Structure of Bis(cyclopropyl)bis(dimethylphenylphosphine)platinum(II), *cis*-$Pt(\overline{CHCH_2CH_2})_2[P(CH_3)_2(C_6H_5)]_2$. Relationship between Structural and $^1J(^{195}Pt-^{31}P)$ Data and Position of Cyclopropyl Group in Trans-Influence Series

Nancy L. Jones and James A. Ibers*

Department of Chemistry, Northwestern University, Evanston, Illinois 60201

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The structure of *cis*-bis(cyclopropyl)bis(dimethylphenylphosphine)platinum(II), *cis*-$Pt(\overline{CHCH_2CH_2})_2(PMe_2Ph)_2$, has been determined crystallographically at −133 (2) °C and consists of discrete molecules of the neutral complex. The complex crystallizes from pentane in the triclinic space group C_i^1-$P\bar{1}$ with two formula units in a unit cell of dimensions a = 11.055 (3) Å, b = 11.457 (3) Å, c = 9.897 (2) Å, α = 112.46 (1)°, β = 96.43 (1)°, γ = 67.73 (1)°. The structure was solved from Patterson and electron density maps. Full-matrix least-squares refinement has led to a final value of the R index on F^2 of 0.068 based on 8749 reflections and 226 variables. The conventional R index on F for those 7210 reflections having $F_o^2 > 3\sigma(F_o^2)$ is 0.039. This complex of Pt(II) possesses nearly square-planar geometry, P(1)–Pt–P(2) = 94.86 (4)°, C(1)–Pt–C(4) = 89.91 (18)°. The cyclopropyl rings are equilateral with average C–C distances of 1.506 (13) Å and C–C–C angles of 60.00 (80)°. Some important molecular parameters are Pt–C(1) = 2.086 (4) Å, Pt–C(4) = 2.070 (4) Å, Pt–P(1) = 2.302 (1) Å, and Pt–P (2) = 2.291 (1) Å. Examination of the structural and $^{31}P\{^1H\}$ NMR data and comparison of these data with those of other Pt(II) complexes suggest placement of the cyclopropyl group in the trans-influence series between metallocycloalkanes and alkyl groups, such as methyl and neopentyl.

Introduction

Recently much interest has focused on metal-assisted rearrangements of cyclopropanes to olefins.[1] Transition-metal σ-cyclopropyl complexes may be intermediates in these rearrangements. Since no simple σ-bound cyclopropyl transition-metal complexes had previously been characterized structurally[2,3] and few such complexes had been synthesized,[4] we undertook a crystallographic study of *cis*-$Pt(\overline{CHCH_2CH_2})_2[P(CH_3)_2(C_6H_5)]_2$[5] to investigate the effect of the metal on the C–C bonding within the cyclopropyl rings. We combined the structural results with $^{31}P\{^1H\}$ NMR data in an attempt to determine the trans influence of the cyclopropyl group. The results of the NMR study and our low temperature structure determination are reported here.

Experimental Section

The complex *cis*-$Pt(\overline{CHCH_2CH_2})_2(PMe_2Ph)_2$ was prepared by the method of Phillips and Puddephatt[5] by reacting *cis*-$PtCl_2(PMe_2Ph)_2$ with 2 equiv of cyclopropyllithium in dry, deaerated diethyl ether under an atmosphere of dinitrogen. Workup included addition of water to the ethereal suspension, evaporation of the solvent from the ether layer, and extraction of the residue into pentane. The ^1H NMR spectrum [(C_6D_6 solution, room temperature) δ(PhP) 6.95 (m), δ(MeP) 1.28 (d, $^2J + {}^4J$(PH) 7.7 Hz), $\delta(C_3H_5)$ 0.97 (m) ppm], the melting point (104 °C), and elemental analysis (calcd for $C_{22}H_{32}P_2Pt$: C, 47.74; H, 5.83; P, 11.19. Found: C, 47.56; H, 5.95; P, 11.18) agree with those reported in the literature.[5] The $^{31}P\{^1H\}$ NMR spectrum (C_6D_6 solution, room temperature) is consistent with the equivalence of the two phosphine ligands (s, −16.6 ppm downfield from external 85% H_3PO_4, J(Pt–P) = 1770 Hz).

Colorless crystals suitable for diffraction study were grown by slow evaporation of a pentane solution of *cis*-$Pt(\overline{CHCH_2CH_2})_2(PMe_2Ph)_2$. Preliminary precession photographic data taken at room temperature from a crystal mounted in air revealed no symmetry, other than the trivial center of symmetry. A Delaunay reduction of the cell constants did not reveal any hidden symmetry. The density, 1.62 (1) g/cm^3, measured by flotation of the crystals in aqueous $ZnCl_2$, may be compared with the density of 1.716 g/cm^3 calculated for two molecules of *cis*-$Pt(\overline{CHCH_2CH_2})_2(PMe_2Ph)_2$ in the low temperature cell.

