$. An isotropic extinction parameter was included in the final refinement which used all nonzero data. In the final cycle the largest shift/error was 0.12 for a hydrogen parameter and 0.02 for nonhydrogen parameters, and the "goodness of fit" was 1.02. A final difference Fourier synthesis revealed a peak of 2.2 e/Å^3 at the platinum site and several peaks of 0.4–1.0 e/Å^3 within 1.5 Å of the metal. No peaks greater than 0.4 e/Å^3 were found beyond 1.5 Å of the platinum.

Final values of the fractional coordinates and isotropic thermal parameters are given in Table I. Anisotropic thermal parameters and observed and calculated structure amplitudes are available.

Description of the Structure

The complex *trans*-Pt(η^1-C_3H_5)Br(PEt_3)$_2$ is depicted from two views in Figures 1 and 2, and the distances and angles are listed in Tables II and III, respectively. Nonbonded contact

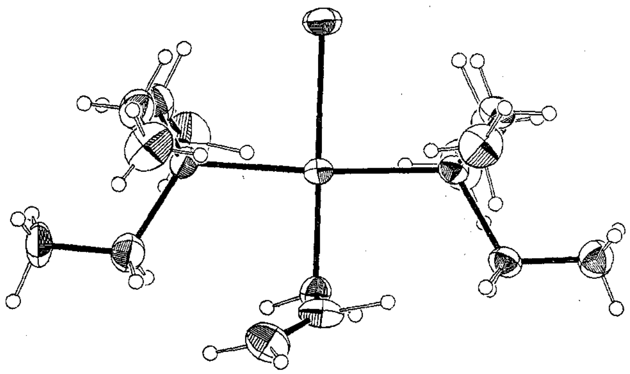

Figure 2. ORTEP drawing of the molecule looking at the Pt–Br–P(1)–P(2)–C(1) plane.

Table III. Bond Angles (deg)

