Crystal and Molecular Structure of Stable Platinum(0) Complexes of Cyclohexyne and Cycloheptyne

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Abstract: The crystal and molecular structures of stable Pt(0) complexes of cyclohexyne (C_6H_8) and cycloheptyne (C_7H_{10}), of the form [(cycloalkyne)Pt{P(C_6H_5)$_3$}$_2$] have been determined by three-dimensional X-ray structural analysis using data collected by counter methods. The cyclohexyne complex crystallizes in the triclinic space group $P\bar{1}$ (C_i^1, No. 2), with a = 9.875 (2) Å, b = 18.141 (4) Å, c = 10.081 (2) Å, α = 89.99 (2)°, β = 80.68 (2)°, γ = 78.28 (2)°, and Z = 2, while the cycloheptyne analog crystallizes in the monoclinic space group $P2_1/c$ (C_{2h}^5, No. 14), with a = 8.951 (2) Å, b = 33.523 (8) Å, c = 13.095 (3) Å, β = 114.24 (2)°, and Z = 4. Both structures were solved by conventional heavy-atom techniques, and were refined by block-diagonal least-squares methods. Only those reflections with $I/\sigma(I) \geq 3.0$ were considered to be statistically significant. For [(cyclohexyne)Pt{P(C_6H_5)$_3$}$_2$], the weighted and unweighted R factors were 0.044 and 0.040, respectively (for 5157 independent reflections), while for [(cycloheptyne)Pt{P(C_6H_5)$_3$}$_2$], the corresponding R factors were 0.030 and 0.024 (4918 unique reflections). The coordination at the central platinum atom of both derivatives is essentially square planar, with the triphenylphosphine groups occupying cis coordination sites. The dihedral angles between the two three-atom planes defined by [Pt,P(1),P(2)] and [Pt,C(1),C(2)] are 4.4 (3) and 7.9 (3)° for [(cyclohexyne)Pt{P(C_6H_5)$_3$}$_2$] and [(cycloheptyne)Pt{P(C_6H_5)$_3$}$_2$], respectively. In the cyclohexyne derivative, the Pt–P distances are 2.264 (2) and 2.271 (2) Å (*cf.* 2.264 (1) and 2.270 (1) Å for the Pt–P distances in the cycloheptyne analog), while the Pt–C distances are 2.034 (7) and 2.044 (7) Å (*cf.* 2.035 (4) and 2.064 (4) Å for the corresponding distances in the cycloheptyne derivative). For [(cyclohexyne)Pt{P(C_6H_5)$_3$}$_2$], the acetylenic C≡C distance is 1.297 (8) Å, while for [(cycloheptyne)Pt{P(C_6H_5)$_3$}$_2$], this distance is 1.283 (5) Å. Within the coordinated cyclic acetylenes, the C—C≡C angles average 127.3° for cyclohexyne and 138.8° for cycloheptyne.

The smallest cyclic acetylene which can be isolated in the free state is cyclooctyne, although there is some indirect evidence for the existence of cycloheptyne and cyclohexyne as short-lived reaction intermediates.[1] The preparation and isolation of stable platinum(0) derivatives of cyclohexyne and cycloheptyne have been previously described.[2]

Single-crystal diffraction studies of [(cyclohexyne)-Pt{P(C_6H_5)$_3$}$_2$] and [(cycloheptyne)Pt{P(C_6H_5)$_3$}$_2$] have now been completed and these confirm the near identity of bond lengths and bond angles in the metal atom first coordination spheres.[3] Indeed, the similarity of the metal–ligand geometry has recently been found to extend to the cyclooctyne analog [(C_8H_{12})Pt{P(C_6H_5)$_3$}$_2$],[4] and also to the acyclic acetylene platinum(0) complexes [($C_6H_5C{\equiv}CCO_2CH_2CH_3$)Pt{P($C_6H_5$)$_3$}$_2$] and [$p$-$NO_2C_6H_4C{\equiv}CCO_2CH_2CH_3$)Pt{P($C_6H_5$)$_3$}$_2$].[5] We now report detailed structural data for both [(C_6H_8)Pt{P(C_6H_5)$_3$}$_2$] and [(C_7H_{10})Pt{P(C_6H_5)$_3$}$_2$].

Experimental Section

Collection and Reduction of X-Ray Intensity Data. Approximate unit cell dimensions for each compound were obtained from preliminary Weissenberg (0*kl*, 1*kl*) and precession (*h*0*l*, *h*1*l*, *hk*0, *hk*1) photographs. Photographs for the cyclohexyne complex showed neither systematic absences nor diffraction symmetry higher than C_i ($\bar{1}$), indicating a triclinic space group. Choice of the centrosymmetric space group $P\bar{1}$ (C_i^1, No. 2) was confirmed by the successful solution and refinement of the structure. In contrast, the systematic absences found for the cycloheptyne analog (*i.e.*, *h*0*l* data, $l = 2n + 1$; 0*k*0 data, $k = 2n + 1$), uniquely define the centrosymmetric monoclinic space group $P2_1/c$ (C_{2h}^5, No. 14). With Z = 2 for the cyclohexyne adduct, and Z = 4 for the cycloheptyne analog, neither molecule has any imposed crystallographic symmetry constraints. Full details of the crystal data for both derivatives are listed in Table I.

Reflection data for both [(cyclohexyne)Pt{P(C_6H_5)$_3$}$_2$] and [(cycloheptyne)Pt{P(C_6H_5)$_3$}$_2$] were collected on a Picker FACS-I fully automatic four-circle diffractometer. In both cases, crystals were mounted on quartz fibers and were aligned with the crystallographic a axis and the instrumental Φ axis approximately coincidental. Accurate unit cell dimensions and crystal orientation matrices were obtained from the least-squares refinement[6] of the 2θ, ω, χ, and Φ values obtained for 12 carefully centered high-angle reflections in each case. The errors quoted in the cell dimensions result from the least-squares process described above.

Full details of the experimental conditions and data collection methods used are outlined in Table II. During data collection, the three standard reflections for each compound showed a regular, isotropic, time-dependent loss of intensity. Before further calculation, reflection data for both complexes were corrected for these decomposition effects.

Data were reduced to values of $|F_o|$ using the program SETUP. The Lorentz-polarization correction is given by

$$(\mathrm{LP}) = [\cos^2 2\theta + \cos^2 2\theta_m]/[\sin 2\theta(1 + \cos^2 2\theta_m)]$$

where θ and θ_m (=13.25°) are the Bragg angles for the reflection and monochromator, respectively. The corrected intensities were assigned individual estimated standard deviations.

$$\sigma(F_o) = \{[\sigma(I)/(\mathrm{LP})]^2 + (\rho|F_o|^2)^2\}^{1/2}/2|F_o|$$

where

$$\sigma(I) = [CT + (t_p/t_b)^2(B1 + B2)]^{1/2}$$

(LP) is the Lorentz-polarization correction, CT is the integrated reflection intensity, $B1$ and $B2$ are the individual background counts, t_p is the reflection counting time, t_b is the total background counting time, and ρ (=$0.001^{1/2}$) is an arbitrarily assigned factor to account for instrumental "unknowns."[7,8] Reflection data for which the individual background counts differed significantly [*i.e.*, if $|B1 - B2|/(B1 + B2)^{1/2} \geq 4.0$] were discarded. The remaining reflection data were sorted to an order convenient for the efficient operation of subsequent programs using the program SORTIE. At the same time, equivalent reflection forms were averaged, and those reflections for which $I/\sigma(I) < 3.0$ {where $I = [CT - (t_p/t_b)(B1 + B2)]$} were rejected as being unobserved. The statistical R factors for the terminal data sets defined as $R_s = \Sigma\sigma_s(F_o)/\Sigma|F_o|$, [where $\sigma_s(F_o) = \sigma(I)/2(\mathrm{LP})(|F_o|)$], are 0.012 and 0.014 for [(cyclohexyne)Pt{P(C_6H_5)$_3$}$_2$] and [(cycloheptyne)Pt{P(C_6H_5)$_3$}$_2$], respectively.

Solution and Refinement of the Structures. Both structures were solved by conventional Patterson and Fourier syntheses and were refined by block-diagonal least-squares methods. A detailed description of the course of the refinements is given in Table III. Atomic scattering factors for the nonhydrogen atoms, with those for Pt and P corrected for the real and imaginary parts of anoma-

Table I. Crystal Data

	$[(C_6H_8)Pt\{P(C_6H_5)_3\}_2]^a$	$[(C_7H_{10})Pt\{P(C_6H_5)_3\}_2]$
a	9.875 (2)[b] Å	8.951 (2) Å
b	18.141 (4) Å	33.523 (8) Å
c	10.081 (2) Å	13.095 (3) Å
α	89.99 (2)°	
β	80.68 (2)°	114.24 (2)°
γ	78.28 (2)°	
Formula weight	799.80	813.83
ρ_{obsd}	1.52 (1) g cm^{-3}	1.50 (1) g cm^{-3}
ρ_{calcd}	1.523 g cm^{-3}	1.508 g cm^{-3}
Z	2	4
Unit cell volume	1743.87 Å^3	3583.05 Å^3
Space group	$P\bar{1}$ (C_i^1, No. 2)	$P2_1/c$ (C_{2h}^5, No. 14)
Imposed symmetry	None	None
Crystal dimensions	0.225 × 0.150 × 0.070 mm[c]	0.275 × 0.075 × 0.137 mm[c]
Absorption coefficient (Cu Kα)	87.62 cm^{-1}	85.24 cm^{-1}

[a] The "reduced" cell, obtained from a Delaunay reduction (B. Delaunay *Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem.*, **84,** 109 (1933)) is a' = 18.811 Å, b' = 12.918 Å, c' = 10.081 Å, α' = 131.03°, β' = 94.87°, γ' = 100.68°, volume of "reduced" cell = 1743.87 Å^3. The structure was solved using the nonreduced cell, and all subsequent data refer to this nonreduced cell. [b] Estimated standard deviations (in parentheses) in this and the following tables, and also in the text, refer to the last significant digit(s) in each case. [c] Crystal dimensions quoted are parallel to a, b, and c, respectively.

lous scattering,[9,10] were taken from the usual compilation.[11] Scattering factors for hydrogen were taken from the tabulation of Stewart, *et al.*[12]

During the refinement process, the reflection data for both derivatives were corrected for absorption effects, using grid sizes of 12 × 8 × 4 and 14 × 4 × 8 points (respectively parallel to a, b^*, c^*) for $[(cyclohexyne)Pt\{P(C_6H_5)_3\}_2]$ and $[(cycloheptyne)Pt\{P(C_6H_5)_3\}_2]$, respectively. The transmission factor (applied to $|F_o|^2$) varied from 0.2237 to 0.6328 for the cyclohexyne derivative and from 0.3029 to 0.5892 for the cycloheptyne analog.

