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CYCLOPROPENYLIDENE—TRANSITION METAL COMPLEXES: SYNTHESIS AND STRUCTURE OF *cis*-DICHLORO(TRI-n-BUTYLPHOSPHINE)(BIS(*N,N*-DIMETHYLAMINO)CYCLOPROPENYLIDENE)-PALLADIUM(II)

ROBERT D. WILSON *, YASUHIRO KAMITORI **, HISANOBU OGOSHI **, ZEN-ICHI YOSHIDA ** and JAMES A. IBERS *,*

Department of Chemistry, Northwestern University, Evanston, Illinois 60201 (U.S.A.) and Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Kyoto (Japan)

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Summary

The synthesis of *cis*-dichloro(tri-n-butylphosphine)(bis(*N,N*-dimethylamino)-cyclopropenylidene)palladium(II), *cis*-$PdCl_2[C(Me_2NC)_2](P\text{-}n\text{-}Bu_3)$, from the reaction of $[PdCl_2(C(Me_2NC)_2)]_2$ with P-n-Bu_3 is described. The first precise analysis of the structure of a cyclopropenylidene—transition metal complex has been carried out. The C_3-ring is bound through the unique carbon atom to the metal center with a Pd—C distance of 1.961(3) Å and is roughly perpendicular to the metal square plane. All C—C ring distances are equivalent within experimental error and average 1.383(2) Å. The dimethylamino groups are sp^2 hybridized at the nitrogen atoms and are coplanar with the carbocyclic fragment. The compound crystallizes in the monoclinic space group C_{2h}^5-$P2_1/c$ with four molecules in a cell of dimensions *a* 7.933(4), *b* 15.524(6), *c* 19.572(7) Å, β 101.05(2)°, *V* 2326 Å^3 (*T*—160°C). The final values of *R* and R_w for the 226 variables and 4383 significant observations are 0.036 and 0.042. Characteristic spectroscopic (IR and NMR) data for the compound are reported.

Introduction

Cyclopropenylidenemetal compounds are rare. We [1] have succeeded in preparing a series of cyclopropenylidene complexes in which the ring system is stabilized by substitution of dialkylamino groups on the carbon atoms away

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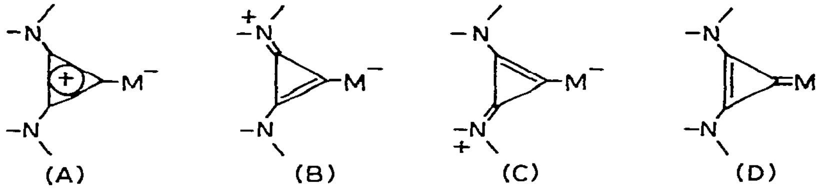
* Northwestern University.

** Kyoto University.

from the metal. A representative member of that series is $PdCl_2[C(Me_2NC)_2]$-$(P\text{-}n\text{-}Bu_3)$, obtained from the chloro-bridged dichloro(bis(dimethylamino)cyclopropenylidene)palladium dimer by nucleophilic cleavage with tri-n-butylphosphine. The dimeric product is first obtained by reaction of 1,2-bis(dimethylamino)-3-chlorocyclopropenium chloride with palladium black [1]. Based on infrared and ^{13}C NMR spectral data the compound was proposed to be the *cis* product and only weak conjugation of the amino substituents to the C_3 ring was inferred. The present X-ray crystallographic study of *cis*-$PdCl_2[C(Me_2NC)_2]$-$(P\text{-}n\text{-}Bu_3)$ was undertaken to provide definitive proof of the structural predictions based on spectroscopic evidence.

The following canonical forms may be written to represent the formal bonding in such a complex:



The only other reported structure known to us of a cyclopropenylidene—metal complex is that of $Cr(CO)_5[C(CPh)_2]$. That structural study, dating to 1969 [2], is not of sufficient accuracy to allow an assessment of the relative importance of the canonical forms A—D in such complexes. The present structural study, carried out at —160°C, is of considerably higher precision. The nature of the bonding as derived from the structural results and from spectroscopic measurements is described here.

Experimental

^{13}C NMR measurements were performed on a JEOL FX-60 spectrometer. The infrared spectra were recorded on a Hitachi Model G-3 spectrophotometer and ultraviolet spectra were taken in CH_2Cl_2 on a Hitachi EPS-3T spectrophotometer.