A colorless crystal, described by faces {100}, {10$\bar{3}$}, ($\bar{1}\bar{5}$2), and ($\bar{2}$5$\bar{3}$), cut from a larger crystal, was mounted on a four-circle, computer-controlled Picker FACS-1 diffractometer.[6] Throughout the data collection the crystal was continuously bathed in a stream of cold (−133 (2) °C) dinitrogen gas.[7] Somewhere between −135 and −157 °C the crystals undergo an irreversible, destructive phase transition. Cell constants at −133 °C were obtained as described elsewhere[8] by a least-squares refinement of 18 centered reflections in the range 30° < 2θ (Mo Kα_1) < 32°. The cell constants are a = 11.055 (3) Å, b = 11.457 (3) Å, c = 9.897 (2) Å, α = 112.46 (1)°, β = 96.43 (1)°, γ = 67.73 (1)°, V = 1071 Å^3.

The θ–2θ scan technique was used to collect intensity data in shells of 2θ. Stationary-counter, stationary-crystal background counts of 10 s were measured at the beginning and end of each scan. For reflections having $I < 3\sigma(I)$, the reflection was rescanned and each background recounted for 20 s. The results of the two scans and two backgrounds were then combined. Six strong reflections were remeasured every 100 reflections during the course of the data collection. Their intensities decreased from the initial

(1) For a recent review, see: Bishop, K. C., III *Chem. Rev.* **1976**, *76*, 461–486.
(2) Attig, T. G.; Ziegler, R. J.; Brock, C. P. *Inorg. Chem.* **1980**, *19*, 2315–2320.
(3) Binger, P.; Doyle, M. J.; McMeeking, J.; Kruger, C.; Tsay, Y.-H. *J. Organomet. Chem.* **1977**, *135*, 405–414.
(4) (a) Cutler, A.; Fish, R. W.; Giering, W. P.; Rosenblum, M. *J. Am. Chem. Soc.*, **1972**, *94*, 4354–4355. (b) Brown, J. M.; Mertis, K. *J. Chem. Soc., Perkin Trans. 2*, **1973**, 1993–2001. (c) Periasamy, M. P.; Walborsky, H. M. *J. Am. Chem. Soc.* **1975**, *97*, 5930–5931. (d) Nuzzo, R. G.; McCarthy, T. J.; Whitesides, G. M., *J. Am. Chem. Soc.* **1981**, *103*, 3404–3410.
(5) Phillips, R. L.; Puddephatt, R. J. *J. Chem. Soc., Dalton Trans.* **1978**, 1732–1735.
(6) The disk-oriented diffractometer control program is from: Lenhert, P. G. *J. Appl. Crystallogr.* **1975**, *8* 568–570.
(7) Huffman, J. C. Ph.D. Thesis, Indiana University, 1974.
(8) Corfield, P. W.; Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 197–204.

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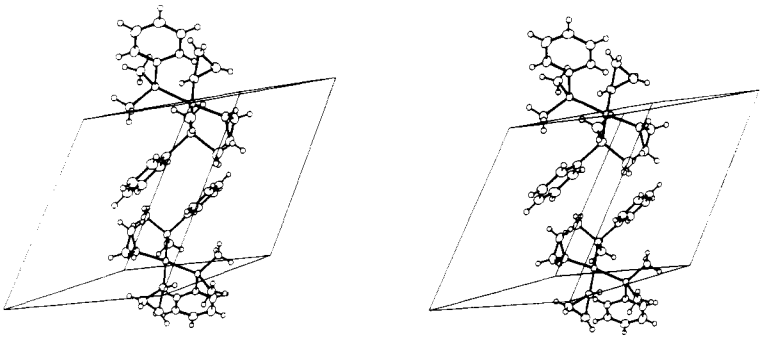


Figure 1. Stereoview of the unit cell of *cis*-Pt(CHCH$_2$CH$_2$)$_2$(PMe$_2$Ph)$_2$. Vibrational ellipsoids are drawn at the 50% probability level, except for hydrogen atoms which have been drawn artificially small.

measured intensities by an average of approximately 2%, and a correction for this decrease was made. Other parameters relevant to the data-collection process are listed in Table I.