When fixed hydrogen atom contributions were added to the refinement, it was assumed that the C–H distances were 1.087 Å.

Table II. Data Collection Details

	$[(C_6H_8)Pt\{P(C_6H_5)_3\}_2]$	$[(C_7H_{10})Pt\{P(C_6H_5)_3\}_2]$
Radiation	Cu Kα	Cu Kα
Wavelength	1.5418 Å	1.5418 Å
Monochromator	Graphite crystal	Graphite crystal
Takeoff angle	3.0°	3.0°
Crystal to counter distance	28.5 cm	28.5 cm
Scan speed	2°/min	2°/min
Scan method	θ–2θ scans	θ–2θ scans
Scan width[a]	From $(2\theta - 1.2)°$ to $(2\theta + 1.2 + \Delta)°$	From $(2\theta - 1.15)°$ to $(2\theta + 1.15 + \Delta)°$
Total background count time[b]	20 sec	20 sec
"Standard" reflections	3 every 40	3 every 40
"Standard" indices	(0,12,3) ($\bar{7}$,$\bar{6}$,0) (0,$\overline{12}$,$\bar{3}$)	(7,1,$\bar{7}$) (0,18,5) (8,0,$\bar{4}$)
Crystal stability	12% isotropic decay during data collection	8% isotropic decay during data collection
2θ scan limit	124°	124°
Form of data collected	$\bar{h}kl$, $\bar{h}\bar{k}l$, hkl, $\bar{h}k\bar{l}$	$h\bar{k}l$, $hk\bar{l}$
Total number of data collected	6343	6674
Number with $I/\sigma(I) \geq 3.0$	5157	4918
ρ^2	0.001	0.001

[a] The scan range was asymmetric. Δ is the 2θ separation (in degrees) of the Cu Kα_1 and Cu Kα_2 peaks at the 2θ value of the reflection concerned. [b] Backgrounds were counted on either "side" of each reflection at the scan range limits and were assumed to be linear between those two points.

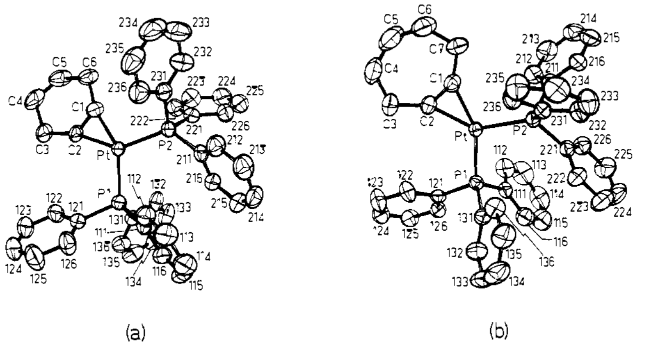

Figure 1. The overall stereochemistry and atom numbering schemes used for the cyclic alkyne platinum(0) derivatives: (a) $[(cyclohexyne)Pt\{P(C_6H_5)_3\}_2]$; (b) $[(cycloheptyne)Pt\{P(C_6H_5)_3\}_2]$. (In both figures, the symbol C has been omitted from phenyl carbon atoms.)

The hydrogen atoms were assigned fixed isotropic temperature factors 10% greater than the carbon atoms to which they are bonded (*i.e.*, $B_H = 1.1B_C$ Å^2). No attempt was made to refine the hydrogen atom coordinates or temperature factors which were recalculated prior to each refinement cycle. On the final refinement cycle for each cyclic acetylene complex, no individual parameter shift was greater than 0.1 of the parameter estimated standard deviation. (Estimated standard deviations are obtained from inversion of the block-diagonal matrices.) The standard deviation of an observation of unit weight, defined as $\{\Sigma w[|F_o| - |F_c|]^2/(m - n)\}^{1/2}$ (where m is the number of observations and n is the number of parameters varied) is 2.40 for $[(cyclohexyne)Pt\{P(C_6H_5)_3\}_2]$ and 1.44 for $[(cycloheptyne)Pt\{P(C_6H_5)_3\}_2]$. An examination of $|F_o|$ and $|F_c|$ showed no evidence of serious extinction effects, and consequently, no correction was applied. Similarly, a weighting scheme analysis showed no serious dependence of $w[|F_o| - |F_c|]^2$ on either $|F_o|$, $\lambda^{-1} \sin \theta$, or Miller index. The final electron-density difference Fourier maps showed no unusual features. For the cyclohexyne derivative, the highest residual peak was 1.2 e/Å^3, near the platinum atom; the remaining peaks were all less than 0.5 e/Å^3. For the cycloheptyne analog, there were no peaks greater than 0.5 e/Å^3.

Table IV lists the final atomic positional and thermal parameters for $[(cyclohexyne)Pt\{P(C_6H_5)_3\}_2]$, while those for $[(cycloheptyne)Pt\{P(C_6H_5)_3\}_2]$ are listed in Table V. The final values of $10|F_o|$ and $10|F_c|$ (in electrons) have been deposited. (For details regarding the availability of supplementary material, see the paragraph at the end of this paper).

Computer Programs. The data reduction and sorting programs SETUP and SORTIE were originally written by Dr. B. M. Foxman, but were modified (Whimp) for operation on the Univac-1108 computer. The Fourier and absorption correction programs, ANUFOR and ACACA, respectively, have been described previously.[13] The block-diagonal least-squares program, BLKLSQ,[13] uses either 4 × 4 or 3 × 3 and 6 × 6 matrices. Figures were produced with ORTEP.[14] Calculations were carried out on the CDC3600 computer of the CSIRO Division of Computing Research, Canberra, and the IBM360/50 and Univac-1108 computers of The Australian National University Computer Centre.

Results

Description of the Structures. The crystal structures of both $[(cyclohexyne)Pt\{P(C_6H_5)_3\}_2]$ and $[(cycloheptyne)Pt\{P(C_6H_5)_3\}_2]$ as defined by the unit cell dimensions, space group symmetry operations, and atom coordinates consist of discrete monomeric molecular units having neither crystallographic nor virtual symmetry higher than C_1. There are no unusually short intermolecular atom–atom contacts. The stereochemical arrangement of one molecule of $[(cyclohexyne)Pt\{P(C_6H_5)_3\}_2]$, together with the atom numbering scheme, is shown in Figure 1a, while a perspective view of this molecule is given by the stereopairs of Figure 2. Similar details for the cycloheptyne analog are shown in Figures 1b and 3. The thermal ellipsoids have been drawn to include 50% of the probability distribution, and,

Table III. Course of Refinement

Set no.	Conditions	$[(C_6H_8)Pt\{P(C_6H_5)_3\}_2]$ R^a	R_w	$[(C_7H_{10})Pt\{P(C_6H_5)_3\}_2]$ R	R_w
1	All atoms isotropic, hydrogen atoms not included, equal (unit) weights	0.086	0.097	0.066	0.073
2	Pt and P anisotropic, C isotropic, hydrogen atoms not included, equal (unit) weights. At this stage of refinement, the reflection data were corrected for absorption effects	0.060	0.074	0.052	0.061
3	Pt and P anisotropic,[b] C isotropic, hydrogen atoms not included, equal unit weights. Individual weights [$w = 1/\sigma^2(F_o)$] were introduced at this point and were used in all subsequent refinement cycles			0.041	0.046
4	Pt and P anisotropic, C isotropic, no hydrogen atom contributions	0.055	0.067	0.041	0.056
5	Pt and P anisotropic, C isotropic, fixed hydrogen atom contributions			0.034	0.046
6	Pt, P, and C anisotropic, no hydrogen atom contributions	0.048	0.061		
7	Pt, P, and C anisotropic, fixed isotropic hydrogen atom contributions included	0.040	0.048	0.024	0.030

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; the function minimized during least-squares refinement was $\Sigma w(|F_o| - |F_c|)^2$. [b] The anisotropic thermal parameter takes the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

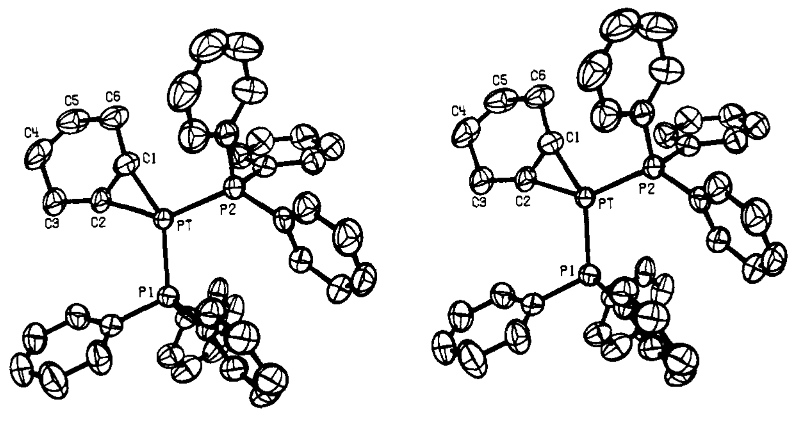

Figure 2. A stereoscopic view of $[(cyclohexyne)Pt\{P(C_6H_5)_3\}_2]$.

