Crystal and Molecular Structure of *trans*-Bromo(*trans*-styryl)bis(triphenylphosphine)platinum(II). Some Stereochemical Aspects of the Addition of Vinyl Halides to Platinum(0) Complexes

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Abstract: The crystal and molecular structure of *trans*-bromo(*trans*-styryl)bis(triphenylphosphine)platinum(II), PtBr(HC=CHC₆H₅)(P(C₆H₅)₃)₂, prepared by the oxidative addition of *trans*-β-bromostyrene to Pt(P(C₆H₅)₃)₃, has been determined from three-dimensional X-ray data collected by counter techniques. Crystal data are the following: monoclinic; space group C_{2h}^5-$P2_1/c$; $a = 14.857$ (3), $b = 16.339$ (5), $c = 16.980$ (4) Å; $\beta = 118.30$ (1)° (temperature 22°); $Z = 4$; $d_{obsd} = 1.64$ (2), $d_{calcd} = 1.650$ g cm⁻³. The structure was refined using 3123 independent reflections for which $F_o^2 > 3\sigma(F_o^2)$ and the refinement converged to a conventional R index of 0.031. The coordination around the platinum atom is tetragonal planar and the σ-styryl group has a trans geometry indicative of stereospecific oxidative addition. The addition of *cis*-β-bromostyrene to the platinum(0) complex is reported, and the mechanistic and stereochemical aspects of the addition of other vinyl halides are discussed.

Though the stereochemistry of the oxidative addition of alkyl halides to d⁸ and d¹⁰ metal systems has received considerable attention,[1] little work has been done on the addition of vinyl halides. With Pt(0) systems of the type PtLₙ ($n = 3$ and 4 and L = alkyl or aryl phosphines), reactions with polyhalogenated olefins,[2] fluorovinyl halides,[3] and some styryl halide derivatives have been studied.[4] Retention of stereochemistry at the trigonal carbon atom of *cis*- and *trans*-β-bromostyrene on nucleophilic substitution by bis-(dimethylglyoximato)cobalt(I) has been observed.[5] An nmr analysis of the product obtained from the addition of *trans*-β-bromostyrene to Pt(P(C₆H₅)₃)₃ shows retention of configuration.[4]

It is our purpose to confirm this last observation by an X-ray crystal structure analysis of the product. We also show that a retention of configuration is observed in the addition of *cis*-β-bromostyrene to Pt(P(C₆H₅)₃)₃,[4] though crystals of the product obtained are unsuitable for X-ray analysis. Moreover, qualitative observations made on the rates of reaction of the bromostyrenes lead us to believe that there exist basic differences between the substitution by Co(I) and addition to Pt(0) species.

The crystal structure determination is also prompted by the fact that only a few structures of hydrocarbon σ-vinyl metal complexes have been reported. Since π-olefin and σ-vinyl complexes have been proposed as intermediates in metal-catalyzed activation of vinyl halides toward substitution[6] and alkylation,[7] the structure should be of interest.

Experimental Section

Preparation of Compounds. *trans*-β-Bromostyrene was obtained by the vacuum distillation of commercial (Eastman Organic Chemicals) β-bromostyrene and subsequent recrystallization from methanol at −40° to give *trans*-β-bromostyrene in 95–98% purity. *cis*-β-Bromostyrene was prepared and purified according to the method described by Cristol and Norris.[8] *trans*-Bromo(*trans*-styryl)bis(triphenylphosphine)platinum(II) was prepared according to the literature method[9] and characterized by its nmr spectrum and elemental analysis.

Anal. Calcd for C₄₄H₃₇P₂BrPt: C, 58.54; H, 4.10; P, 6.87; Br, 8.85. Found: C, 58.5; H, 4.1; P, 6.8; Br, 8.7; mp 225°. *cis*-β-Bromostyrene was added to Pt(P(C₆H₅)₃)₃ and a microcrystalline product was isolated in a manner similar to that described for *trans*-bromo(*trans*-styryl)bis(triphenylphosphine)platinum(II).

Anal. Calcd for C₄₄H₃₇P₂BrPt·0.25CH₂Cl₂: C, 57.6; H, 4.05; P, 6.72; Br, 8.68; Cl, 1.92. Found: C, 57.9; H, 4.0; P, 6.5; Br, 8.65; Cl, 1.96.

The solvent CH₂Cl₂ is seen in the nmr spectrum also; mp 178–180°. ¹H nmr spectra were recorded either on a Varian T-60 60-MHz spectrometer or on a Bruker 90-MHz spectrometer. Powder diffraction spectra were recorded on a Norelco powder diffractometer.

Collection and Reduction of X-Ray Data. Crystals of *trans*-bromo(*trans*-styryl)bis(triphenylphosphine)platinum(II) suitable for X-ray analysis were obtained by vapor diffusion of ether into a CH₂Cl₂ solution of the compound in a desiccator. The crystals had to be screened very carefully since a fair number of them were twinned. A needle-shaped crystal of dimensions 0.5 × 0.1 × 0.1 mm was mounted under atmospheric conditions. The 0.5-mm axis, [001], was along the spindle axis; the girdle faces belong to the forms {100} and {110}.

A series of Weissenberg and precession photographs was taken using Cu Kα radiation. These showed the crystal to be monoclinic with 2/m Laue symmetry. The systematic absences observed were *h0l* for *l* odd and 0*k*0 for *k* odd. These absences are consistent with the space group C_{2h}^5-$P2_1/c$. Since the linear absorption coefficient for Cu radiation ($\mu = 95$ cm⁻¹) is nearly twice that for Mo radiation ($\mu = 51.1$ cm⁻¹), all subsequent X-ray work was carried out using Mo Kα radiation. Transmission factors for the crystal used ranged from 0.473 to 0.625.