Br(1)	Pt(1)	P(1)	87.78 (4)	C(6)	C(7)	H(14)	106 (4)
Br(1)	Pt(1)	P(2)	87.92 (5)	C(6)	C(7)	H(15)	119 (6)
Br(1)	Pt(1)	C(1)	175.66 (18)	H(13)	C(7)	H(14)	118 (6)
P(1)	Pt(1)	P(2)	172.73 (6)	H(13)	C(7)	H(15)	98 (8)
P(1)	Pt(1)	C(1)	91.88 (20)	H(14)	C(7)	H(15)	111 (7)
P(2)	Pt(1)	C(1)	92.84 (20)	P(1)	C(8)	H(16)	110 (3)
Pt(1)	P(1)	C(4)	118.41 (22)	P(1)	C(8)	H(17)	106 (4)
Pt(1)	P(1)	C(6)	109.11 (26)	C(9)	C(8)	H(16)	104 (3)
Pt(1)	P(1)	C(8)	114.18 (27)	C(9)	C(8)	H(17)	113 (4)
C(4)	P(1)	C(6)	104.30 (34)	H(16)	C(8)	H(17)	111 (6)
C(4)	P(1)	C(8)	104.94 (35)	C(8)	C(9)	H(18)	109 (4)
C(6)	P(1)	C(8)	104.64 (35)	C(8)	C(9)	H(19)	120 (4)
Pt(1)	P(2)	C(10)	113.16 (27)	C(8)	C(9)	H(20)	109 (5)
Pt(1)	P(2)	C(12)	118.20 (25)	H(18)	C(9)	H(19)	110 (5)
Pt(1)	P(2)	C(14)	112.05 (28)	H(18)	C(9)	H(20)	111 (6)
C(10)	P(2)	C(12)	104.52 (38)	H(19)	C(9)	H(20)	97 (6)
C(10)	P(2)	C(14)	102.70 (39)	P(2)	C(10)	H(21)	108 (6)
C(12)	P(2)	C(14)	104.70 (38)	P(2)	C(10)	H(22)	100 (4)
C(1)	C(2)	C(3)	129.05 (75)	C(11)	C(10)	H(21)	112 (6)
P(1)	C(4)	C(5)	116.98 (50)	C(11)	C(10)	H(22)	112 (4)
P(1)	C(6)	C(7)	113.29 (55)	H(21)	C(10)	H(22)	111 (7)
P(1)	C(8)	C(9)	112.75 (53)	C(10)	C(11)	H(23)	111 (6)
P(2)	C(10)	C(11)	113.37 (60)	C(10)	C(11)	H(24)	109 (4)
P(2)	C(12)	C(13)	116.73 (62)	C(10)	C(11)	H(25)	109 (6)
P(2)	C(14)	C(15)	113.78 (67)	H(23)	C(11)	H(24)	104 (7)
C(2)	C(1)	H(1)	107 (6)	H(23)	C(11)	H(25)	117 (8)
C(2)	C(1)	H(2)	112 (4)	H(24)	C(11)	H(25)	106 (7)
H(1)	C(1)	H(2)	113 (7)	P(2)	C(12)	H(26)	106 (4)
C(1)	C(2)	H(3)	114 (3)	P(2)	C(12)	H(27)	107 (5)
C(3)	C(2)	H(3)	117 (3)	C(13)	C(12)	H(26)	108 (4)
C(2)	C(3)	H(4)	123 (4)	C(13)	C(12)	H(27)	107 (5)
C(2)	C(3)	H(5)	116 (5)	H(26)	C(12)	H(27)	113 (6)
H(4)	C(3)	H(5)	121 (6)	C(12)	C(13)	H(28)	107 (7)
P(1)	C(4)	H(6)	106 (4)	C(12)	C(13)	H(29)	113 (6)
P(1)	C(4)	H(7)	104 (4)	C(12)	C(13)	H(30)	110 (6)
C(5)	C(4)	H(6)	108 (4)	H(28)	C(13)	H(29)	104 (9)
C(5)	C(4)	H(7)	112 (4)	H(28)	C(13)	H(30)	104 (8)
H(6)	C(4)	H(7)	109 (5)	H(29)	C(13)	H(30)	117 (9)
C(4)	C(5)	H(8)	115 (3)	P(2)	C(14)	H(31)	103 (5)
C(4)	C(5)	H(9)	111 (5)	P(2)	C(14)	H(32)	99 (5)
C(4)	C(5)	H(10)	111 (5)	C(15)	C(14)	H(31)	112 (5)
H(8)	C(5)	H(9)	102 (6)	C(15)	C(14)	H(32)	114 (5)
H(8)	C(5)	H(10)	105 (5)	H(31)	C(14)	H(32)	114 (7)
H(9)	C(5)	H(10)	113 (7)	C(14)	C(15)	H(33)	105 (8)
P(1)	C(6)	H(11)	104 (3)	C(14)	C(15)	H(34)	103 (5)
P(1)	C(6)	H(12)	107 (4)	C(14)	C(15)	H(35)	114 (6)
C(7)	C(6)	H(11)	108 (3)	H(33)	C(15)	H(34)	102 (10)
C(7)	C(6)	H(12)	117 (4)	H(33)	C(15)	H(35)	107 (9)
H(11)	C(6)	H(12)	107 (5)	H(34)	C(15)	H(35)	124 (8)
C(6)	C(7)	H(13)	106 (5)				

distances are normal, showing the data crystal to be composed of an array of neutral molecules. Excluding the allyl group, the molecule exhibits a striking near C_{2v} symmetry, with the twofold rotation axis passing through the Pt–Br bond.

The platinum has a square-planar coordination with a slight tetrahedral distortion, the deviations from the least-squares plane defined by the four-coordinated atoms and the metal being small (±0.1 Å) as listed in Table IV.

Table IV. Least-Squares Planes through the Molecule

Atom	Dev, Å	Atom	Dev, Å
(1) Plane through the Square-Planar Coordination Sites			
Equation of Plane:[b] $8.961X + 9.391Y - 9.224Z = 8.728$			
Pt(1)	−0.012	P(2)	0.103
Br(1)	−0.092	C(1)	−0.103
P(1)	0.103		
(2) Plane Defined by C(1)–C(2)–C(3)			
Equation of Plane:[b] $10.724X - 7.136Y - 10.226Z = 8.919$			
C(1)	0.000	H(1)[a]	0.647
C(2)	0.000	H(2)[a]	0.080
C(3)	0.000	H(3)[a]	0.041
		H(4)[a]	0.113
		H(5)[a]	−0.012

[a] Atoms not included in refinement. [b] Crystallographic coordinates.