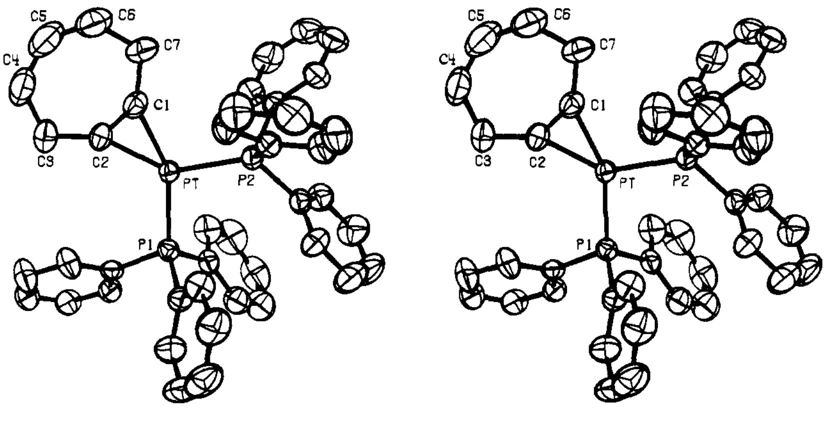

Figure 3. A stereoscopic view of $[(cycloheptyne)Pt\{P(C_6H_5)_3\}_2]$.

for clarity, hydrogen atoms have been omitted from all figures.

Both complexes exhibit near identical coordination at the central platinum atom; the ligand arrangement is essentially square planar, with the donor phosphine groups occupying mutually cis coordination sites; the coordinated alkyne groups are only slightly rotated from the P-Pt-P planes (*vide infra*). Bond length and bond angle data are listed in Tables VI-VIII. It should be noted that as atom-atom correlations have been neglected, both in the (block-diagonal) least-squares refinement process, and in the subsequent calculation of bond distance and interbond angle estimated standard deviations, the tabulated esd's will certainly be underestimated. The results of weighted least-squares planes calculations are collected in Table IX.[15] Torsion angles within each cyclic alkyne ring are collected in Table X.

Discussion

In the complexes $[(cycloheptyne)Pt\{P(C_6H_5)_3\}_2]$ and $[(cyclohexyne)Pt\{P(C_6H_5)_3\}_2]$, the disposition of ligands in the first coordination sphere is entirely characteristic of alkyne- and alkene-platinum(0) (d^{10}) complexes. In both de-

Table IV. Fractional Atomic Positional and Thermal Parameters for [(cyclohexyne)Pt{P(C_6H_5)$_3$}$_2$]

(a) Refined Positional and Anisotropic Thermal Parameters

ATOM	X	Y	Z	BETA11	BETA22	BETA33	BETA12	BETA13	BETA23
PT	0.00471(2)	0.25100(1)	0.14374(2)	0.00521(7)	0.00227(1)	0.00749(2)	-0.00040(1)	-0.00018(2)	0.00064(1)
P(1)	-0.00912(4)	0.15275(7)	0.28024(13)	0.00685(15)	0.00224(4)	0.00843(13)	-0.00067(6)	-0.00066(11)	0.00050(6)
P(2)	-0.20176(4)	0.33613(7)	0.18136(13)	0.00588(15)	0.00262(4)	0.00877(13)	-0.00029(6)	-0.00030(11)	0.00058(6)
C(1)	0.1295(6)	0.3013(3)	0.0079(6)	0.0097(7)	0.0035(2)	0.0090(6)	-0.0014(3)	-0.0015(5)	0.0013(3)
C(2)	0.2010(6)	0.2359(3)	0.0320(6)	0.0061(6)	0.0036(2)	0.0094(6)	-0.0003(3)	0.0007(5)	0.0004(3)
C(3)	0.3505(6)	0.2030(4)	-0.0271(7)	0.0067(7)	0.0047(3)	0.0126(8)	-0.0002(3)	0.0006(6)	0.0008(4)
C(4)	0.3919(7)	0.2531(4)	-0.1424(7)	0.0080(8)	0.0073(4)	0.0136(9)	-0.0027(4)	0.0027(7)	0.0019(5)
C(5)	0.3354(8)	0.3361(4)	-0.1186(8)	0.0109(9)	0.0062(3)	0.0165(10)	-0.0036(5)	-0.0023(8)	0.0044(5)
C(6)	0.1749(7)	0.3583(4)	-0.0845(6)	0.0106(8)	0.0045(3)	0.0117(7)	-0.0025(4)	-0.0016(6)	0.0025(3)
C(111)	-0.1771(5)	0.1244(3)	0.3309(5)	0.0063(6)	0.0024(2)	0.0100(6)	-0.0004(3)	0.0004(5)	0.0004(3)
C(112)	-0.2636(6)	0.1252(3)	0.2362(6)	0.0091(7)	0.0035(2)	0.0114(7)	-0.0017(3)	-0.0018(6)	0.0006(3)
C(113)	-0.3899(7)	0.1035(4)	0.2674(7)	0.0096(8)	0.0044(3)	0.0166(9)	-0.0022(4)	-0.0036(7)	0.0014(4)
C(114)	-0.4339(7)	0.0815(4)	0.3959(8)	0.0089(8)	0.0038(2)	0.0212(11)	-0.0022(4)	-0.0019(8)	0.0019(4)
C(115)	-0.3505(7)	0.0810(4)	0.4918(7)	0.0112(9)	0.0044(3)	0.0151(9)	-0.0017(4)	0.0013(7)	0.0032(4)
C(116)	-0.2218(7)	0.1018(3)	0.4620(6)	0.0099(8)	0.0033(2)	0.0117(7)	-0.0009(3)	-0.0010(6)	0.0017(3)
C(121)	0.1066(6)	0.0638(3)	0.2143(5)	0.0093(7)	0.0025(2)	0.0082(5)	-0.0003(3)	-0.0002(5)	0.0007(2)
C(122)	0.2513(6)	0.0549(3)	0.1892(7)	0.0082(7)	0.0033(2)	0.0146(8)	-0.0002(3)	-0.0002(6)	0.0006(3)
C(123)	0.3407(7)	-0.0068(4)	0.1421(7)	0.0091(8)	0.0044(3)	0.0157(9)	0.0004(4)	0.0011(7)	-0.0004(4)
C(124)	0.2907(8)	-0.0698(4)	0.1169(8)	0.0127(10)	0.0039(3)	0.0163(10)	0.0013(4)	0.0021(8)	-0.0010(4)
C(125)	0.1498(9)	-0.0664(4)	0.1407(10)	0.0160(12)	0.0033(2)	0.0248(14)	-0.0008(4)	0.0017(11)	-0.0028(5)
C(126)	0.0577(7)	-0.0003(3)	0.1894(8)	0.0093(8)	0.0034(2)	0.0187(10)	-0.0011(3)	0.0012(7)	-0.0021(4)
C(131)	0.0478(6)	0.1660(3)	0.4395(5)	0.0084(7)	0.0028(2)	0.0086(5)	-0.0012(3)	-0.0005(5)	0.0003(3)
C(132)	0.0156(6)	0.2412(4)	0.4974(6)	0.0081(7)	0.0044(2)	0.0114(7)	-0.0024(3)	0.0008(6)	-0.0024(3)
C(133)	0.0459(8)	0.2483(4)	0.6257(7)	0.0116(9)	0.0065(4)	0.0112(7)	-0.0030(4)	-0.0006(7)	-0.0027(4)
C(134)	0.1135(8)	0.1912(5)	0.6923(7)	0.0145(11)	0.0081(4)	0.0101(7)	-0.0057(6)	-0.0014(7)	-0.0003(4)
C(135)	0.1511(9)	0.1207(5)	0.6335(7)	0.0167(12)	0.0064(4)	0.0114(8)	-0.0038(5)	-0.0045(8)	0.0018(4)
C(136)	0.1167(7)	0.1077(4)	0.5085(6)	0.0128(9)	0.0041(2)	0.0109(7)	-0.0018(4)	-0.0032(7)	0.0012(3)
C(211)	-0.3651(5)	0.3150(3)	0.2725(5)	0.0054(6)	0.0025(2)	0.0101(6)	0.0001(2)	-0.0003(5)	0.0002(3)
C(212)	-0.4843(6)	0.3181(4)	0.2172(6)	0.0074(7)	0.0041(2)	0.0118(7)	-0.0011(3)	-0.0013(6)	0.0004(3)
C(213)	-0.6057(7)	0.3003(4)	0.2888(8)	0.0077(8)	0.0048(3)	0.0170(10)	-0.0014(4)	-0.0012(7)	-0.0001(4)
C(214)	-0.6038(7)	0.2778(4)	0.4211(7)	0.0096(8)	0.0038(2)	0.0153(9)	-0.0015(4)	0.0042(7)	-0.0002(4)
C(215)	-0.4850(7)	0.2751(4)	0.4789(6)	0.0107(8)	0.0038(2)	0.0115(7)	-0.0008(4)	0.0028(6)	0.0006(3)
C(216)	-0.3667(6)	0.2931(3)	0.4054(6)	0.0083(7)	0.0032(2)	0.0095(6)	-0.0005(3)	0.0003(5)	0.0006(3)
C(221)	-0.1911(6)	0.4209(3)	0.2746(5)	0.0098(7)	0.0026(2)	0.0093(6)	-0.0007(3)	-0.0015(5)	0.0009(3)
C(222)	-0.0616(7)	0.4409(3)	0.2692(7)	0.0106(8)	0.0032(2)	0.0131(8)	-0.0010(3)	-0.0019(6)	0.0000(3)
C(223)	-0.0503(8)	0.5054(4)	0.3380(8)	0.0136(10)	0.0044(3)	0.0162(10)	-0.0022(4)	-0.0037(8)	0.0001(4)
C(224)	-0.1685(9)	0.5489(4)	0.4131(7)	0.0210(13)	0.0031(2)	0.0132(8)	-0.0019(4)	-0.0019(9)	-0.0009(3)
C(225)	-0.2965(9)	0.5304(4)	0.4182(7)	0.0192(12)	0.0028(2)	0.0148(9)	-0.0007(4)	0.0021(9)	-0.0007(3)
C(226)	-0.3088(7)	0.4675(3)	0.3487(7)	0.0119(9)	0.0030(2)	0.0137(8)	-0.0007(3)	0.0005(7)	-0.0001(3)
C(231)	-0.2509(6)	0.3704(3)	0.0218(5)	0.0058(6)	0.0035(2)	0.0095(6)	-0.0004(3)	-0.0004(5)	0.0009(3)
C(232)	-0.2953(9)	0.4461(4)	-0.0013(7)	0.0181(12)	0.0039(3)	0.0142(9)	-0.0009(4)	-0.0034(9)	0.0022(4)
C(233)	-0.3318(10)	0.4678(5)	-0.1268(9)	0.0219(15)	0.0059(4)	0.0175(11)	-0.0005(6)	-0.0061(11)	0.0045(5)
C(234)	-0.3210(9)	0.4163(5)	-0.2268(8)	0.0147(11)	0.0089(5)	0.0123(8)	-0.0010(6)	-0.0034(8)	0.0048(5)
C(235)	-0.2791(8)	0.3412(5)	-0.2053(7)	0.0116(10)	0.0085(4)	0.0103(7)	-0.0014(5)	-0.0019(7)	0.0005(5)
C(236)	-0.2402(7)	0.3174(4)	-0.0797(6)	0.0121(9)	0.0050(3)	0.0105(7)	-0.0006(4)	-0.0020(7)	0.0001(4)