The cell constants and their standard deviations were determined by the least-squares refinement of the setting angles of 15 reflections (in the range $17.5° \le 2\theta \le 24°$) that had been centered on a Picker FACS-1 automatic diffractometer, using procedures previously de-

(1) See, for example, (a) R. G. Pearson and W. R. Muir, *J. Amer. Chem. Soc.*, **92**, 5519 (1970); (b) J. S. Bradley, D. E. Connor, D. Dolphin, J. A. Labinger, and J. A. Osborn, *J. Amer. Chem. Soc.*, **94**, 4043 (1972).

(2) W. J. Bland and R. D. W. Kemmitt, *J. Chem. Soc. A*, 1278 (1968).

(3) A. J. Mukhedkar, M. Green, and F. G. A. Stone, *J. Chem. Soc. A*, 947 (1970).

(4) B. E. Mann, B. L. Shaw, and N. I. Tucker, *J. Chem. Soc. A*, 2667 (1971).

(5) K. Nguyen van Duong and A. Gaudemer, *J. Organometal. Chem.*, **22**, 473 (1970); M. D. Johnson and B. S. Meeks, *J. Chem. Soc. A*, 185 (1971).

(6) E. W. Stern, M. L. Stern, and H. P. Leftin, *J. Catal.*, **6**, 152 (1966).

(7) J. Klein and R. Levene, *J. Amer. Chem. Soc.*, **94**, 2520 (1972).

(8) S. J. Cristol and W. P. Norris, *J. Amer. Chem. Soc.*, **75**, 2645 (1953).

(9) C. D. Cook and G. S. Jauhal, *Can. J. Chem.*, **45**, 301 (1967).

Table II. Positional, Thermal, and Group Parameters for *trans*-PtBr(*trans*-HC=CHC$_6$H$_5$)(P(C$_6$H$_5$)$_3$)$_2$

Atom	x	y	z	$10^4\beta_{11}{}^a$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Pt	0.22546 (2)^b	0.25098 (2)	−0.04763 (2)	34.3 (2)	24.3 (1)	33.9 (2)	−1.2 (2)	16.9 (1)	1.3 (2)
Br	0.23493 (7)	0.40155 (6)	−0.01780 (7)	58.3 (7)	27.6 (4)	64.5 (6)	−6.2 (5)	35.8 (5)	−9.9 (4)
P(1)	0.38840 (14)	0.24534 (14)	−0.03213 (13)	37.9 (12)	27.1 (8)	38.0 (10)	−0.7 (11)	18.1 (9)	2.5 (10)
P(2)	0.06348 (15)	0.24002 (13)	−0.06254 (13)	37.5 (12)	30.0 (10)	37.1 (10)	−1.4 (10)	18.1 (9)	−1.5 (9)
CS(1)	0.2239 (6)	0.1275 (5)	−0.0561 (6)	33 (5)	34 (4)	44 (5)	−2 (4)	19 (4)	2 (3)
CS(2)	0.2508 (7)	0.0773 (5)	0.0144 (6)	57 (7)	35 (4)	53 (5)	5 (4)	30 (5)	10 (4)
C(1)	0.2522 (7)	−0.0131 (6)	0.0116 (7)	69 (7)	35 (4)	78 (7)	7 (5)	55 (6)	12 (5)
C(2)	0.1907 (9)	−0.0578 (7)	−0.0644 (8)	94 (10)	42 (5)	98 (9)	−8 (6)	39 (8)	−1 (6)
C(3)	0.1935 (10)	−0.1424 (8)	−0.0629 (10)	103 (11)	40 (7)	142 (11)	−15 (6)	76 (9)	−14 (7)
C(4)	0.2594 (11)	−0.1825 (7)	0.0134 (12)	142 (14)	38 (6)	190 (14)	16 (7)	126 (12)	28 (7)
C(5)	0.3223 (11)	−0.1391 (8)	0.0873 (10)	159 (14)	56 (7)	128 (11)	46 (8)	97 (11)	46 (7)
C(6)	0.3194 (9)	−0.0554 (7)	0.0877 (8)	103 (10)	45 (5)	93 (8)	16 (6)	60 (8)	19 (5)

Group	$x_c{}^c$	y_c	z_c	δ	ϵ	η
R(1)	0.3942 (3)	0.1074 (2)	−0.1650 (3)	0.366 (5)	2.387 (3)	−1.868 (5)
R(2)	0.4705 (3)	0.4066 (2)	−0.0874 (2)	−1.713 (4)	−2.768 (4)	−2.563 (4)
R(3)	0.5572 (3)	0.1968 (2)	0.1671 (2)	−1.795 (5)	2.339 (3)	1.507 (5)
R(4)	−0.1015 (3)	0.1369 (2)	−0.2295 (2)	−1.713 (5)	2.286 (3)	−0.941 (6)
R(5)	0.0911 (3)	0.1581 (2)	0.1199 (2)	2.722 (4)	2.804 (3)	1.875 (4)
R(6)	−0.0732 (3)	0.4021 (2)	−0.0970 (2)	−0.653 (12)	1.847 (4)	2.823 (13)

^{a} The form of the 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} Numbers in parentheses given here and in other tables are estimated standard deviations in the least significant figures. ^{c} x_c, y_c, z_c are the fractional coordinates of the ring center; δ, ϵ, η (in radians) have been defined previously.[16]

scribed.[10] Mo Kα_1 radiation (λ 0.70930 Å) was monochromatized from the (002) face of a mosaic graphite crystal. The results were $a = 14.857$ (3) Å, $b = 16.339$ (5) Å, $c = 16.980$ (4) Å, $\beta = 118.30$ (1)°, and $V = 3629.1$ Å^3. An observed density of 1.64 (2) g cm^{-3}, obtained by flotation of the crystals in CCl$_4$–C$_6$H$_5$I, is in good agreement with that of 1.650 g cm^{-3} calculated for four formula units in the cell.