Solution and refinement of the structure were carried out by procedures standard in this laboratory.[9] The position of the platinum atom was derived from an origin-removed sharpened Patterson map, on the assumption that the space group is the centrosymmetric one, C_i^1–$P\bar{1}$. This choice was confirmed ultimately by the successful refinement of the structure. Positions for the nonhydrogen atoms were obtained from Fourier and difference Fourier syntheses interspersed with structure-factor calculations and cycles of least-squares refinement. The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are, respectively, the observed and calculated structure amplitudes and where $w = 4F_o^2/\sigma^2(F_o^2)$. Atomic scattering factors were taken from the usual tabulation.[10] Initial refinements were on F and utilized only one-fourth of those reflections having $F_o^2 > 3\sigma(F_o^2)$. Refinement was continued until the conventional R index was 0.08. At this stage of refinement anomalous dispersion terms were included for the Pt and two P atoms;[10] in addition an absorption correction[9] was made. Atoms were now assigned an anisotropic model for their thermal motion. One cycle of least-squares refinement on one-third of those reflections having $F_o^2 > 3\sigma(F_o^2)$ yielded values for R and R_w on F of 0.044 and 0.049, respectively. On a resultant difference electron density map hydrogen atoms appeared with peak heights in the range 1.2 to 0.7 e/Å^3. These hydrogen atoms were placed in idealized locations (C–H 0.95 Å), each was given an isotropic thermal parameter B 1.0 Å^2 greater than that of its attached carbon atom, and all were held fixed during subsequent refinement. The function $\sum w(F_o^2 - F_c^2)^2$, where $w = 1/\sigma^2(F_o^2)$, was minimized in the final cycle of least-squares refinement, which involved 226 variables and 8749 observations (including those for which $F_o^2 < 0$). This refinement converged to values of R and R_w (on F_o^2) of 0.068 and 0.082, respectively, to an error in an observation of unit weight of 1.34 electrons^2, and for those reflections having $F_o^2 > 3\sigma(F_o^2)$ to values of the conventional R and R_w indices on $|F_o|$ of 0.039 and 0.040, respectively. The final difference electron density map is essentially featureless with the highest peak (4.2 eÅ^{-3}) near the Pt atom. This height may be compared with that of about 22 eÅ^{-3} for a typical C atom on an earlier electron density map. Analysis of R indices as a function of Miller indices, F_o^2, and setting angles revealed no unexpected trends. The final positional and thermal parameters of all atoms are listed in Table II. Table III lists values of $10|F_o|$ and $10|F_c|$;[11] a negative entry for $|F_o|$ indicates $F_o^2 < 0$.

Description of the Structure

The crystal structure consists of discrete molecules of *cis*-Pt(CHCH$_2$CH$_2$)$_2$[P(CH$_3$)$_2$(C$_6$H$_5$)]$_2$. The crystal packing is shown in Figure 1. The shortest intermolecular interaction is calculated to be 2.33 Å between two hydrogen atoms, H(1)C(5) and HC(11). The shortest Pt···H(cyclopropyl) distance is 2.46 Å [Pt–HC(4)], beyond the range of a metal–hydrogen interaction.

Figure 2 is a drawing of an individual molecule. Figure 3 is a drawing of the inner coordination sphere and displays some pertinent bond distances and angles. Bond angles and lengths are listed in Table IV. The coordination

Table I. Summary of Crystal Data and Intensity Collection for *cis*-Pt(CHCH$_2$CH$_2$)$_2$(P(CH$_3$)$_2$(C$_6$H$_5$))$_2$

compound	*cis*-Pt(CHCH$_2$CH$_2$)$_2$(PMe$_2$Ph)$_2$
formula	C$_{22}$H$_{32}$P$_2$Pt
formula wt	553.54 amu
a	11.055 (3) Å
b	11.457 (3) Å
c	9.897 (2) Å
α	112.46 (1)°
β	96.43 (1)°
γ	67.73 (1)°
V	1071 Å^3
Z	2
ρ_{calcd}	1.716 g/cm^3 (−133 °C)
ρ_{obsd}	1.62 (1) g/cm^3 (23 °C)
space group	C_i^1-$P\bar{1}$
crystal dimensions	0.28 × 0.45 × 0.23 mm along direct crystal axes
crystal shape	approximated as a 6-sided prism with major faces {100}, {10$\bar{3}$}, ($\bar{1}$5$\bar{2}$), ($\bar{2}$5$\bar{3}$)
crystal vol	0.0096 mm^3
temp	−133 °C[a]
radiation	graphite-monochromated Mo Kα, λ(Mo Kα_1) 0.7093 Å
linear absorption coefficient	67.6 cm^{-1}
transmission factors	0.197 – 0.449
receiving aperture	5.5 × 5.5 mm; 32 cm from crystal
take-off angle	3.1°
scan speed	2.0° in 2θ/min
2θ limits	3.5° < 2θ < 68.0°
scan range	1.1° below Kα_1 to 0.9° above Kα_2
background counts	10 s at each end of scan with rescan option[b]
unique data used in final refinement[c]	8749 $\pm h, \pm k, +l$
unique data, $F_o^2 > 3\sigma(F_o^2)$	7210
final number of variables	226
R (on F_o^2, all data)	0.068
R_w (on F_o^2, all data)	0.082
R (on F_o for $F_o^2 > 3\sigma(F_o^2)$)	0.039
error in observation of unit weight	1.34 electrons^2

[a] See ref 7. [b] See ref 6. [c] This includes reflections with $F_o^2 < 0$.