(b) Calculated Hydrogen Atom Coordinates and Fixed Isotropic Thermal Parameters[a]

ATOM	X	Y	Z	B(A**2)	ATOM	X	Y	Z	B(A**2)
H(31)	0.417	0.203	0.049	5.1	H(1133)	0.018	0.304	0.673	6.1
H(32)	0.360	0.146	-0.065	5.1	H(1134)	0.139	0.201	0.791	6.8
H(41)	0.506	0.244	-0.162	6.5	H(1135)	0.204	0.074	0.686	6.6
H(42)	0.355	0.235	-0.231	6.5	H(1136)	0.145	0.052	0.462	5.1
H(51)	0.379	0.355	-0.035	6.5	H(1212)	-0.484	0.335	0.114	4.6
H(52)	0.369	0.364	-0.209	6.5	H(1213)	-0.699	0.303	0.243	5.7
H(61)	0.129	0.358	-0.176	5.1	H(1214)	-0.697	0.263	0.479	5.5
H(62)	0.143	0.414	-0.036	5.1	H(1215)	-0.485	0.258	0.582	5.1
H(1112)	-0.229	0.143	0.135	4.4	H(1216)	-0.273	0.290	0.451	4.1
H(1113)	-0.456	0.104	0.191	5.6	H(1222)	0.031	0.406	0.211	4.8
H(1114)	-0.534	0.065	0.421	6.0	H(1223)	0.052	0.520	0.334	6.1
H(1115)	-0.385	0.064	0.593	5.9	H(1224)	-0.160	0.599	0.467	6.2
H(1116)	-0.156	0.101	0.538	4.6	H(1225)	-0.389	0.566	0.477	6.3
H(1122)	0.291	0.110	0.208	4.9	H(1226)	-0.411	0.453	0.353	5.1
H(1123)	0.453	-0.009	0.123	5.8	H(1232)	-0.302	0.487	0.079	6.3
H(1124)	0.362	-0.122	0.079	6.4	H(1233)	-0.368	0.527	-0.145	8.2
H(1125)	0.110	-0.116	0.121	7.6	H(1234)	-0.348	0.434	-0.324	7.9
H(1126)	-0.055	0.002	0.208	5.7	H(1235)	-0.273	0.300	-0.285	7.0
H(1132)	-0.037	0.288	0.445	4.8	H(1236)	-0.204	0.258	-0.061	5.6

[a] The hydrogen atoms are numbered according to the carbon atoms to which they are bonded.

rivatives, the platinum atoms, the alkyne carbon atoms, and their substituents (*e.g.*, the atoms Pt, C(1), C(2), C(3), and C(6) in the cyclohexyne complex), form near planar systems (*vide infra*). In turn, the acetylenic carbon atoms (*i.e.*, C(1) and C(2) in both derivatives) lie very close to the plane of Pt, P(1), and P(2); the dihedral angle between the planes (Pt, C(1), C(2)) and (Pt, P(1), P(2)) is 4.4 (3)° for the cyclohexyne adduct and 7.9 (3)° for the cycloheptyne analog. Similar values have been observed for the corresponding dihedral angle in [($C_6H_5C{\equiv}CCO_2CH_2CH_3$)Pt{P($C_6H_5$)$_3$}$_2$] (5.2°) and [($p$-$NO_2C_6H_4$-$C{\equiv}CCO_2CH_2CH_3$)Pt{P($C_6H_5$)$_3$}$_2$] (9.1°),[5] and also for the platinum(0)-olefin derivatives [(tetracyanoethylene)-Pt{P(C_6H_5)$_3$}$_2$] (8.3°),[16,17] and [($Cl_2C{=}CCl_2$)Pt{P(C_6-

Table V. Fractional Atomic Positional and Thermal Parameters for [(cycloheptyne)Pt{P(C_2H_5)$_3$}$_2$]