Intensities were collected in the manner described previously,[10,11] using monochromatized Mo Kα radiation. The takeoff angle was 2.6°. The counter was positioned 32 cm from the crystal and preceded by an aperture of dimensions 4.8 × 5.2 mm. The scan range was from 0.8° below Kα_1 to 0.8° above Kα_2 in the range 2.0° $\leq 2\theta \leq 38.5°$ and from 0.9° below Kα_1 to 0.8 above Kα_2 in the range 38.5° $\leq 2\theta \leq 45.0°$. The scan rate was 2°/min in 2θ. Background counts of 10 and 20 sec each were taken in the ranges 2.0° $\leq 2\theta \leq 33.8°$ and 33.8° $\leq 2\theta \leq 45.0°$, respectively, at the extremes of each scan. Unique intensities (with the exception of the 00l Friedel pairs and 0kl, 0$k\bar{l}$ symmetry equivalent pairs) were collected out to 45° in 2θ. Less than 15% of the reflections were above background immediately past this point. A total of 5205 reflections was collected. Throughout the data collection six standard reflections were measured at intervals of 75 observations as a check on crystal and electronic stability. The intensities of these standards remained constant within counting statistics.

The data were processed in the usual manner,[10,11] using a p of 0.04. An analysis of the intensities of the 0kl and 0$k\bar{l}$ symmetry equivalent pairs (a total of 444 observations) showed an average deviation of 2.9% (which decreased to 2.4% after an absorption correction).

Of the 4983 independent reflections observed, 3123 had $F^2 > 3\sigma(F^2)$ and these were used in subsequent calculations.

Solution of Refinement of Structure. Initially, a solution by direct methods was attempted. This proved abortive owing to the rather uneven distribution among the eight parity groups of 200 reflections with highest E values. There were no l odd reflections among these reflections. A sharpened, origin-removed Patterson function[12] was computed. The position of the platinum atom (with $y \approx 1/4$) but not the positions of the Br and P atoms could be found. In subsequent least-squares calculations the function

minimized was $\Sigma w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes and where the weights w are taken as $4F_o^2/\sigma^2(F_o^2)$. In all calculations of F_o the atomic scattering factors for the atoms were taken from those compiled by Cromer and Waber.[13] The effects of anomalous dispersion were included in F_c[14] and the values of $\Delta f'$ and $\Delta f''$ for platinum, bromine, phosphorus, and carbon were taken from the calculations of Cromer and Liberman.[15]

A structure factor calculation was next made using the position of the platinum atom and rejecting all the reflections with l odd. A subsequent difference Fourier map revealed the positions of two phosphorus atoms and also two bromine positions (as was expected owing to the false mirror symmetry resulting from the Pt atom at $y = 1/4$). Using one of these positions for bromine and the ones found for the phosphorus and platinum atoms, a cycle of least-squares refinement was carried out using variable isotropic thermal parameters for the atoms. This converged to values of the reliability indices R_1 and R_2 of 0.179 and 0.253, respectively, where

$$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$$

and the weighted R

$$R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2)^{1/2}$$

A difference map at this point revealed the positions of all the other nonhydrogen atoms, indicating that the correct position for the bromine atom had been chosen. The seven phenyl groups found in the asymmetric unit were now treated as rigid groups[16] of D_{6h} symmetry with C–C = 1.397 Å. A refinement in which all non-group atoms were assigned variable isotropic thermal parameters, as was each group, converged to R_1 and R_2 values of 0.064 and 0.081, respectively.

Refinement proceeded normally. In the final model all non-group, nonhydrogen atoms were allowed to vibrate anisotropically, the carbon atoms of the triphenylphosphine ligands were restricted to rigid groups although each carbon atom was assigned a variable isotropic thermal parameter, and contributions from idealized positions of the hydrogen atoms (C–H = 1.0 Å; B(H) = B(C)) were added to the structure factors as fixed contributions. The final refinement converged to values of R_1 and R_2 of 0.031 and 0.038, respectively.

(10) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

(11) R. J. Doedens and J. A. Ibers, *Inorg. Chem.*, **6**, 204 (1967).

(12) In addition to various local programs, Patterson functions and Fourier syntheses were calculated using a local version of Zalkin's FORDAP. Refinement and structure factor calculations were carried out with our least-squares program, NUCLS, which, in its nongroup form, resembles the Busing–Levy ORFLS. Errors in derived quantities were obtained from the Busing–Levy ORFFE program, and drawings were made with the use of Johnson's ORTEP program. Absorption corrections were arrived at by using the AGNOST program.

(13) D. T. Cromer and J. T. Waber, "International Tables for X-Ray Crystallography," Vol. IV, Kynoch Press, Birmingham, England, in press, Table 2.2A.

(14) J. A. Ibers and W. A. Hamilton, *Acta Crystallogr.*, **17**, 781 (1964).

(15) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).

(16) See, for example, R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **4**, 773 (1965).
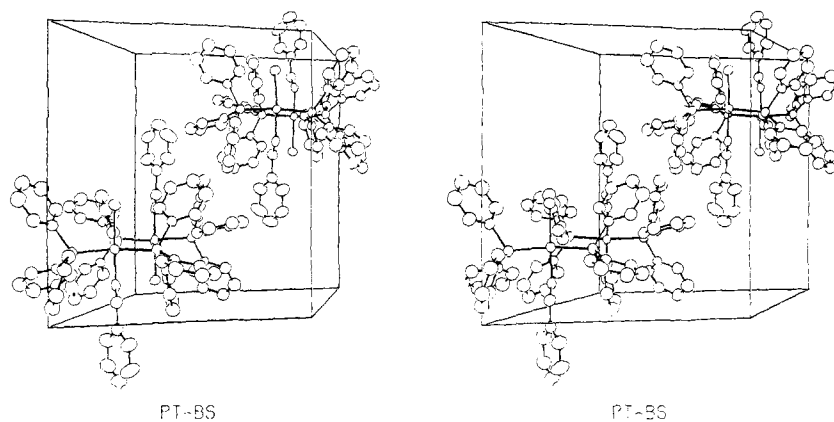
Figure 1. A stereoscopic view of the contents of a unit cell of *trans*-PtBr(*trans*-CH=CHC₆H₅)(P(C₆H₅)₃)₂. Hydrogen atoms have been omitted for the sake of clarity. The other atoms are drawn at their 50% probability levels. In this drawing x goes from left to right, y from bottom to top, and z comes out of the paper.