The Pt–P bond lengths of 2.301 (2) and 2.294 (2) Å are normal in comparison with 2.300 (19) Å in *trans*-$PtCl_2(PEt_3)_2$ and 2.315 (4) Å in *trans*-$PtBr_2(PEt_3)_2$.[15] In contrast, the Pt–Br bond length of 2.543 (1) Å is large relative to 2.388 (5) Å for $[PtBr_2(\mu\text{-}SEt_2)]_2$[16] and 2.428 (2) Å for *trans*-$PtBr_2(PEt_3)_2$[15] but comparable to that found in *trans*-$PtHBr(PEt_3)_2$ (2.56 Å).[17] Thus, the trans influence of the allyl group approximates that of the hydride ligand. This is in accord with the large trans influence of the allyl moiety encountered in *trans*-$Pt(\eta^1\text{-}C_3H_5)Cl(PPh_3)_2$[9] and $Pt(\eta^1\text{-}C_3H_5)(PPh_3)Cl(CNCH_3)$.[4]

The Pt–C bond length of 2.086 (7) Å is in line with that found in other platinum(II) σ-alkyls[18] and similar to that (2.090 (4) Å) in *trans*-$Pt(\eta^1\text{-}C_3H_5)Cl(PPh_3)$.[9] The geometry of the allyl group is reasonably close to that expected for an idealized σ-allyl group containing sp^3 and sp^2 hybridized tetracoordinate and tricoordinate carbons, viz., C(1)–C(2) = 1.486 (9) Å, C(2)–C(3) = 1.298 (10) Å, and C(1)–C(2)–C(3) angle = 129.05 (75)°. Consistent with this structural aspect, there appears to be no unusual interaction of the platinum center with the vinylic double bond or any of the allyl hydrogens, the orientation of the allyl group in the molecule being α (the angle between the plane of the allyl group and the least-squares coordination plane) equal to 73° and β (the torsion angle about the C(1)–C(2) bond) equal to 110°.

The bonding and orientation parameters for the allyl group are quite similar in each of the three monomeric σ-allyl platinum derivatives studied heretofore. In fact, the data are accurate enough for $Pt(\eta^1\text{-}C_3H_5)Cl(PPh_3)_2$ and $Pt(\eta^1\text{-}C_3H_5)Br(PEt_3)_2$ to allow a detailed comparison of the two. We conclude that the allyl groups are essentially equivalent in the two complexes, except for a small difference in their orientation. In all three compounds, the allyl group is present as a saturated σ-alkyl group; i.e., there is no interaction of the C=C double bond with the platinum atom, and the Pt–C bond length is normal.[18]

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Registry No. *trans*-$Pt(\eta^1\text{-}C_3H_5)Br(PEt_3)_2$, 63324-94-7.

Supplementary Material Available: Tables listing anisotropic thermal parameters and observed and calculated structure factor amplitudes (18 pages). Ordering information is given on any current masthead page.

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Steric Effects in the Synthesis of Ortho and Para Isomers of Unsymmetrically Substituted Borazines

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The investigation of the effects of substituents and reagents on the reactivity and properties of unsymmetrically substituted borazines presents some unique challenges to the synthetic chemist. There are a variety of data which are consistent with the hypothesis that the π electrons of borazines are delocalized, at least partially. A substitutent on boron can interact with the π system by means of a resonance effect to alter the electron density at the other positions around the ring. Correlations of NMR data[1-3] provided the initial evidence for π-electron delocalization. Further comparisons of NMR data for similarly substituted borazines and amine–boranes supported the hypotheses of delocalization and resonance effects instead of simple field effects.[4]

Chemical reactivity studies have demonstrated that a substitutent on one boron has a definite influence on the reactions of the groups bound to the other boron atoms. For example $H_3B_3N_3H_3$ reacts readily with silver salts[2,3] such as AgCN to form $H_2(CN)B_3N_3H_3$ in very high yields. In contrast, $H_2(CN)B_3N_3H_3$ is totally unreactive toward silver salts under similar conditions. The compound $Cl_3B_3N_3H_3$ reacts with a stoichiometric quantity of $N(CH_3)_2H$ to form $Cl_2[N(CH_3)_2]B_3N_3H_3$ in essentially quantitative yields.[5] The dimethylamino group, an electron-donating substituent, apparently alters the chemical properties of the borazine ring to make a chlorine bound to boron in $Cl_2[N(CH_3)_2]B_3N_3H_3$ much less reactive than one in $Cl_3B_3N_3H_3$. It is certainly clear that a substituent on one boron influences the reactivity at another boron position, positions meta to each other.