(a) Refined Positional and Anisotropic Thermal Parameters

ATOM	X	Y	Z	BETA11	BETA22	BETA33	BETA12	BETA13	BETA23
PT	0.090399(17)	0.095997(4)	0.158528(11)	0.008151(23)	0.000574(1)	0.003899(10)	-0.000013(15)	0.001536(13)	0.000043(3)
P(1)	0.124121(112)	0.144960(26)	0.050790(69)	0.009260(143)	0.000618(8)	0.004367(59)	0.000130(28)	0.002321(77)	0.000069(17)
P(2)	0.292677(117)	0.109078(27)	0.329417(71)	0.009877(147)	0.000608(8)	0.004228(60)	-0.000157(28)	0.001571(78)	-0.000006(17)
C(1)	-0.02572(47)	0.04741(11)	0.18465(31)	0.01040(64)	0.00078(4)	0.00684(31)	-0.00036(13)	0.00246(37)	-0.00001(9)
C(2)	-0.08617(45)	0.05356(11)	0.07862(30)	0.00812(58)	0.00079(4)	0.00633(29)	-0.00002(12)	0.00180(34)	-0.00015(8)
C(3)	-0.21066(54)	0.03424(13)	-0.02261(35)	0.01336(77)	0.00111(5)	0.00766(34)	-0.00049(16)	0.00270(43)	-0.00086(10)
C(4)	-0.25504(76)	-0.00760(18)	0.00393(48)	0.02742(130)	0.00185(8)	0.01205(49)	-0.00399(27)	0.00962(69)	-0.00253(16)
C(5)	-0.26721(82)	-0.01659(17)	0.10840(50)	0.02837(140)	0.00124(6)	0.01703(67)	-0.00261(25)	0.00636(82)	-0.00007(17)
C(6)	-0.13223(81)	-0.01682(15)	0.21773(45)	0.03637(156)	0.00107(5)	0.01219(51)	-0.00202(24)	0.01199(77)	-0.00023(13)
C(7)	-0.04307(65)	0.02068(14)	0.26870(38)	0.02286(105)	0.00099(5)	0.00931(40)	-0.00141(19)	0.00516(54)	0.00070(11)
C(111)	0.12668(48)	0.19518(10)	0.10531(28)	0.01320(68)	0.00060(3)	0.00465(25)	0.00014(12)	0.00193(34)	-0.00003(7)
C(112)	0.00581(62)	0.20296(13)	0.14374(36)	0.01933(94)	0.00100(5)	0.00963(40)	0.00085(18)	0.00646(51)	-0.00039(11)
C(113)	-0.01334(77)	0.24139(15)	0.17758(45)	0.03116(142)	0.00118(6)	0.01358(56)	0.00200(24)	0.00991(76)	-0.00089(14)
C(114)	0.08819(78)	0.27146(15)	0.17383(39)	0.03872(173)	0.00089(5)	0.01026(48)	0.00128(23)	0.00582(76)	-0.00066(12)
C(115)	0.21236(84)	0.26381(14)	0.14146(41)	0.03905(164)	0.00085(5)	0.01079(48)	-0.00157(23)	0.00606(74)	-0.00063(12)
C(116)	0.23306(66)	0.22529(13)	0.10687(35)	0.02594(110)	0.00082(4)	0.00785(36)	-0.00090(18)	0.00607(53)	-0.00041(10)
C(121)	-0.04069(44)	0.15021(10)	-0.08992(28)	0.00898(57)	0.00077(4)	0.00462(24)	-0.00004(12)	0.00291(31)	0.00034(7)
C(122)	-0.08747(51)	0.11590(14)	-0.15408(29)	0.01619(83)	0.00099(4)	0.00500(29)	0.00092(15)	0.00175(40)	-0.00014(9)
C(123)	-0.21425(65)	0.11694(15)	-0.26081(34)	0.02358(108)	0.00118(5)	0.00544(31)	0.00036(20)	0.00105(48)	-0.00042(10)
C(124)	-0.29172(58)	0.15206(14)	-0.30454(33)	0.01566(85)	0.00137(6)	0.00553(31)	-0.00027(18)	-0.00022(42)	0.00045(10)
C(125)	-0.24810(54)	0.18644(13)	-0.24226(34)	0.01299(75)	0.00111(5)	0.00706(33)	0.00025(16)	0.00111(41)	0.00091(10)
C(126)	-0.12056(50)	0.18557(12)	-0.13456(30)	0.01322(72)	0.00084(4)	0.00599(29)	-0.00007(14)	0.00243(38)	0.00024(9)
C(131)	0.30376(46)	0.14175(11)	0.01860(30)	0.01077(62)	0.00073(4)	0.00572(27)	-0.00017(12)	0.00401(35)	-0.00025(8)
C(132)	0.32325(55)	0.16498(13)	-0.06343(35)	0.01554(80)	0.00097(4)	0.00825(35)	0.00018(15)	0.00603(45)	0.00021(10)
C(133)	0.46259(63)	0.16207(15)	-0.08255(41)	0.02071(100)	0.00130(5)	0.01127(46)	-0.00099(20)	0.01068(58)	0.00006(13)
C(134)	0.58521(60)	0.13604(15)	-0.02084(45)	0.01736(93)	0.00129(6)	0.01401(52)	-0.00093(19)	0.01088(61)	-0.00106(14)
C(135)	0.56885(55)	0.11179(15)	0.06009(40)	0.01190(76)	0.00124(5)	0.01100(45)	0.00053(17)	0.00535(49)	-0.00031(12)
C(136)	0.42509(51)	0.11463(12)	0.07787(33)	0.01310(72)	0.00082(4)	0.00734(33)	0.00052(14)	0.00394(41)	0.00008(9)
C(211)	0.22371(47)	0.10948(10)	0.44388(29)	0.01198(66)	0.00059(3)	0.00574(28)	-0.00040(12)	0.00340(36)	-0.00012(7)
C(212)	0.06365(54)	0.12143(14)	0.42046(35)	0.01356(78)	0.00135(5)	0.00759(35)	0.00022(17)	0.00475(44)	-0.00001(11)
C(213)	0.01362(62)	0.12563(17)	0.50712(44)	0.01695(93)	0.00157(6)	0.01206(48)	-0.00025(20)	0.00910(57)	-0.00063(14)
C(214)	0.11734(66)	0.11726(14)	0.61503(38)	0.02701(117)	0.00111(5)	0.00921(40)	-0.00054(20)	0.01068(60)	-0.00026(12)
C(215)	0.27515(68)	0.10478(13)	0.63867(35)	0.02590(114)	0.00104(5)	0.00625(34)	-0.00036(18)	0.00656(53)	0.00019(10)
C(216)	0.32629(56)	0.10109(11)	0.55390(32)	0.01639(82)	0.00088(4)	0.00531(29)	-0.00013(14)	0.00343(41)	0.00008(8)
C(221)	0.41551(44)	0.15515(11)	0.36169(27)	0.01090(64)	0.00066(3)	0.00455(25)	-0.00013(12)	0.00126(33)	0.00004(7)
C(222)	0.54692(52)	0.15930(12)	0.33297(35)	0.01297(73)	0.00082(4)	0.00865(36)	-0.00073(14)	0.00416(43)	-0.00010(10)
C(223)	0.63535(61)	0.19479(15)	0.35299(41)	0.01646(91)	0.00114(5)	0.01237(49)	-0.00117(18)	0.00529(56)	0.00026(13)
C(224)	0.59236(66)	0.22615(14)	0.40264(41)	0.02248(110)	0.00087(5)	0.01257(51)	-0.00203(19)	0.00507(62)	-0.00025(12)
C(225)	0.45966(68)	0.22279(13)	0.42902(41)	0.02686(119)	0.00072(4)	0.01161(47)	-0.00068(18)	0.00802(63)	-0.00069(11)
C(226)	0.37176(56)	0.18787(12)	0.40927(33)	0.01729(84)	0.00072(4)	0.00768(34)	-0.00008(15)	0.00416(44)	-0.00013(9)
C(231)	0.44927(45)	0.06981(11)	0.37005(27)	0.01078(62)	0.00067(3)	0.00454(24)	0.00003(12)	0.00205(32)	0.00017(7)
C(232)	0.60803(51)	0.07469(12)	0.45258(30)	0.01365(73)	0.00087(4)	0.00564(29)	0.00021(14)	0.00246(38)	0.00006(9)
C(233)	0.71915(54)	0.04355(13)	0.48145(34)	0.01365(76)	0.00105(5)	0.00681(32)	0.00066(15)	0.00135(41)	0.00010(10)
C(234)	0.67569(57)	0.00701(13)	0.42920(35)	0.01655(87)	0.00096(4)	0.00885(37)	0.00115(16)	0.00434(48)	0.00038(11)
C(235)	0.51837(59)	0.00147(12)	0.34778(35)	0.01840(91)	0.00078(4)	0.00896(38)	0.00060(16)	0.00370(48)	-0.00016(10)
C(236)	0.40566(49)	0.03300(12)	0.31645(31)	0.01339(73)	0.00073(4)	0.00624(29)	0.00028(13)	0.00181(39)	-0.00005(8)

(b) Calculated Hydrogen Atom Coordinates and Fixed Isotropic Thermal Parameters[a]

ATOM	X	Y	Z	B(A**2)	ATOM	X	Y	Z	B(A**2)
H(31)	-0.321	0.053	-0.054	4.9	H(132)	0.227	0.186	-0.112	4.6
H(32)	-0.162	0.032	-0.086	4.9	H(133)	0.477	0.181	-0.146	5.9
H(41)	-0.373	-0.015	-0.062	7.8	H(134)	0.695	0.134	-0.036	6.2
H(42)	-0.162	-0.028	0.000	7.8	H(135)	0.665	0.091	0.108	5.4
H(51)	-0.354	0.005	0.115	8.7	H(136)	0.410	0.096	0.141	4.2
H(52)	-0.320	-0.046	0.098	8.7	H(212)	-0.020	0.128	0.334	5.1
H(61)	-0.180	-0.029	0.276	7.4	H(213)	-0.111	0.135	0.489	6.3
H(62)	-0.041	-0.037	0.212	7.4	H(214)	0.076	0.120	0.682	5.8
H(71)	0.078	0.013	0.331	5.9	H(215)	0.358	0.098	0.725	5.4
H(72)	-0.111	0.036	0.309	5.9	H(216)	0.451	0.091	0.572	4.2
H(112)	-0.075	0.179	0.145	5.4	H(222)	0.581	0.134	0.295	4.5
H(113)	-0.110	0.248	0.205	7.6	H(223)	0.739	0.198	0.331	6.2
H(114)	0.073	0.301	0.201	7.7	H(224)	0.661	0.254	0.419	6.5
H(115)	0.294	0.288	0.141	7.6	H(225)	0.425	0.248	0.467	6.1
H(116)	0.330	0.219	0.079	5.5	H(226)	0.268	0.185	0.431	4.6
H(122)	-0.024	0.088	-0.119	4.5	H(232)	0.643	0.103	0.494	4.1
H(123)	-0.251	0.090	-0.311	5.9	H(233)	0.842	0.048	0.546	4.9
H(124)	-0.390	0.153	-0.388	5.5	H(234)	0.763	-0.017	0.452	5.1
H(125)	-0.311	0.214	-0.277	5.0	H(235)	0.483	-0.027	0.307	5.2
H(126)	-0.084	0.213	-0.085	4.1	H(236)	0.283	0.029	0.252	4.1

[a] The hydrogen atoms are numbered according to the carbon atoms to which they are bonded.

$H_5)_3\}_2$] (12.3°).[18] Energy minimization calculations for the complexes [($CH_3C{\equiv}CCH_3$)Pt(PH_3)$_2$] and [($CH_2{=}CH_2$)Pt(PH_3)$_2$] have shown that there is a single energy minimum when the alkyne or alkene bond lies in the plane of the platinum and phosphorus atoms.[19,20] In contrast, in the platinum(II) (d^8) alkyne and alkene derivatives, the corresponding dihedral angle is close to 90°.[21]

In terms of the Dewar-Chatt-Duncanson model[22,23] for

Table VI. Comparison of Important Bond Distances and Interbond Angles for [(cyclohexyne)Pt{P(C_6H_5)$_3$}$_2$] and [(cycloheptyne)Pt{P(C_6H_5)$_3$}$_2$]

(a) Bond Distances, Å

Atoms	[(cyclohexyne)-Pt{P(C_6H_5)$_3$}$_2$]	[(cycloheptyne)-Pt{P(C_6H_5)$_3$}$_2$]
Pt–P(1)	2.264 (1)	2.264 (1)
Pt–P(2)	2.271 (1)	2.270 (1)
Pt–C(1)	2.034 (6)	2.035 (4)
Pt–C(2)	2.044 (5)	2.064 (4)
P(1)–C(111)	1.829 (5)	1.825 (4)
P(1)–C(121)	1.832 (5)	1.836 (3)
P(1)–C(131)	1.816 (5)	1.825 (4)
P(2)–C(211)	1.834 (5)	1.841 (4)
P(2)–C(221)	1.832 (5)	1.842 (4)
P(2)–C(231)	1.827 (6)	1.835 (4)
C(1)–C(2)	1.297 (8)	1.283 (5)
C(1)–C(6)	1.480 (9)	
C(1)–C(7)		1.476 (6)
C(2)–C(3)	1.499 (8)	1.485 (6)
C(3)–C(4)	1.530 (10)	1.536 (7)
C(4)–C(5)	1.500 (11)	1.448 (8)
C(5)–C(6)	1.535 (10)	1.445 (9)
C(6)–C(7)		1.492 (7)