Table III. Derived Parameters for Ring Carbon Atoms

Ring atom	x	y	z	$B,^a$ Å²
R(1)C(1)^b	0.3984 (4)^c	0.1686 (3)	−0.1060 (3)	2.7 (2)
R(1)C(2)	0.3722 (5)	0.1884 (3)	−0.1943 (4)	4.2 (2)
R(1)C(3)	0.3680 (5)	0.1271 (4)	−0.2533 (3)	4.8 (2)
R(1)C(4)	0.3900 (5)	0.0461 (3)	−0.2240 (4)	4.7 (2)
R(1)C(5)	0.4162 (4)	0.0264 (2)	−0.1357 (4)	5.1 (2)
R(1)C(6)	0.4204 (4)	0.0876 (3)	−0.0766 (3)	4.3 (2)
R(2)C(1)	0.4367 (4)	0.3381 (3)	−0.0595 (4)	2.8 (2)
R(2)C(2)	0.3683 (3)	0.3821 (3)	−0.1348 (4)	4.1 (2)
R(2)C(3)	0.4021 (4)	0.4506 (3)	−0.1627 (3)	4.4 (2)
R(2)C(4)	0.5042 (5)	0.4750 (3)	−0.1153 (4)	5.1 (2)
R(2)C(5)	0.5726 (3)	0.4310 (4)	−0.0400 (4)	5.8 (2)
R(2)C(6)	0.5388 (4)	0.3626 (3)	−0.0121 (3)	4.3 (2)
R(3)C(1)	0.4840 (4)	0.2158 (3)	0.0797 (3)	2.9 (2)
R(3)C(2)	0.4579 (3)	0.2178 (4)	0.1486 (4)	3.9 (2)
R(3)C(3)	0.5311 (5)	0.1988 (4)	0.2360 (3)	5.1 (2)
R(3)C(4)	0.6304 (4)	0.1779 (4)	0.2545 (3)	5.0 (2)
R(3)C(5)	0.6565 (3)	0.1759 (4)	0.1856 (4)	4.8 (2)
R(3)C(6)	0.5833 (4)	0.1948 (4)	0.0982 (3)	3.8 (2)
R(4)C(1)	−0.0281 (4)	0.1794 (3)	−0.1554 (3)	3.1 (2)
R(4)C(2)	−0.1249 (4)	0.1651 (4)	−0.1636 (3)	4.4 (2)
R(4)C(3)	−0.1982 (3)	0.1226 (4)	−0.2376 (4)	5.1 (2)
R(4)C(4)	−0.1749 (4)	0.0944 (4)	−0.3035 (3)	5.9 (2)
R(4)C(5)	−0.0781 (5)	0.1088 (4)	−0.2953 (3)	5.6 (2)
R(4)C(6)	−0.0047 (4)	0.1513 (4)	−0.2213 (4)	4.7 (2)
R(5)C(1)	0.0757 (4)	0.1932 (3)	0.0394 (3)	2.7 (2)
R(5)C(2)	0.0478 (4)	0.1118 (3)	0.0413 (3)	4.1 (2)
R(5)C(3)	0.0633 (5)	0.0767 (3)	0.1217 (4)	5.2 (2)
R(5)C(4)	0.1065 (5)	0.1229 (4)	0.2003 (3)	4.9 (2)
R(5)C(5)	0.1344 (5)	0.2043 (3)	0.1985 (3)	4.5 (2)
R(5)C(6)	0.1189 (4)	0.2394 (2)	0.1180 (4)	4.3 (2)
R(6)C(1)	−0.0122 (4)	0.3323 (3)	−0.0787 (4)	3.1 (2)
R(6)C(2)	−0.0580 (5)	0.3512 (3)	−0.0256 (3)	4.5 (2)
R(6)C(3)	−0.1190 (5)	0.4210 (4)	−0.0439 (4)	5.9 (2)
R(6)C(4)	−0.1342 (4)	0.4719 (3)	−0.1153 (4)	5.3 (2)
R(6)C(5)	−0.0883 (5)	0.4531 (3)	−0.1683 (4)	5.6 (2)
R(6)C(6)	−0.0273 (5)	0.3833 (4)	−0.1500 (4)	4.9 (2)

^{a} B is the refined isotropic thermal parameter for the individual ring carbon atom. ^{b} R(1)C(1) is attached to P. Other C atoms are numbered consecutively so that C(4) is para to C(1). ^{c} The estimated standard deviations are derived from those of the group parameters.