(9) See, for example: Waters, J. M.; Ibers, J. A. *Inorg. Chem.* **1977**, *16*, 3273–3277.

(10) Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2A and 2.3.1. For hydrogen atoms, see: Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175–3186.

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

Table II. Positional and Thermal Parameters for the Atoms of *cis*-Pt($\overline{CHCH_2CH_2}$)$_2$(P(CH$_3$)$_2$(C$_6$H$_5$))$_2$

ATOM	X[A]	Y	Z	B11[B] OR B,A^2	B22	B33	B12	B13	B23
PT	-0.244346(14)	-0.020781(15)	0.058603(16)	38.81(12)	39.00(13)	43.24(15)	-17.10(9)	8.61(9)	6.62(10)
P(1)	-0.386480(95)	0.15418(10)	0.25977(11)	41.95(81)	40.19(87)	51.5(11)	-15.27(69)	10.74(73)	10.12(80)
P(2)	-0.10739(10)	-0.17290(11)	0.15716(12)	41.74(84)	47.58(97)	60.3(12)	-14.68(73)	1.95(78)	11.52(88)
C(1)	-0.36162(42)	0.11943(42)	-0.03290(48)	63.6(39)	50.6(38)	66.2(49)	-25.0(31)	-4.3(35)	26.7(37)
C(4)	-0.11878(38)	-0.12022(43)	-0.12412(46)	48.6(32)	54.8(40)	62.9(46)	-21.8(29)	12.8(30)	6.2(36)
C(2)	-0.36054(47)	0.26292(45)	0.02034(55)	75.2(45)	52.4(40)	87.1(60)	-25.3(34)	3.2(41)	22.7(41)
C(3)	-0.31777(52)	0.16587(49)	-0.13438(53)	100.8(53)	69.6(46)	72.9(55)	-36.9(41)	13.9(43)	24.9(42)
C(5)	-0.09980(45)	-0.26327(48)	-0.23490(49)	64.1(43)	69.0(47)	69.2(48)	-22.5(37)	22.7(36)	2.0(39)
C(6)	-0.15565(44)	-0.14133(47)	-0.28064(46)	75.2(41)	76.6(45)	58.2(43)	-39.1(35)	13.2(33)	8.8(36)
C(7)	-0.42452(45)	0.01790(46)	0.36154(52)	64.5(43)	53.4(43)	72.7(56)	-22.2(35)	16.6(39)	17.7(41)
C(8)	-0.55135(35)	0.20778(41)	0.23004(49)	42.0(29)	59.1(38)	81.8(52)	-14.0(27)	5.8(31)	19.2(36)
C(9)	-0.33264(38)	0.22972(38)	0.40367(42)	46.8(34)	39.3(34)	55.3(40)	-12.9(28)	11.2(29)	7.5(31)
C(10)	-0.22429(39)	0.25361(42)	0.37944(46)	49.9(34)	48.7(39)	59.0(45)	-17.2(30)	7.1(31)	13.1(35)
C(11)	-0.18359(42)	0.34919(46)	0.48928(53)	56.5(38)	54.9(45)	72.6(58)	-24.5(34)	-1.5(38)	19.8(43)
C(12)	-0.25038(51)	0.42113(49)	0.62293(52)	79.6(53)	53.1(46)	76.9(51)	-30.9(41)	-4.9(41)	4.6(40)
C(13)	-0.35784(58)	0.39913(57)	0.64852(59)	100.8(61)	74.5(58)	83.3(62)	-42.0(50)	37.2(48)	-23.7(49)
C(14)	-0.39870(49)	0.30318(53)	0.54074(54)	76.9(48)	73.3(54)	78.4(55)	-39.9(42)	30.4(41)	-11.4(44)
C(15)	-0.03689(46)	-0.09244(48)	0.32520(50)	62.9(43)	66.9(47)	82.1(50)	-29.4(37)	-19.2(37)	23.4(40)
C(16)	0.03939(47)	-0.30643(52)	0.05362(57)	49.9(43)	74.9(52)	100.9(62)	-6.2(39)	10.9(41)	18.5(46)
C(17)	-0.17752(38)	-0.27373(39)	0.20341(44)	47.2(34)	37.2(34)	56.9(42)	-7.2(27)	1.5(30)	9.8(32)
C(18)	-0.26083(45)	-0.32864(44)	0.10592(50)	59.9(42)	52.6(41)	75.0(50)	-21.5(34)	-12.6(36)	21.4(37)
C(19)	-0.31208(47)	-0.40993(49)	0.13507(58)	62.9(45)	58.3(47)	111.2(65)	-28.4(38)	-10.3(43)	21.8(46)
C(20)	-0.28546(46)	-0.43469(43)	0.26364(52)	66.4(44)	48.2(39)	104.2(54)	-16.8(33)	14.3(39)	20.8(38)
C(21)	-0.20580(51)	-0.37858(49)	0.36255(53)	88.0(52)	64.0(47)	77.2(54)	-24.0(40)	10.3(42)	25.5(42)
C(22)	-0.15178(45)	-0.29980(43)	0.33202(48)	77.4(43)	62.6(39)	61.2(48)	-30.8(34)	-10.8(36)	20.7(36)
HC1	-0.444	0.109	-0.046	3.2					
H1C2	-0.438	0.339	0.042	3.8					
H2C2	-0.295	0.284	0.089	3.8					
H1C3	-0.227	0.127	-0.165	4.0					
H2C3	-0.370	0.182	-0.212	4.0					
HC4	-0.045	-0.096	-0.089	3.1					
H1C5	-0.014	-0.324	-0.270	3.7					
H2C5	-0.154	-0.306	-0.231	3.7					
H1C6	-0.245	-0.111	-0.304	3.5					
H2C6	-0.136	-0.129	-0.343	3.5					
H1C7	-0.502	0.079	0.422	3.7					
H2C7	-0.440	-0.059	0.295	3.7					
H3C7	-0.355	-0.007	0.421	3.7					
H1C8	-0.604	0.244	0.316	3.3					
H2C8	-0.548	0.278	0.205	3.3					
H3C8	-0.587	0.151	0.152	3.3					
HC10	-0.176	0.201	0.289	3.2					
HC11	-0.111	0.369	0.471	3.5					