(b) Interbond Angles, Degrees

Atoms	[(cyclohexyne)-Pt{P(C_6H_5)$_3$}$_2$]	[(cycloheptyne)-Pt{P(C_6H_5)$_3$}$_2$]
P(1)–Pt–P(2)	109.54 (5)	102.58 (3)
P(1)–Pt–C(1)	146.6 (2)	153.2 (1)
P(1)–Pt–C(2)	109.7 (2)	117.0 (1)
P(2)–Pt–C(1)	103.6 (2)	104.2 (1)
P(2)–Pt–C(2)	140.7 (2)	140.2 (1)
C(1)–Pt–C(2)	37.1 (2)	36.5 (1)
Pt–P(1)–C(111)	120.1 (2)	114.1 (1)
Pt–P(1)–C(121)	114.3 (2)	115.9 (1)
Pt–P(1)–C(131)	112.7 (2)	117.2 (1)
C(111)–P(1)–C(121)	102.2 (2)	100.4 (2)
C(111)–P(1)–C(131)	103.2 (2)	105.9 (2)
C(121)–P(1)–C(131)	102.2 (2)	101.2 (2)
Pt–P(2)–C(211)	123.5 (2)	113.9 (1)
Pt–P(2)–C(221)	112.7 (2)	123.2 (1)
Pt–P(2)–C(231)	110.2 (2)	110.6 (1)
C(211)–P(2)–C(221)	100.9 (2)	100.1 (2)
C(211)–P(2)–C(231)	102.9 (2)	103.9 (2)
C(221)–P(2)–C(231)	104.7 (2)	102.8 (2)
Pt–C(1)–C(2)	71.9 (4)	73.0 (2)
Pt–C(2)–C(1)	71.0 (4)	70.6 (2)
C(1)–C(2)–C(3)	126.4 (5)	136.4 (4)
C(2)–C(1)–C(6)	128.1 (6)	
C(2)–C(1)–C(7)		141.4 (4)
C(2)–C(3)–C(4)	106.7 (5)	111.4 (4)
C(3)–C(4)–C(5)	115.9 (6)	122.0 (5)
C(4)–C(5)–C(6)	114.4 (6)	125.5 (5)
C(1)–C(6)–C(5)	106.5 (5)	
C(5)–C(6)–C(7)		121.0 (5)
C(1)–C(7)–C(6)		112.3 (4)

platinum(0)–alkyne bonding, the π-bond from the platinum atom to the acetylene will be strong, while the σ-bond in the reverse direction will be weak. This will lead to a significant increase in electron density in the acetylene pπ^* (antibonding) orbitals, and a concomitant decrease in the alkyne bond strength. The decrease in acetylene bond strength is indicated not only by the lowering of the C≡C stretching frequency (1721 cm^{-1} for the cyclohexyne adduct; 1770 cm^{-1} for the cycloheptyne analog; *cf.* 2200 cm^{-1} (approximately) for free acetylenes),[2,24] but also by the increased carbon–carbon distance. Thus, the distances C(1)–C(2) (1.297 (8) Å for the cyclohexyne complex, 1.283 (5) Å for the cyclopheptyne derivative) are equal within experimental error (3.0σ), and are intermediate between the values normally expected for simple carbon–carbon triple (1.202 (5) Å)[25a] and double (1.335 (5) Å)[25b] bonds. Similar bond lengthening has been observed[5] for the coordinated acyclic acetylenes $C_6H_5C{\equiv}CCO_2CH_2CH_3$ (1.286 (8) Å) and *p*-$NO_2C_6H_4C{\equiv}CCO_2CH_2CH_3$ (1.313 (7) Å). We note that the Pt(0)–alkyne interactions are appreciably more energetic than those in the Pt(II)–alkyne series. For the divalent species, the C≡C distance is much shorter, *e.g.*, for $[(CH_3)(CH_3C{\equiv}CCH_3)Pt\{P(CH_3)_2(C_6H_5)\}_2]PF_6$ the distance is 1.22 (3) Å,[21] reflecting the expected enhancement, in the Pt(0) complexes, of the acetylene pπ^* orbital charge density.

The Pt–C distances in the two complexes range from 2.034 (6) to 2.064 (4) Å. Although this range exceeds the limits of statistical significance, there is no obvious electronic rationale for these differences, and the apparent distortion is most probably a consequence of crystal packing effects. The observed Pt–C distances in the present complexes are in excellent agreement with those found for $[(C_6H_5C{\equiv}CC_6H_5)Pt\{P(C_6H_5)_3\}_2]$ (2.01 and 2.06 Å).[26] As expected, the C–Pt–C angles are *ca.* 40° (C(1)–Pt–C(2): 37.1 (1)° for the cyclohexyne complex, 36.5 (1)° for the cycloheptyne analog), and are in good agreement with the corresponding angle in $[(C_6H_5C{\equiv}CC_6H_5)Pt\{P(C_6H_5)_3\}_2]$ (39°).[26] These angles are, in turn, only slightly less than those found for Pt(0)–olefin complexes, *e.g.*, 41.5° for [(tetracyanoethylene)Pt{P(C_6H_5)$_3$}$_2$][16,17] and 47° for $[(Cl_2C{=}CCl_2)Pt\{P(C_6H_5)_3\}_2]$.[18]

Consistent with increased electron density in the alkyne pπ^* orbitals, the mean deformation (from 180°) of the internal C≡C—C angles for the coordinated cyclic acetylenes (52.7° for the cyclohexyne complex, 41.3° for the cyclopheptyne analog) is, in each case, some 12–16° in excess of that calculated for the hypothetical free ligands (40° for free cyclohexyne, 25° for free cycloheptyne).[27] A similar result has been found for the cyclooctyne complex [(cy-

Table VII. Bond Lengths (Å) and Interbond Angles (deg) in the Phenyl Rings of [(cyclohexyne)Pt{P(C_6H_5)$_3$}$_2$]

	$m = 1, n = 1$	$m = 1, n = 2$	$m = 1, n = 3$	$m = 2, n = 1$	$m = 2, n = 2$	$m = 2, n = 3$
P(*m*)–C(*mn*1)	1.829 (5)	1.832 (5)	1.816 (5)	1.834 (5)	1.832 (5)	1.827 (6)
C(*mn*1)–C(*mn*2)	1.379 (8)	1.397 (8)	1.438 (8)	1.373 (8)	1.392 (9)	1.387 (9)
C(*mn*2)–C(*mn*3)	1.372 (9)	1.378 (9)	1.386 (9)	1.393 (9)	1.392 (9)	1.405 (11)
C(*mn*3)–C(*mn*4)	1.384 (11)	1.373 (10)	1.354 (11)	1.396 (10)	1.378 (11)	1.351 (12)
C(*mn*4)–C(*mn*5)	1.367 (10)	1.362 (11)	1.363 (12)	1.385 (9)	1.366 (12)	1.369 (13)
C(*mn*5)–C(*mn*6)	1.384 (9)	1.386 (10)	1.390 (10)	1.376 (9)	1.374 (9)	1.423 (10)
C(*mn*6)–C(*mn*1)	1.412 (8)	1.384 (8)	1.388 (8)	1.397 (8)	1.394 (9)	1.380 (9)
	$m = 1, n = 1$	$m = 1, n = 2$	$m = 1, n = 3$	$m = 2, n = 1$	$m = 2, n = 2$	$m = 2, n = 3$
P(*m*)–C(*mn*1)–C(*mn*2)	118.3 (4)	118.7 (4)	117.3 (4)	124.0 (4)	119.2 (5)	123.1 (5)
P(*m*)–C(*mn*1)–C(*mn*6)	123.1 (4)	123.1 (5)	123.7 (5)	117.6 (4)	122.5 (4)	117.4 (5)
C(*mn*2)–C(*mn*1)–C(*mn*6)	118.6 (5)	118.2 (6)	119.0 (5)	118.3 (5)	118.3 (5)	119.5 (6)
C(*mn*1)–C(*mn*2)–C(*mn*3)	121.0 (6)	119.9 (6)	115.8 (6)	122.4 (6)	120.5 (6)	119.6 (7)
C(*mn*2)–C(*mn*3)–C(*mn*4)	120.3 (7)	121.4 (7)	124.5 (7)	118.0 (6)	119.4 (7)	121.1 (8)
C(*mn*3)–C(*mn*4)–C(*mn*5)	119.7 (6)	119.2 (7)	119.1 (7)	120.3 (6)	120.7 (6)	120.1 (8)
C(*mn*4)–C(*mn*5)–C(*mn*6)	120.9 (6)	120.5 (8)	120.1 (7)	120.2 (6)	120.2 (6)	120.0 (7)
C(*mn*5)–C(*mn*6)–C(*mn*1)	119.4 (6)	120.9 (7)	121.0 (6)	120.7 (5)	120.8 (6)	119.5 (7)