An analysis of $\Sigma w(|F_o| - |F_c|)^2$ as a function of $|F_o|$, setting angles, and Miller indices indicates no unusual trends. The error in an observation of unit weight is 1.28 e for the 181 variables and 3123 observations. The maximum density on a final difference Fourier map is 0.67 (4) e/Å³, less than 20% of the height of a C atom on previous maps. A structure factor calculation for the 1935 reflections omitted from the calculations which have $F_o^2 < 3\sigma(F_o^2)$ reveals that 1924 of them have $|F_o^2 - F_c^2| < 3\sigma(F_o^2)$. Of the 11 reflections with $|F_o^2 - F_c^2| > 3\sigma(F_o^2)$, five have $|F_o^2 - F_c^2|$
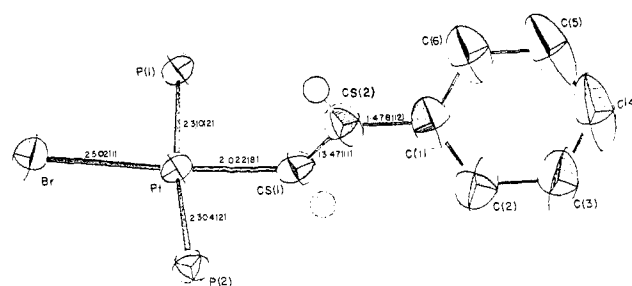
Figure 2. Inner coordination sphere of *trans*-PtBr(*trans*-CH= CHC₆H₅)(P(C₆H₅)₃)₂ showing the labeling scheme and with the exception of the styryl hydrogen atoms the vibrational ellipsoids at their 50% probability level. Hydrogen atoms on the styryl phenyl group have been omitted.

$< 4\sigma(F_o^2)$ and six are low angle reflections with uneven background counts.

The values of $10|F_o|$ and $10|F_c|$ for the 3123 reflections used in the analysis are given in Table I.[17] Table II presents the positional and thermal parameters derived from the last cycle of least-squares refinement, along with the associated standard deviations, as derived from the inverse matrix. The derived parameters for the triphenyl-phosphine ring C atoms and the idealized positions of the H atoms are shown in Tables III and IV,[17] respectively.

Description of the Structure

No crystallographic symmetry is imposed on the discretely packed molecules of PtBr(HC=CHPh)(PPh₃)₂ (where Ph = C₆H₅). A stereoscopic pair of views of the contents of a unit cell is given in Figure 1. Figure 2 shows the inner coordination sphere. An overall view of the molecule, with the exclusion of hydrogen atoms, along with the labeling scheme is shown in Figure 3. There are no unusual intermolecular contacts. The shortest of these is a H⋯H contact of 2.26 Å. A selection of bond distances, nonbonded contacts, and angles, together with standard deviations, is given in Table V. The root-mean-square amplitudes of vibration along the principal axes of vibration for atoms refined anisotropically are given in Table VI. The shapes of the thermal ellipsoids in Figures 2 and 3 also depict the directions of vibration.

The coordination about the platinum atom is close to tetragonal planar, the CS(1) atom deviating slightly from the plane. The best weighted least-squares plane

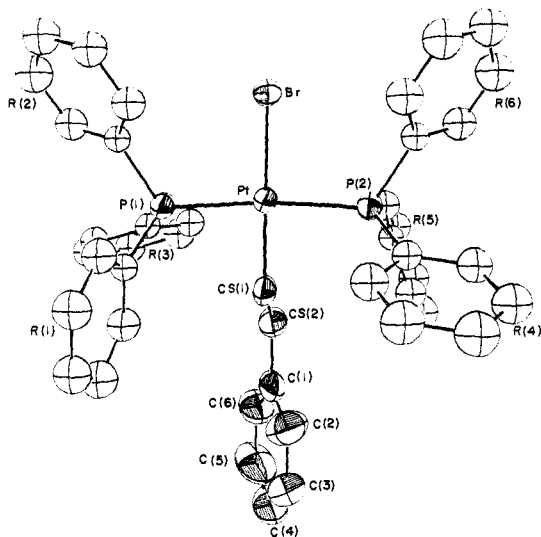(17) See paragraph at end of paper regarding supplementary material.

Figure 3. An overall view of the *trans*-PtBr(*trans*-CH=CHC$_6$H$_5$)-(P(C$_6$H$_5$)$_3$)$_2$ molecule. Hydrogen atoms have been omitted for the sake of clarity.

Table V. Selected Interatomic Distances (Å) and Angles (deg) in *trans*-PtBr(*trans*-HC=CHC$_6$H$_5$)(P(C$_6$H$_5$)$_3$)$_2$

Atoms	Distance	Atoms	Angle
		Br–Pt–P(1)	93.49 (6)
Pt–Br	2.5021 (12)	Br–Pt–P(2)	93.11 (6)
Pt–P(1)	2.310 (2)	Br–Pt–CS(1)	173.3 (2)
Pt–P(2)	2.304 (2)	P(1)–Pt–CS(1)	86.8 (2)
Pt–CS(1)	2.022 (8)	P(2)–Pt–CS(1)	86.5 (2)
		P(1)–Pt–P(2)	173.25 (8)
Br···P(1)[a]	3.507 (2)		
Br···P(2)	3.492 (2)	Pt–CS(1)–CS(2)	123.8 (6)
P(1)···CS(1)	2.983 (8)	CS(1)–CS(2)–C(1)	125.7 (9)
P(2)···CS(1)	2.971 (8)	CS(2)–C(1)–C(2)	123.0 (9)
		CS(2)–C(1)–C(6)	118.9 (10)
CS(1)–CS(2)	1.347 (11)		
CS(2)–C(1)	1.478 (12)	C(1)–C(2)–C(3)	120.6 (12)
		C(2)–C(3)–C(4)	119.9 (10)
C(1)–C(2)	1.385 (14)	C(3)–C(4)–C(5)	119.8 (12)
C(2)–C(3)	1.383 (15)	C(4)–C(5)–C(6)	121.2 (13)
C(3)–C(4)	1.364 (18)	C(5)–C(6)–C(1)	120.2 (12)
C(4)–C(5)	1.356 (18)	C(6)–C(1)–C(2)	118.1 (10)
C(5)–C(6)	1.368 (15)	Av C–C–C	120.0 (11)
C(6)–C(1)	1.387 (14)		
Av C–C[b]	1.374 (17)	Pt–P(1)–R(1)C(1)	111.8 (2)
		Pt–P(1)–R(2)C(1)	117.0 (2)
		Pt–P(1)–R(3)C(1)	112.8 (2)
P(1)–R(1)C(1)	1.828 (8)	Pt–P(2)–R(4)C(1)	116.9 (2)
P(1)–R(2)C(1)	1.829 (8)	Pt–P(2)–R(5)C(1)	107.5 (2)
P(1)–R(3)C(1)	1.816 (8)	Pt–P(2)–R(6)C(1)	119.3 (2)
P(2)–R(4)C(1)	1.812 (7)		
P(2)–R(5)C(1)	1.821 (7)	R(1)C(1)–P(1)–R(2)C(1)	103.0 (5)
P(2)–R(6)C(1)	1.822 (8)	R(1)C(1)–P(1)–R(3)C(1)	104.9 (5)
Av P–RC(1)	1.821 (7)	R(2)C(1)–P(1)–R(3)C(1)	106.3 (5)
		R(4)C(1)–P(2)–R(5)C(1)	107.0 (5)
		R(4)C(1)–P(2)–R(6)C(1)	99.6 (5)
		R(5)C(1)–P(2)–R(6)C(1)	105.5 (5)