ATOM	X	Y	Z	B,A^2
HC12	-0.222	0.488	0.594	4.0
HC13	-0.405	0.451	0.742	4.7
HC14	-0.475	0.289	0.557	4.2
H1C15	0.029	-0.159	0.353	3.7
H2C15	0.000	-0.036	0.309	3.7
H3C15	-0.103	-0.038	0.400	3.7
H1C16	0.016	-0.368	-0.029	4.2
H2C16	0.089	-0.267	0.024	4.2
H3C16	0.092	-0.353	0.115	4.2
HC18	-0.282	-0.311	0.019	3.6
HC19	-0.367	-0.448	0.067	4.0
HC20	-0.320	-0.490	0.281	3.7
HC21	-0.187	-0.395	0.449	4.0
HC22	-0.096	-0.263	0.401	3.4

[A] ESTIMATED STANDARD DEVIATIONS IN THE LEAST SIGNIFICANT FIGURE(S) ARE GIVEN IN PARENTHESES IN THIS AND ALL SUBSEQUENT TABLES. [B] THE FORM OF THE ANISOTROPIC THERMAL ELLIPSOID IS: EXP[-(B11H^2+B22K^2+B33L^2+2B12HK+2B13HL+2B23KL)]. THE QUANTITIES GIVEN IN THE TABLE ARE THE THERMAL COEFFICIENTS X 10^4.

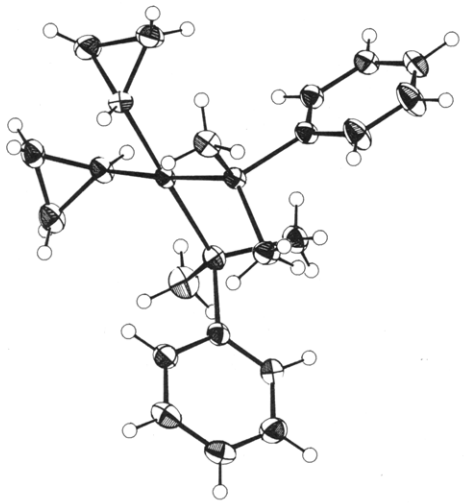


Figure 2. Drawing of an individual molecule of *cis*-Pt($\overline{CHCH_2CH_2}$)$_2$(PMe$_2$Ph)$_2$.

about the Pt atom is essentially planar. The average deviation of the Pt, two P, and two C atoms attached to the

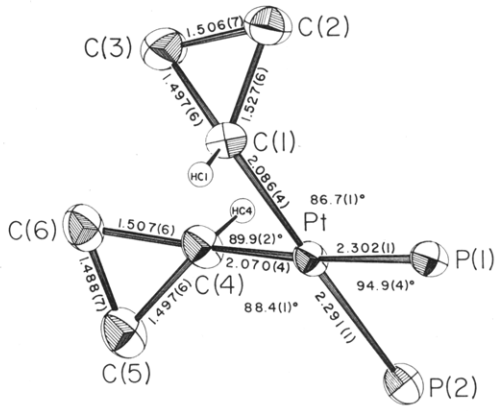


Figure 3. Coordination sphere of *cis*-Pt($\overline{CHCH_2CH_2}$)$_2$(PMe$_2$Ph)$_2$ with some bond distances and angles.