Table VIII. Bond Lengths (Å) and Interbond Angles (deg) in the Phenyl Rings of [(cycloheptyne)Pt{ P(C_6H_5)$_3$}$_2$]

	m = 1, *n* = 1	*m* = 1, *n* = 2	*m* = 1, *n* = 3	*m* = 2, *n* = 1	*m* = 2, *n* = 2	*m* = 2, *n* = 3
P(*m*)–C(*mn*1)	1.825 (4)	1.836 (3)	1.825 (4)	1.841 (4)	1.842 (4)	1.835 (2)
C(*mn*1)–C(*mn*2)	1.392 (6)	1.384 (5)	1.395 (6)	1.395 (6)	1.381 (6)	1.398 (5)
C(*mn*2)–C(*mn*3)	1.396 (7)	1.393 (6)	1.373 (7)	1.388 (7)	1.393 (6)	1.383 (6)
C(*mn*3)–C(*mn*4)	1.371 (8)	1.367 (7)	1.375 (7)	1.364 (7)	1.371 (7)	1.379 (6)
C(*mn*4)–C(*mn*5)	1.367 (9)	1.373 (6)	1.390 (7)	1.381 (8)	1.371 (8)	1.386 (6)
C(*mn*5)–C(*mn*6)	1.406 (7)	1.404 (6)	1.402 (6)	1.369 (6)	1.374 (6)	1.401 (6)
C(*mn*6)–C(*mn*1)	1.382 (6)	1.384 (5)	1.384 (5)	1.383 (5)	1.395 (5)	1.394 (5)

	m = 1, *n* = 1	*m* = 1, *n* = 2	*m* = 1, *n* = 3	*m* = 2, *n* = 1	*m* = 2, *n* = 2	*m* = 2, *n* = 3
P(*m*)–C(*mn*1)–C(*mn*2)	115.3 (3)	116.6 (3)	123.1 (3)	118.7 (3)	121.1 (3)	123.6 (3)
P(*m*)–C(*mn*1)–C(*mn*6)	125.3 (3)	124.7 (3)	118.2 (3)	123.1 (3)	120.8 (3)	117.8 (3)
C(*mn*2)–C(*mn*1)–C(*mn*6)	119.4 (4)	118.7 (3)	118.8 (4)	118.0 (3)	118.0 (3)	118.6 (3)
C(*mn*1)–C(*mn*2)–C(*mn*3)	120.2 (5)	120.5 (4)	120.7 (4)	119.8 (4)	121.1 (4)	120.8 (4)
C(*mn*2)–C(*mn*3)–C(*mn*4)	119.8 (5)	120.4 (4)	120.2 (5)	121.0 (5)	119.7 (5)	120.7 (4)
C(*mn*3)–C(*mn*4)–C(*mn*5)	120.6 (5)	120.2 (4)	120.7 (5)	119.5 (5)	119.8 (5)	119.4 (4)
C(*mn*4)–C(*mn*5)–C(*mn*6)	120.3 (5)	119.7 (4)	118.6 (4)	119.8 (4)	120.7 (5)	120.4 (4)
C(*mn*5)–C(*mn*6)–C(*mn*1)	119.6 (4)	120.5 (3)	120.9 (4)	121.8 (4)	120.6 (4)	120.1 (4)

Table IX. Least-Squares Planes

(a) Best Weighted Least-Squares Planes

Plane[a]	Atoms defining plane	Equation[b]
I-1	Pt, P(1), P(2)	$-0.5583X - 0.4447Y - 0.7004Z + 3.6353 = 0$
I-2	C(1), C(2), C(3), C(6)	$-0.5325X - 0.3929Y - 0.7498Z + 3.4334 = 0$
I-3	Phenyl ring C(111)–C(116)	$0.2172X - 0.9382Y - 0.2696Z + 3.0205 = 0$
I-4	Phenyl ring C(121)–C(126)	$-0.1534X + 0.3105Y - 0.9381Z + 1.9203 = 0$
I-5	Phenyl ring C(131)–C(136)	$0.8832X + 0.1893Y - 0.4291Z - 0.2627 = 0$
I-6	Phenyl ring C(211)–C(216)	$0.0863X - 0.9437Y - 0.3192Z + 6.2331 = 0$
I-7	Phenyl ring C(221)–C(226)	$-0.1767X + 0.5692Y - 0.8030Z - 1.9987 = 0$
I-8	Phenyl ring C(231)–C(236)	$0.9407X + 0.0865Y - 0.3281Z + 0.5121 = 0$
II-1	Pt, P(1), P(2)	$0.7818X - 0.5860Y - 0.2129Z + 2.3253 = 0$
II-2	C(1), C(2), C(3), C(7)	$0.7996X - 0.5971Y - 0.0641Z + 2.0765 = 0$
II-3	Phenyl ring C(111)–C(116)	$-0.2622X + 0.2296Y - 0.9373Z - 0.1597 = 0$
II-4	Phenyl ring C(121)–C(126)	$0.9041X + 0.1927Y - 0.3813Z - 1.4909 = 0$
II-5	Phenyl ring C(131)–C(136)	$-0.1680X - 0.7062Y - 0.6878Z + 3.9339 = 0$
II-6	Phenyl ring C(211)–C(216)	$-0.2770X + 0.9520Y - 0.1304Z + 4.0707 = 0$
II-7	Phenyl ring C(221)–C(226)	$-0.2589X + 0.3313Y - 0.9073Z + 2.6430 = 0$
II-8	Phenyl ring C(231)–C(236)	$0.6575X + 0.2947Y - 0.6934Z + 1.0448 = 0$

(b) Distances (Å) of Atoms from Best Planes

Atom	Plane I-1	Plane II-1	Atom	Plane I-2	Plane II-2
Pt	0.0000 (2)	0.0000 (2)	C(1)	−0.006 (6)	0.009 (8)
P(1)	0.000 (1)	0.000 (1)	C(2)	0.006 (6)	−0.008 (4)
P(2)	0.000 (1)	0.000 (1)	C(3)	−0.003 (7)	0.004 (5)
C(1)	−0.140 (6)	−0.031 (4)	C(6)	0.003 (7)	
C(2)	−0.069 (6)	0.142 (4)	C(7)		−0.005 (6)
C(3)	−0.109 (7)	0.337 (5)	Pt	−0.0127 (2)	−0.0037 (2)
C(6)	−0.243 (7)		P(1)	−0.180 (1)	−0.198 (1)
C(7)		−0.194 (6)	P(2)	0.004 (1)	0.311 (1)
			C(4)	0.276 (7)	0.391 (7)
			C(5)	−0.363 (8)	−0.045 (7)
			C(6)		0.368 (7)

Atom	Plane I-3 *m* = 1, *n* = 1	Plane I-4 *m* = 1, *n* = 2	Plane I-5 *m* = 1, *n* = 3	Plane I-6 *m* = 2, *n* = 1	Plane I-7 *m* = 2, *n* = 2	Plane I-8 *m* = 2, *n* = 3
C(*mn*1)	0.002 (5)	−0.001 (5)	−0.017 (6)	0.001 (5)	−0.008 (5)	−0.003 (6)
C(*mn*2)	−0.006 (6)	0.004 (7)	0.033 (6)	0.000 (6)	0.002 (6)	0.004 (9)
C(*mn*3)	0.005 (7)	−0.005 (7)	−0.027 (8)	−0.005 (7)	0.009 (7)	−0.007 (10)
C(*mn*4)	0.001 (7)	0.003 (8)	−0.007 (8)	0.007 (7)	−0.009 (7)	0.011 (9)
C(*mn*5)	−0.005 (7)	0.002 (9)	0.025 (9)	−0.005 (6)	−0.004 (7)	−0.013 (8)
C(*mn*6)	0.002 (6)	−0.002 (8)	−0.001 (7)	0.000 (6)	0.012 (6)	0.009 (7)
P(*m*)	0.015 (1)	−0.023 (1)	−0.141 (1)	0.041 (1)	−0.002 (1)	0.001 (1)

Atom	Plane II-3 *m* = 1, *n* = 1	Plane II-4 *m* = 1, *n* = 2	Plane II-5 *m* = 1, *n* = 3	Plane II-6 *m* = 2, *n* = 1	Plane II-7 *m* = 2, *n* = 2	Plane II-8 *m* = 2, *n* = 3
C(*mn*1)	0.016 (3)	−0.002 (4)	−0.013 (4)	−0.006 (4)	−0.008 (3)	−0.004 (4)
C(*mn*2)	−0.017 (5)	0.003 (5)	0.007 (4)	0.010 (5)	0.006 (4)	−0.001 (4)
C(*mn*3)	−0.008 (6)	−0.007 (6)	0.007 (5)	−0.006 (6)	0.007 (5)	0.002 (5)
C(*mn*4)	0.023 (5)	0.007 (5)	−0.011 (5)	−0.003 (5)	−0.014 (5)	0.004 (5)
C(*mn*5)	−0.009 (5)	−0.005 (5)	−0.004 (5)	0.004 (5)	0.006 (5)	−0.011 (5)
C(*mn*6)	−0.016 (4)	0.003 (5)	0.014 (3)	0.001 (4)	0.007 (4)	0.010 (4)
P(*m*)	0.169 (1)	−0.032 (1)	−0.055 (1)	−0.155 (1)	0.068 (1)	−0.054 (1)

[a] Planes numbered I-*n* (*n* = 1–8) refer to [(cyclohexyne)Pt{P(C_6H_5)$_3$}$_2$]; those numbered II-*n* (*n* = 1–8) refer to the cycloheptyne derivative.

[b] The equations of the planes, $LX + MY + NZ + D = 0$, refer to orthogonal coordinates: for [(cyclohexyne)Pt{P(C_6H_5)$_3$}$_2$] $X = 9.8747x + 3.6844y + 1.6331z$, $Y = 0.0x + 17.7628y - 0.3377z$, $Z = 0.0x + 0.0y + 9.9421z$; for [(cycloheptyne)Pt{(PC_6H_5)$_3$}$_2$] $X = 8.9153x + 0.0y - 5.3770z$, $Y = 0.0x + 33.5228y + 0.0z$, $Z = 0.0x + 0.0y + 11.9407z$.

Table X. Torsion Angles in the Cyclic Acetylene Rings

				Torsion angle, degrees[a]	
Atom 1	Atom 2	Atom 3	Atom 4	[(cyclohexyne)-Pt{P(C_6H_5)$_3$}$_2$]	[(cycloheptyne)-Pt{P(C_6H_5)$_3$}$_2$]
C(6)	C(1)	C(2)	C(3)	1.6 (10)	
C(7)	C(1)	C(2)	C(3)		−3.3 (11)
C(1)	C(2)	C(3)	C(4)	−11.9 (9)	−13.9 (8)
C(2)	C(3)	C(4)	C(5)	38.4 (9)	37.4 (7)
C(3)	C(4)	C(5)	C(6)	−57.2 (9)	−67.2 (8)
C(4)	C(5)	C(6)	C(7)		65.9 (9)
C(4)	C(5)	C(6)	C(1)	40.9 (8)	
C(5)	C(6)	C(7)	C(1)		−36.8 (9)
C(5)	C(6)	C(1)	C(2)	−15.4 (9)	
C(6)	C(7)	C(1)	C(2)		17.9 (9)

[a] The sign of the torsion angle is positive if, when looking from atom 2 to atom 3, a clockwise rotation of atom 1 would superimpose it on atom 4.

clooctyne)Pt{P(C_6H_5)$_3$}$_2$], where the deformation of the C≡C—C angle in the coordinated alkyne is 34°;[4] *cf.* an estimated 15° for free cyclooctyne.[27] For the diphenylacetylene complex,[26] the corresponding deformation is 40°.