Interplanar Angles

Planes	Angle
CS(2), Pt, CS(1)–C(1), CS(2), CS(1)	0.9 (6)
C(1), CS(2), CS(1)–C(6), C(1), C(2)	27.1 (9)

[a] Broken line indicates nonbonded contacts. [b] A number in parentheses associated with an average quantity is the standard deviation of a single observation obtained on the assumption that the quantities averaged are from the same population.

through the atoms Pt, Br, P(1), P(2), and CS(1) is given by the equation $-1.400x - 2.900y + 15.404z = -1.776$ Å with the deviations from the plane, in Å, for

Table VI. Root-Mean-Square Amplitudes of Vibration (Å)

Atom	Min	Intermed	Max
Pt	0.1667 (6)	0.1819 (6)	0.1981 (5)
Br	0.183 (1)	0.207 (1)	0.277 (1)
P(1)	0.178 (3)	0.189 (4)	0.213 (3)
P(2)	0.178 (3)	0.199 (3)	0.209 (3)
CS(1)	0.16 (1)	0.21 (1)	0.23 (1)
CS(2)	0.20 (1)	0.21 (1)	0.26 (1)
C(1)	0.18 (1)	0.21 (1)	0.31 (1)
C(2)	0.23 (2)	0.29 (2)	0.35 (2)
C(3)	0.22 (2)	0.27 (2)	0.40 (2)
C(4)	0.21 (2)	0.25 (2)	0.48 (2)
C(5)	0.21 (2)	0.29 (2)	0.44 (2)
C(6)	0.22 (2)	0.26 (2)	0.34 (1)

the atoms being -0.0013 (3), 0.008 (1), 0.026 (2), 0.028 (2), and 0.228 (9), respectively. Moreover, CS(1) is $+0.237$ (9) Å and $+0.188$ (9) Å from the planes defined by the atoms Pt, P(1), Br, and P(1), Br, P(2), respectively.

The bond angles around the platinum atom deviate considerably from 90°. This is not unusual since triphenylphosphine ligands have a tendency to distort away from heavy halogen ligands, bromine in this case.[16,18] For instance, the two P–Pt–Cl angles in PtHCl(P(C$_6$H$_5$)$_2$C$_2$H$_5$)$_2$ are 92.6 (4) and 94.5 (4)°.[16]

The styryl moiety is well behaved with the normally expected bond distances and bond angles, though a lengthening of the CS(1)–CS(2) distance is observed. The dihedral angle between the planes formed by atoms CS(2), Pt, and CS(1) and C(1), CS(2), and CS(1) is 0.9 (6)° which is consistent with these atoms being coplanar to within 0.02 Å. The styryl phenyl group is also planar as indicated by the fact that the maximum distance of any C atom from a weighted least-squares plane through the six carbon atoms is 0.016 (12) Å. The rather large thermal ellipsoids for the C atoms in the plane of styryl phenyl ring prompted a correction for librational effects. Using the six carbon atoms on the phenyl ring, CS(1), CS(2), and Pt all as a rigid group,[19] the C–C distances on the phenyl ring are within one standard deviation of the distances obtained without any applied correction. The trend of the distances around the ring is not altered on applying the correction for librational motion. The angle between the plane of this phenyl ring and the plane formed by the atoms C(1), CS(2), and CS(1) is 27.1 (9)°.

The observed Pt–Br bond distance of 2.502 Å is longer than that for normal Pt–Br distances in Pt$_6$Br$_{12}$[20] (2.447 (12) Å) or in K$_2$PtBr$_6$[21] (2.463 (3) Å). This lengthening can be attributed to the trans influence of the styryl group. The Pt–CS(1) distance is 0.1 Å shorter than a typical Pt–CH$_3$ bond distance (2.12 Å[22]) and this is the expected difference between sp^2 and sp^3 carbon atoms. The Pt–CS(1) distance, along with the Pt–CS(1)–CS(2) angle of 123.8°, indicates a single bond between Pt and CS(1). If any bond order greater than one is to be invoked, this should be manifested in

(18) M. L. Schneider and H. M. M. Shearer, *J. Chem. Soc., Dalton Trans.*, 354 (1973).

(19) The Dunitz–White version (TMA) of the Trueblood–Schomaker rigid body analysis was used.

(20) G. Thiele and P. Woditsch, *Angew. Chem., Int. Ed. Engl.*, **8**, 672B (1969).

(21) H. D. Grundy and I. D. Brown, *Can. J. Chem.*, **48**, 115 (1970).