Pt center from the best-weighted least-squares plane is 0.033 Å. The maximum deviation is that of atom C(4) (0.083 Å). Angles around the Pt atom are distorted from 90°. The angle P(1)–Pt–C(1) also differs slightly from the angle P(2)–Pt–C(4), 86.69 (13)° and 88.45 (13)°, respectively. The Pt–P(1) and Pt–P(2) bond distances, 2.302 (1)

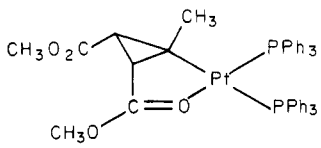
Table IV. Selected Distances (Å) and Angles (Deg) in *cis*-Pt(CHCH$_2$CH$_2$)$_2$(P(CH$_3$)$_2$(C$_6$H$_5$))$_2$

Bond Distances		
Pt-P(1)	2.302 (1)	2.296 (8)[a]
Pt-P(2)	2.291 (2)	
Pt-C(1)	2.086 (4)	2.078 (11)
Pt-C(4)	2.070 (4)	
C(1)-C(2)	1.527 (6)	1.506 (13)
C(2)-C(3)	1.506 (7)	
C(3)-C(1)	1.497 (6)	
C(4)-C(5)	1.508 (6)	
C(5)-C(6)	1.488 (7)	
C(6)-C(4)	1.507 (6)	
P(1)-C(7)	1.827 (5)	1.823 (5)
P(1)-C(8)	1.823 (4)	
P(1)-C(9)[b]	1.829 (4)	
P(2)-C(15)	1.818 (4)	
P(2)-C(16)	1.821 (5)	
P(2)-C(17)[b]	1.819 (4)	
C(9)-C(10)	1.389 (5)	1.387 (8)
C(10)-C(11)	1.392 (6)	
C(11)-C(12)	1.378 (7)	
C(12)-C(13)	1.372 (7)	
C(13)-C(14)	1.387 (7)	
C(14)-C(9)	1.402 (6)	
C(17)-C(18)	1.397 (6)	
C(18)-C(19)	1.383 (7)	
C(19)-C(20)	1.384 (7)	
C(20)-C(21)	1.379 (7)	
C(21)-C(22)	1.386 (6)	
C(22)-C(17)	1.391 (6)	
Bond Angles		
P(1)-Pt-P(2)	94.86 (4)	
C(1)-Pt-C(4)	89.91 (18)	
P(1)-Pt-C(1)	86.69 (13)	
P(1)-Pt-C(4)	175.89 (13)	
P(2)-Pt-C(1)	177.36 (12)	
P(2)-Pt-C(4)	88.45 (13)	
C(2)-C(1)-C(3)	59.73 (30)	60.00 (80)
C(1)-C(2)-C(3)	59.13 (29)	
C(1)-C(3)-C(2)	61.14 (30)	
C(5)-C(4)-C(6)	59.15 (30)	
C(4)-C(5)-C(6)	60.41 (30)	
C(4)-C(6)-C(5)	60.45 (30)	
Pt-P(1)-C(7)	119.68 (15)	
Pt-P(1)-C(8)	116.83 (15)	
Pt-P(1)-C(9)	113.38 (13)	
Pt-P(2)-C(15)	112.68 (16)	
Pt-P(2)-C(16)	119.55 (19)	
Pt-P(2)-C(17)	116.78 (13)	
C(7)-P(1)-C(8)	100.12 (21)	
C(8)-P(1)-C(9)	102.05 (18)	
C(7)-P(1)-C(9)	102.18 (20)	
C(15)-P(2)-C(16)	100.70 (22)	
C(16)-P(2)-C(17)	100.04 (22)	
C(15)-P(2)-C(17)	104.76 (21)	
C(14)-C(9)-C(10)	118.51 (36)	120.00 (98)
C(9)-C(10)-C(11)	120.26 (39)	
C(10)-C(11)-C(12)	120.38 (40)	
C(11)-C(12)-C(13)	120.11 (41)	
C(12)-C(13)-C(14)	120.17 (47)	
C(13)-C(14)-C(9)	120.55 (43)	
C(22)-C(17)-C(18)	117.86 (39)	
C(17)-C(18)-C(19)	120.62 (43)	
C(18)-C(19)-C(20)	120.68 (42)	
C(19)-C(20)-C(21)	119.34 (43)	
C(20)-C(21)-C(22)	120.10 (44)	
C(21)-C(22)-C(17)	121.37 (39)	