Table I

Isomer Distribution for $H_2XB_3N_3H_2CH_3$

Isomer	Statistical	Reagent HgCl$_2$[6]	SnCl$_4$	BCl$_3$	BBr$_3$
% ortho	67	34	42	56	52
% para	33	66	58	44	48

Isomer Distribution for $HX_2B_3N_3H_2CH_3$

Isomer	Reagent HgCl$_2$	SnCl$_4$	BCl$_3$	BBr$_3$
% ortho,ortho	45	54	53	54
% ortho,para	55	46	47	46

There is much less research on the effects of substituents on the ring nitrogen atoms on the reactivity at the boron atoms, the relative ortho and para positions. The reaction of $H_3B_3N_3H_2CH_3$ with $HgCl_2$ yields a mixture of isomers[6] of $H_2ClB_3N_3H_2CH_3$, 70% para and 30% ortho. It was suggested that this isomer distribution must be due to some type of directive influence operative during the course of the reaction.[6] If the reaction had been random, there should have been a 67% yield of the ortho isomer and 33% of the para isomer. For comparison the chlorination of toluene[7] using $FeCl_3$ leads to the formation of 87% *p*-chlorotoluene. The directive influences in this reaction are based on electronic and steric effects of all reactants. There is some relevant chemistry which demonstrates that a steric effect[8,9] in the borazine reagent is an important factor determining reactivity. The reaction of 1,3-dimethyl-5-cyclohexylborazine[9] with either methyl or ethyl Grignard reagents leads to the formation of 80% para and 20% ortho isomers. The compound 1,3-diethyl-5-cyclohexylborazine[9] was attacked less selectively by the methyl or ethyl Grignard reagents as 60% para and 40% ortho isomers were formed.

It is clear that substituents on nitrogen have a significant steric effect on the course of substitution reactions. Substituents on boron apparently have important electronic effects which alter the reactivity at the corresponding meta positions. In this paper we report results which demonstrate the significance of a steric effect of the reagent which reacts with the borazine. We have studied the halogenation of 1-methylborazine using BCl_3, BBr_3, $SnCl_4$, and $HgCl_2$. Our data clearly indicate that the nature of the halogenating reagent has an important influence on the isomer distribution from the substitution reaction.

The compound $H_3B_3N_3H_2CH_3$ was reacted with a variety of halogenating reagents such as $HgCl_2$, $SnCl_4$, BCl_3, and BBr_3. The chlorinated products $H_2ClB_3N_3H_2CH_3$ and $HCl_2B_3N_3H_2CH_3$ were isolated by vacuum distillation and then converted to the corresponding dimethylamino derivative for isomer identification.[6] Previous research[6] has shown that the ortho and para isomers of $H_2ClB_3N_3H_2CH_3$ cannot be quantitatively separated or identified. However, the relative amounts of isomers[6] in a given sample can be determined from the relative intensities of the ^1H NMR lines of the isomers of $H_2[(CH_3)_2N]B_3N_3H_2CH_3$. The reaction for the preparation of the dimethylamino derivative uses extremely mild conditions and there is no isomerization during reaction.[6] In all cases, the entire yield of $H_2ClB_3N_3H_2CH_3$ and $HCl_2B_3N_3H_2CH_3$ from a given reaction was converted to $H_2[(CH_3)_2N]B_3N_3H_2CH_3$ and $H[(CH_3)_2N]_2B_3N_3H_2CH_3$ to ensure against loss of a given isomer. Table I gives the relative yields of isomers. The percentages are the averages from three separate preparative reactions. Percentages of a given isomer using a specific halogenating reagent did not vary by more than ±3%.

The isomer distributions of $H_2XB_3N_3H_2CH_3$ (X = Cl, Br) clearly demonstrate that steric effects in the halogenating agent play a major role in determining the site of substitution. As