(22) M. R. Snow, J. McDonald, F. Basolo, and J. A. Ibers, *J. Amer. Chem. Soc.*, **94**, 2526 (1972); M. R. Churchill, *Perspect. Struct. Chem.*, **3**, 91 (1970).

the CS(1)–CS(2) bond length. Here, a direct comparison with the parent molecule, styrene, is not possible since no good structural data are available for styrene or its derivatives. The CS(1)–CS(2) bond length is, however, longer than that observed in the cinnamate ion[23] or in a phenylallyl moiety.[24] The CS(2)–C(1) bond length is within 1σ of the expected single bond length of 1.48 Å between two sp^2 carbon atoms. The twist angle of 27.1° between the plane of the phenyl ring and the plane formed by the atoms CS(1), CS(2), and C(1), though larger than the 13.1 and 17° observed in the phenylallyl[24] and cinnamate[23] groups, is not unusual. Though this twist need not impede conjugation, save for the long CS(1)–CS(2) bond length there appears to be no extensive conjugation.

Some comparisons of coordinated vinyl groups with this present structure are given in Table VII. With

Table VII. Geometry of Some Hydrocarbon σ-Vinyl Groups

Compound	C=C (Å)	M—C=C angle (deg)
(π-C$_5$H$_5$)Fe(CO)$_2$C$_4$H$_5$SO$_2$[a]	1.31 (1)	129.7 (7)
Pt(C$_6$H$_9$)(CH$_2$COC$_6$H$_5$)(diphos)[b]	1.32 (2)	?
(BAE)[b](Co(CH=CH$_2$)(H$_2$O)[c]	1.33 (2)	127.2 (9)
[(π-C$_5$H$_5$)Fe(CO)$_2$]$_2$C$_4$H$_4$[d]	1.340 (7)	131.8 (4)
PtBr(trans-CH=CHC$_6$H$_5$)(P(C$_6$H$_5$)$_3$)$_2$[e]	1.347 (11)	123.8 (6)

[a] diphos = diphenylphosphinoethane: M. R. Churchill and J. Wormald, *J. Amer. Chem. Soc.*, **93**, 354 (1971). [b] M. A. Bennett, G. B. Robertson, P. O. Whimp, and T. Yoshida, *ibid.*, **95**, 3028 (1973). [c] BAE = *N,N'*-ethylenebis(acetylacetoneiminato): S. Brückner, M. Calligaris, G. Nardin, and L. Randaccio, *Inorg. Chim. Acta*, **2**, 416 (1968). [d] Bridging vinyl group: J. H. Nelson and H. B. Jonassen, *Coord. Chem. Rev.*, **6**, 27 (1971). [e] This work.

insufficient data, no conjectures as to back donation from the metal to the styryl group can be made.

Stereochemistry of Oxidative Addition

The stereochemistry of the nucleophilic substitution of vinylic halides by ordinary nucleophiles has been the subject of several reviews.[25,26] Such reactions usually lead to retention of configuration at trigonal carbon atoms. In recent years, metal complexes have been used as nucleophiles in these substitutions.[4,5,7] As noted earlier, the reaction of cis- and trans-β-bromostyrene with the "supernucleophile" bis(dimethylglyoximato)cobalt(I) anion has been observed to give β-styrylpyridinecobaloxime(III) with retention of stereochemistry at the trigonal carbon atom.[5] Our crystal structure determination confirms the conclusion reached by Mann, Shaw, and Tucker,[4] viz., retention of stereochemistry on the addition of trans-β-bromostyrene to Pt(P(C$_6$H$_5$)$_3$)$_3$ (I).

To establish the stereochemistry of this reaction further, cis-β-bromostyrene was added to I to give product II with the same analysis as that of the trans-styrylplatinum complex (III) but with different physical properties (Experimental Section). The crystals of II appear to be sensitive to X-rays, becoming opaque and powdery over a period of 1–2 hr exposure. A rapid

X-ray powder diffraction spectrum obtained for II and for III shows them to be different. The nmr spectrum of III shows a doublet, assigned to the vinyl proton attached to CS(2) at 5.54 ppm (in δ, with respect to TMS), with J_{H-H} = 15.5 Hz. II shows a doublet for the vinylic proton at 6.5 ppm with J_{H-H} = 10.5 Hz (solutions of II in CDCl$_3$ could not be obtained in high enough concentrations to observe platinum satellites). The smaller coupling constant observed for II is consistent with a cis-styryl group attached to platinum,[5] indicating again a retention of configuration. The nmr signals of the vinylic protons attached to CS(1) could not be resolved, as previously noted.[4]

Despite the retention of configuration observed in both the Pt(0) and the cobaloxime systems, there seem to be few other similarities between the two systems. Although no detailed kinetic study of the β-bromostyrene reactions with cobaloximes is available, Dodd and Johnson[27] have observed that this reaction is considerably slower than that of most alkyl halides. This is the behavior found in reactions of normal nucleophiles as well. In contrast, the rate of addition of β-bromostyrene to I is at least 2 orders of magnitude greater than that observed for methyl iodide addition. Qualitatively, there appears to be no difference between the rates of addition of cis- and trans-β-bromostyrene. The rapidity of this reaction prevented us from making a more detailed kinetic study by conventional methods. Hence, we feel that the addition–elimination mechanism proposed for the substitution of styryl halides by the Co(I) systems[4,5] cannot be invoked for the Pt(0) systems. Addition of radical inhibitors such as galvinoxyl does not retard the reaction with the Pt(0) complex. β-Bromostyrene does not add to Ir(I) complexes of the type IrCl(CO)L$_2$ (L = P(C$_6$H$_5$)$_3$ or P(p-tolyl)$_3$) as evidenced by the absence of any shift in the carbonyl stretching frequency over a period of 36 hr. Nor does there appear to be a reaction with IrCl(N$_2$)(P-(C$_6$H$_5$)$_3$)$_2$.