There is, clearly, very little accumulated ring strain in the coordinated cyclohexyne moiety. The C-C-C angles are all within 6° of the regular tetrahedral value, and the distances C(3)-C(4), C(4)-C(5), and C(5)-C(6) are within 3.5σ of the value normally expected for carbon-carbon single bonds (1.537 (5) Å).[25b] In contrast, the coordinated cycloheptyne group appears to be quite severely strained. The internal angles at C(4), C(5), and C(6) each differ substantially (by 11-16°) from the tetrahedral value. In addition, the distances C(4)-C(5) and C(5)-C(6) (1.448 (8) and 1.445 (8) Å, respectively) have apparently undergone substantial compression. To a lesser extent, the bond C(6)-C(7) (1.492 (7) Å) also appears to be compressed.

The bonds adjacent to the alkyne linkage (C(1)-C(6) (1.480 (9)), C(2)-C(3) (1.499 (8)) for cyclohexyne; C(1)-C(7) (1.476 (6)), C(2)-C(3) (1.485 (6) Å) for cycloheptyne) appear uniformly longer than those commonly observed in acyclic acetylenes (1.459 (5) Å),[25c] but they do not differ significantly from the expected value (*ca.* 1.47-1.48 Å) for bonds between sp (tending toward sp^2) and sp^3 hybridized carbon atoms.[28]

The atoms C(1), C(2), C(3), and C(6) of the coordinated cyclohexyne group are planar within experimental error, the maximum deviation from this plane being −0.006 (6) Å at C(1). The platinum atom is −0.0127 (2) Å from this plane, while C(4) and C(5) are respectively 0.276 (7) and −0.363 (8) Å from this plane.

Similarly, in the cycloheptyne complex, C(1), C(2), C(3), and C(7) are planar within experimental error; the maximum deviation from the plane is 0.009 (4) Å (C(1)). The platinum atom is only −0.0037 (2) Å from this plane, while C(4) and C(6) are respectively 0.391 (7) and 0.369 (7) Å above the plane and C(5) is 0.045 (7) Å below the plane. The cycloheptyne ring has, therefore, a distorted chair conformation.

The Pt-P distances average 2.267 Å, and range from 2.264 (1) to 2.271 (1) Å. Values of 2.28 and 2.27 Å were found for the Pt-P distances in the diphenylacetylene derivative.[26] In all three examples, however, the observed Pt-P distances are very much shorter than the value of 2.49 Å calculated from the sum of the appropriate covalent radii for simple σ-bonds. The angle P(1)-Pt-P(2) for the cyclohexyne derivative (109.54 (5)°) is larger than the corresponding angles in the cycloheptyne analog (102.58 (3)°) or the diphenylacetylene derivative (102°).[26] It is unlikely that this discrepancy is electronic in origin, and, as similar differences have been observed for the P-Pt-P angles in the platinum(0) complexes of $C_6H_5C{\equiv}CCO_2CH_2CH_3$ (109.84°) and p-$NO_2C_6H_4C{\equiv}CCO_2CH_2CH_3$ (103.42°), we suggest that the apparent anomaly is steric in origin, arising from differing crystal packing effects.

The P-C distances average 1.828 Å for the cyclohexyne adduct and 1.834 Å for the cycloheptyne analog. These values are in excellent agreement with those observed for numerous coordinated triphenylphosphine groups and also for free triphenylphosphine where the average P-C distance is 1.828 Å.[29] The angles at the phosphorus atoms show the customary deformations from regular tetrahedral values, with the Pt-P-C angles being significantly greater and the C-P-C angles being significantly less than 109° 27′. The phenyl carbon-carbon distances average 1.384 Å for the cyclohexyne derivative and 1.385 Å for the cycloheptyne complex. This apparent contraction relative to the benzene value (1.397 Å) results from a progressive shortening of the C-C distances toward the ring extremities and is characteristic of libration shortening. Deviations of the internal phenyl ring angles from 120° (particularly the angle C(*mn*2)-C(*mn*1)-C(*mn*6)) are, likewise, characteristic of joint libration effects and electronegativity differences between P- and H-bonded carbon atoms.[30]

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Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $7.00 for photocopy or $2.00 for microfiche, referring to code number JACS-75-1051.

References and Notes

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$$A = \sum_{\substack{\text{all}\\\text{atoms}}} \{(f_0 + \Delta f')\cos\phi - \Delta f''\sin\phi\}$$

$$B = \sum_{\substack{\text{all}\\\text{atoms}}} \{(f_0 + \Delta f')\sin\phi + \Delta f''\cos\phi\}$$

where $\phi = 2\pi(hx + ky + lz)$

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Steric *vs.* Electronic Effects in Palladium–Thiocyanate Complexes. The Crystal Structures of Dithiocyanato[bis(diphenylphosphino)methane]palladium(II), Isothiocyanatothiocyanato[1,2-bis(diphenylphosphino)ethane]palladium(II), and Diisothiocyanato[1,3-bis(diphenylphosphino)propane]palladium(II)

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Abstract: The crystal structures of the series $(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2Pd(CNS)_2$, CNS represents the thiocyanate ion without specifying the mode of attachment (n = 1–3), have been determined by X-ray diffraction techniques. The most important observation is that the thiocyanate coordination changes from S,S when n = 1 to S,N for n = 2 and N,N with n = 3. The conclusion is that the mode of thiocyanate coordination in palladium thiocyanate-phosphine complexes is determined by steric rather than electronic effects. The crystals of $(C_6H_5)_2PCH_2P(C_6H_5)_2Pd(SCN)_2$ are monoclinic, space group $P2_1/n$, with a = 10.426 (8) Å, b = 29.353 (10) Å, c = 9.884 (6) Å, and β = 119.86 (4)°. The final R value for the 2814 reflections used in the analysis was 0.039. The complex $(C_6H_5)P(CH_2)_2P(C_6H_5)Pd(SCN)(NCS)$ crystallizes with the orthorhombic space group $P2_12_12_1$. The cell dimensions are a = 17.773 (6), b = 23.212 (15), and c = 8.502 (4) Å. A total of 2249 reflections was used in the analysis and the final R value was 0.056. The last compound $(C_6H_5)_2P(CH_2)_3P(C_6H_5)_2Pd(NCS)_2$ is monoclinic with the space group $I2/a$ and cell dimensions of a = 14.774 (6) Å, b = 9.181 (5) Å, c = 21.182 (10) Å, and β = 95.48 (2)°. The molecule has twofold symmetry, as required for four molecules per unit cell. The final R value for the 1781 reflections used in the analysis was 0.025. The Pd–P bond distances are a function of the nature of the trans atom, a σ-bond rather than a π-bond effect. The Pd–S distances appear to be independent of the tip of the thiocyanate ion from the coordination plane. A comparison of the angular changes in the three compounds is easily interpreted in terms of increasing steric effects with an increase in the chain length between the phosphorus atoms. The changing mode of the thiocyanate ion is explainable in terms of steric effects without invoking any π-bonding arguments.

The thiocyanate ion is an ambidentate ligand that can coordinate either through the sulfur or nitrogen atom.[2] This ambidentate nature can be interpreted in terms of the "soft–hard" concepts developed by Pearson.[3] Therefore, in the case of class b or "soft" metals, such as Pd(II) or Pt(II), coordination of thiocyanate is expected to occur through the "soft" sulfur atom. Indeed, Pd(II) complexes with many amine ligands form S-bonded thiocyanates. In contrast, a limited number of phosphine complexes of Pd(II) were found to have N-bonded thiocyanates, a fact which has been rationalized on the basis of π-bonding,[4] polyelectronic perturbation theory,[5] and the so-called antisymbiosis effects.[6]

A study of palladium- and platinum–thiocyanate complexes involving PPh_3, $AsPh_3$, and $SbPh_3$ was complicated by the fact that the steric and electronic factors operated in the same direction.[7] Nevertheless, steric control was used to prepare the N-bonded complex $Pd[(C_2H_5)_2NCH_2CH_2NHCH_2CH_2N(C_2H_5)_2](NCS)^+$ rather than the usual S-bonded thiocyanates.[8] However, despite this early evidence that steric effects could explain the changes in thiocyanate coordination, π-bonding arguments continued to be invoked.[9,10] In fact contrary evidence such as nmr coupling constants which suggested that π-bonding in Pt(π)–phosphine complexes was minimal at best[11] was ignored. The presence of both N-bonded and S-bonded thiocyanates in Pd(dppn)(NCS)(SCN), dppn is $(C_6H_5)_2PCH_2CH_2CH_2N(CH_3)_2$,[12] appeared to support these π-bonding arguments and has also been used as an example of "antisymbiosis."[6] However, the existence of both N- and S-bonded thiocyanates in Pd(dpe)(NCS)(SCN),[13] dpe is $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$, suggested that steric effects were extremely important and tended to refute the "antisymbiosis" arguments, at least for palladium complexes.

The problem in all of the previous studies has been the difficulty in separating steric from electronic effects. Therefore, after the completion of our study of Pd(dpe)(NCS)(SCN), we undertook an investigation of two other closely related complexes $Pd(dpm)(SCN)_2$, dpm is $(C_6H_5)_2PCH_2P(C_6H_5)_2$, and $Pd(dpp)(NCS)_2$, dpp is $(C_6H_5)_2PCH_2CH_2CH_2P(C_6H_5)_2$. The series of complexes $(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2Pd(CNS)_2$, CNS does not specify the mode of attachment, will have approximately equivalent electronic effects but vastly different steric require-