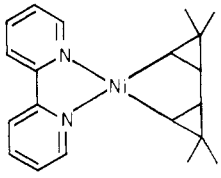
[a] The estimated standard deviation given in parentheses is the larger of that calculated for an individual observation on the assumption that the values averaged are from the same population or of that calculated from the inverse lease-squares matrix. [b] Atoms C(9)-C(14) and C(17)-C(22) constitute the phenyl rings.

and 2.291 (1) Å, respectively, differ slightly, the P atom attached through the longer bond being trans to the C atom attached through the shorter Pt-C bond [2.070 (4) vs. 2.086 (4) Å]. The differences in the Pt-P bond lengths may be caused by steric crowding. The Pt-C(1) and Pt-C(4) bond lengths are typical for Pt-C σ bonds. The C-C bond lengths within the cyclopropyl rings do not differ significantly. Similarly, the C-C-C bond angles are also equal. There does not appear to be any orbital overlap between the phosphine phenyl rings and the cyclopropyl rings.

The platinum σ-cyclopropyl complex [2,3-bis(methoxycarbonyl)-1-methylcyclopropyl]bis(triphenylphosphine)platinum(II) tetrafluoroborate (A), studied by Attig, Ziegler, and Brock,[2] contains a functionalized cyclopropyl ring. The oxygen atom of one ester group interacts with the platinum center, causing the ring to be distorted. Thus direct comparison of that structure with the present one is impossible. The structural characterization of the nickel σ-cyclopropyl complex α,α'-bipyridyl-5-nickela-3,3,7,7-tetramethyl-*trans*-tricyclo[4.1.0.0^{2,4}]heptane (B), carried



A



B

out by Binger et al.,[3] has revealed functionalized cyclopropyl rings constrained by a C-C bond between the rings. No distortion of the rings is apparent. The cyclopropyl rings are equilateral with an average C-C bond distance of 1.52 Å and an average C-C-C bond angle of 60°.

Upon comparison with Pt-P bond lengths (Table V) in other compounds,[12-20] we can place the σ-bound cyclopropyl group (Pt-P 2.302 (1) and 2.291 (1) Å) in the trans-influence series between metallocycloalkanes and alkyl groups, such as methyl and neopentyl groups.[21] A comparison of the $^1J(^{195}Pt-^{31}P)$ coupling constant (1770 Hz) with the coupling constants of other alkyl(bis(tertiary

(12) Manojlović-Muir, L.; Muir, K. W.; Solomun, T.; Meek, D. W.; Peterson, J. L. *J. Organomet. Chem.* **1978**, *146*, C26-C28.
(13) Crociani, B.; Nicolini, M.; Clemente, D. A.; Bandoli, G. *J. Organomet. Chem.* **1973**, *49*, 249-256.
(14) Gee, R. J. D.; Powell, H. M. *J. Chem. Soc. A* **1971**, 1956-1960.
(15) Bresciani-Pahor, N.; Plazzotta, M.; Randaccio, L.; Bruno, G.; Ricevuto, V.; Romeo, R.; Belluco, U. *Inorg. Chim. Acta* **1978**, *31*, 171-175.
(16) Howard, J.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1973**, 1840-1843.
(17) Ibers, J. A.; DiCosimo, R.; Whitesides, G. M. *Organometallics* **1982**, *1*, 13.
(18) Yarrow, D. J.; Ibers, J. A.; Lenarda, M.; Graziani, M. *J. Organomet. Chem.* **1974**, *70*, 133-145.
(19) Bielfeld, C. G.; Eick, H. A.; Grubbs, R. H. *Inorg. Chem.* **1973**, *12*, 2166-2170.
(20) Barker, G. K.; Green, M.; Howard, J. A. K.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1978**, 1839-1847.
(21) The electron-withdrawing groups, —C≡N and —CH=CH$_2$, present in the metallocyclic compounds, *cis*-Pt(C(CN)$_2$CH$_2$C(CN)$_2$)(PPh$_3$)$_2$ and *cis*-Pt(CH(CHCH$_2$)(CH$_2$)$_2$CH(CHCH$_2$))(PMe$_3$)$_2$, may bring about Pt-P bond lengths longer than those present in the unsubstituted platinum metallocycles.