When 1-bromo-1-propene was allowed to react with I in benzene, evaporation of solvent yielded starting material only. But free ethylene was observed in the nmr spectrum of a reaction mixture of Pt(C$_2$H$_4$)(P(p-tolyl)$_3$)$_2$ and 1-bromo-1-propene, indicating displacement of C$_2$H$_4$ by the propene. Accordingly we attempted the reaction of neat 1-bromo-1-propene with I. A rapid dissipation of the orange color of I was observed and the Pt(II) vinyl species was isolated, as judged from the similarity of its nmr spectrum to that of the Pt(II) complex with vinyl bromide prepared by this method.[4]

These observations indicate that the cleavage of the carbon–halogen bonds in the oxidative addition to I is activated by different processes for alkyl and vinyl halides. It has been observed in the reactions of polyhalogenated olefins and fluoro vinyl halides with Pt(0) complexes that both Pt(0) olefin complexes as well as Pt(II) vinyl complexes are formed.[3,28–30] In these reactions, the formation of the vinyl complexes is pro-

(23) R. F. Bryan, H. H. Mills, and J. C. Speakman, *J. Chem. Soc.*, 4350 (1963).

(24) M. R. Churchill and J. Wormald, *Inorg. Chem.*, **10**, 572 (1971).

(25) Z. Rappoport, *Advan. Phys. Org. Chem.*, **7**, 1 (1969).

(26) G. Modena, *Accounts Chem. Res.*, **4**, 73 (1971).

(27) D. Dodd and M. D. Johnson, *J. Organometal. Chem.*, **52**, 26 (1973).

(28) W. J. Bland, J. Burgess, and R. D. W. Kemmitt, *J. Organometal Chem.*, **14**, 201 (1968).

(29) M. Green, R. B. L. Osborn, A. J. Rest, and F. G. A. Stone, *J. Chem. Soc. A*, 2525 (1968).

(30) M. J. Hacker, G. W. Littlecott, and R. D. W. Kemmitt, *J. Organometal. Chem.*, **47**, 189 (1973).

posed to occur by the rearrangement of an intermediate Pt(0) olefin complex. Evidence for this mechanism comes from the observation that some of these Pt(0) olefin complexes isolated rearrange to the vinyl complexes under varying conditions.[3,28,30] The half-life for the rearrangement of $Pt(C_2Cl_4)(P(C_6H_5)_3)_2$ to $PtCl(C_2Cl_3)(P(C_6H_5)_3)_2$ is on the order of 3–4 hr in ethanol.[28] Conditions required for these rearrangements in some cases are quite drastic. Since incorporation of Ag^+ enhances the rearrangement, a heterolytic cleavage of the C–X (X = halogen) bond is proposed as the key step in the mechanism.[3] Vinyl chloride, normally inert to nucleophilic substitution, undergoes facile substitution by nucleophiles such as OAc^- in the presence of $PdCl_2$. A π-olefin $PdCl_2$ complex intermediate is proposed.[6]

It is very possible that the reaction of β-bromostyrene with I goes through a Pt(0) olefin intermediate. But the rearrangement to the Pt(II) styryl complex, since the reaction is very fast even in a nonpolar medium such as benzene, probably goes *via* an intramolecular route not involving an explicit heterolytic cleavage of the carbon–halogen bond[31] (Scheme I). The trans stereochemistry

Scheme I. Reaction of Vinyl Halides with Pt(0) Complexes
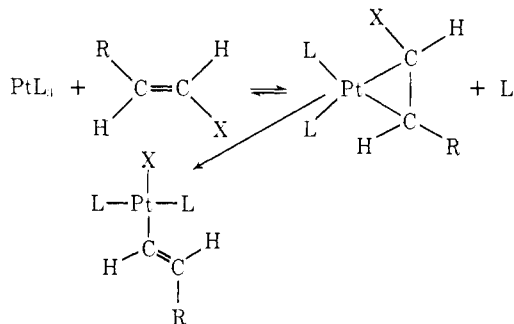
of the vinyl and halogen ligands is somewhat surprising on this basis, since a cis isomer would be expected. However the trans isomer would be the thermodynamically more stable one.[32] A rearrangement of the

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(31) The equilibrium constant for the first step shown, when ethylene is the olefin involved, is 0.12: C. A. Tolman, W. C. Seidel, and D. H. Gerlach, *J. Amer. Chem. Soc.*, **94**, 2669 (1972). The exchange has been observed to be rapid for other olefins also: R. Ugo, *Coord. Chem. Rev.*, **3**, 319 (1968), and references therein.

(32) R. G. Pearson, *Inorg. Chem.*, **12**, 712 (1973).

olefin complex is compatible with the retention of configuration observed at the trigonal carbon atom of β-bromostyrene. A direct reaction of PtL_3 with the vinyl halide is not excluded. If a five-coordinate product is formed initially, it could easily isomerize from a cis grouping to a trans arrangement about platinum.

With the 1-bromo-1-propene, the reversibly formed Pt(0) olefin complex fails to rearrange to the vinyl complex in benzene solution and this rearrangement also appears to be slow in the addition of vinyl bromide.[4]

Klein and Levene[7] have shown that the methylation of a large number of substituted vinyl halides by $Cu(CH_3)_2^-$ goes stereospecifically with retention of configuration. Since $Cu(CH_3)_2^-$ is a d^{10} system as are the Pt(0) systems, an attractive mechanism for the methylation reaction is initial oxidative addition of the vinyl halide to give an unstable Cu(II) or Cu(III) intermediate followed by methyl migration to give the product, both these steps proceeding with retention of configuration at the trigonal carbon atom.

Failure to inhibit the reaction of *trans*-β-bromostyrene and Pt(0) with galvinoxyl is evidence against a free radical mechanism.[1b] The observed stereospecificity also seems to rule out a free radical intermediate. However, it should be pointed out that vinyl free radicals do not isomerize immediately.[33] A rapid reaction of a styryl radical with Pt(0) could prevent isomerization.

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(33) R. C. Neumann, Jr., and G. D. Holmes, *J. Org. Chem.*, **33**, 4317 (1968).