Table V. Selected Pt-P Bond Distances in Other Complexes, *cis*-$PtXY(PR_3)_2$

X	Pt-P (trans to X), Å	Y	PR_3	ref
CH_3	2.327 (1)	$PMe_2(C_6F_5)$	$PMe_2(C_6F_5)$	12
C_6H_5	2.330 (20)	$PbPh_3$	PPh_3	13
C_6H_5	2.317 (5)	$GePh_3OH$	PEt_3	14
$CH_3C_6H_5$	2.320 (9)	Cl	PEt_3	15
C_6F_5	2.326 (7)	Cl	PEt_3	15
$CH(CF_3)_2$	2.310 (7)	F	PPh_3	16
CF_3	2.326 (1)	X	$PMe_2(C_6F_5)$	12
$CH_2C(CH_3)_3$	2.322 (1)	X	PEt_3	17
$CHCH_2CH_2$	2.302 (1), 2.291 (1)	X	PMe_2Ph	this work
$C(CN)_2CH_2C(CN)_2$	2.314 (2), 2.291 (2)		PPh_3	18
$CH_2C(CH_3)_2CH_2$	2.287 (1), 2.282 (2)		PEt_3	17
$CH_2(CH_2)_2CH_2$	2.279 (5), 2.285 (6)		PPh_3	19
$CH(CHCH_2)(CH_2)_2CH(CHCH_2)$	2.294 (2), 2.306 (2)		PMe_3	20

Table VI. Selected $^1J(^{195}Pt-^{31}P)$ Coupling Constants for Complexes *cis*-$PtXY(PR_3)_2$[a]

X	^1J(Pt-P(trans to X)), Hz	Y	^1J(Pt-P(trans to Y)), Hz	PR_3	ref
C_6H_5	1577	Cl	4138	PEt_3	22
C_6H_5	1705	X		PEt_3	22
2,4,6-$C_6H_2(CH_3)_3$	1603	Br	4234	PEt_3	22
$CH(CH_2)_3CH_2$	1616	X		PEt_3	4d
$CH_2C(CH_3)_3$	1638	X		PEt_3	23
$CH(CH_2)_2CH_2$	1647	X		PEt_3	4d
CH_3	1719	Cl	4179	PEt_3	22
CH_3	1856	X		PEt_3	22
CH_3	1865	$PMe_2(C_6F_5)$	2822	$PMe_2(C_6F_5)$	12
$CHCH_2CH_2$	1770	X		PMe_2Ph	this work
$CHCH_2CH_2$	1790	X		PEt_3	4d
$CH_2C(CH_3)_2CH_2$	1868			PEt_3	23
Cl	3454	$P(Bu\text{-}n)_3$	2270	$P(Bu\text{-}n)_3$	22

[a] No correction has been made to account for the different phosphine groups or different NMR solvents used.

phosphine))platinum(II) compounds[4d,12,22,23] (Table VI) supports this placement of the σ-bound cyclopropyl group in the trans-influence series, although more data are needed. Interpretation of these data indicates that the cyclopropyl group tends to weaken the bond trans to itself (i.e., lengthen the Pt-P bond) by an inductive effect. The ^1J(Pt-P) coupling constant depends mainly on the covalency and s character of the Pt-P bond, as determined by the inductive effect of the group trans to the phosphine.[24] The Cl^- ligand is considered to be low in the trans-influence series[25] and Pt-P bond lengths trans to the Cl^- ligand are shorter than the bond lengths we report here. For example, the Pt-P bond lengths reported for *cis*-$PtCl_2[PMe_2(C_6F_5)]_2$ are 2.231 (1) and 2.240 (1) Å and a ^1J(Pt-P) coupling constant of 3586 Hz is also reported.[12] The phenyl group is placed high in the trans-influence series, and this is reflected in the low ^1J(P-P) coupling constants measured[22] (1577 and 1705 Hz for Pt(II)-phenyl complexes) and the lengthening of the Pt-P bond in *cis*-$Pt(C_6H_5)(GePh_2OH)(PEt_3)_2$ to 2.317 (5) Å.[14] The ^1J(Pt-P) value of 1770 Hz for *cis*-$Pt(CHCH_2CH_2)_2(PMe_2Ph)_2$ reported here fits in nicely between that of 1638 Hz for *cis*-$Pt[CH_2C(CH_3)_3]_2(PEt_3)_2$ and a ^1J(Pt-P) of 1868 Hz for $Pt[CH_2C(CH_3)_2CH_2](PEt_3)_2$.[23]

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(22) Allen, F. H.; Pidcock, A. *J. Chem. Soc. A* **1968**, 2700–2704.
(23) Foley, P.; DiCosimo, R.; Whitesides, G. M. *J. Am. Chem. Soc.* **1980**, *102*, 6713–6725.
(24) Mason, R.; Meek, D. W. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 183–194.
(25) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335–422.

Registry No. *cis*-$Pt(CHCH_2CH_2)_2(PMe_2Ph)_2$, 64522-77-6; *cis*-$PtCl_2(PMe_2Ph)_2$, 15393-14-3.

Supplementary Material Available: Table III, listing of $10|F_o|$ vs. $10|F_c|$ values (30 pages). Ordering information is given on any current masthead page.