Synthesis of $[PdCl_2(C(Me_2NC)_2)]_2$ *(I)*. A mixture of 1,2-bis(dimethylamino)-3-chlorocyclopropenium chloride (1 mmol) and palladium black (1.2 mmol) in freshly distilled acetonitrile (20 ml) was refluxed for 16 h under an argon atmosphere. The reaction mixture was concentrated and then chromatographed on silica gel with methylene chloride/ether (1/1). Crystallization from methylene chloride/ether gave reddish orange crystals of $[PdCl_2(C(Me_2NC)_2)]_2$ in 44% yield: m.p. 210°C (dec.); IR (KBr): 2930, 1890, 1570, 1409, 1375, 1216 cm^{-1}; PMR ($CDCl_3$): δ 3.09, 3.32 ppm (s, CH_3); ^{13}C NMR ($CDCl_3$): δ 150.9 ($N—C_{ring}$), 99.9 ($Pd—C_{ring}$) 41.3, 42.2 ppm (br, CH_3); UV (CH_2Cl_2): $\lambda_{max}(\epsilon_{max})$ 366 nm (3080), 306 (sh, 1000); Anal. Found: C, 28.03; H, 4.28; Cl, 23.57; N, 9.26. $C_{14}H_{24}Cl_4N_4Pd_2$ calcd.: C, 27.89; H, 4.01; Cl, 23.52; N, 9.29%.

Synthesis of cis-$PdCl_2[C(Me_2NC)_2](P\text{-}n\text{-}Bu_3)$ *(II)*. A solution of I (0.5 mmol) in methylene chloride (20 ml) was cooled to —60°C. To this solution was added tri-n-butylphosphine (1.0 mmol) under vigorous stirring. The reaction mixture was allowed to warm to 25°C and stirred for an additional 2 h. The solvent was removed under reduced pressure and the residue was chromatographed on silica gel with methylene chloride/ether (3/1). Recrystallization from chloroform/ether afforded white crystals in 85% yield: m.p. 172°C; IR (KBr): 2960, 2935, 2875, 1903, 1557, 1419, 1409, 1378, 1211 cm^{-1}; PMR ($CDCl_3$): δ 3.24 (br, CH_3), 0.75—1.05 ppm (m, n-Bu); ^{13}C NMR ($CDCl_3$): δ 150.6 (N—C_{ring}), 125.0 (Pd—C_{ring}, ^{2}J(C—P) 6.0 Hz), 41.2 (br, CH_3), 26.4, 25.7, 24.7, 23.7, 13.6 ppm (n-Bu); UV (CH_2Cl_2): $\lambda_{max}(\epsilon_{max})$ 309 nm (2550). Anal. Found: C, 44.74; H, 7.68; Cl, 14.07; N, 5.62. $C_{19}H_{39}Cl_2N_2PPd$ calcd.: C, 45.30; H, 7.80; Cl, 14.07; N, 5.56%.

Data collection and structure analysis of cis-$PdCl_2[C(Me_2NC)_2](P\text{-}n\text{-}Bu_3)$. Clear, colorless, well-formed crystals of the air-stable compound were grown from acetone/hexane. Preliminary precession photographs revealed Laue symmetry $2/m$. The extinction conditions observed, $l = 2n + 1$ for $h0l$, and $k = 2n + 1$ for $0k0$, are consistent with the space group C_{2h}^5-$P2_1/c$. Least-squares refinement of the setting angles of nine reflections ($20° < 2\theta(\text{Mo-}K_\alpha) < 27°$) with the sample at 22°C and of thirteen ($19° < 2\theta(\text{Mo-}K_\alpha) < 31°$) at —160°C resulted in the unit cell parameters of Table 1. Acquisition of a low temperature

TABLE 1

CRYSTAL DATA, DATA COLLECTION PROCEDURES, AND REFINEMENT RESULTS FOR *cis*-$PdCl_2[C(Me_2NC)_2](P\text{-}n\text{-}Bu_3)$

Formula	$C_{19}H_{39}Cl_2N_2P_1Pd_1$
Formula weight	503.82 amu
Space group	C_{2h}^5-$P2_1/c$
Cell constants at —160°C [22°C]	
a	7.933(4) Å [8.126(3) Å]
b	15.524(6) Å [15.527(7) Å]
c	19.572(7) Å [19.864(8) Å]
β	101.05(2)° [101.43(2)°]
V	2336 Å^3 [2457 Å^3]
Z	4
ρ_c (room temperature)	1.367 g/cm^3
ρ_0 (room temperature)	1.36 g/cm^3
ρ_c (—160°C)	1.414 g/cm^3
Data collection temperature	—160 ± 1°C
Crystal shape	a regular parallelepiped of approx. edge dimensions 0.20 mm × 0.18 mm × 0.16 mm, bounded by the faces $\{100\}$, $\{011\}$
Crystal volume	0.0052 mm^3
Radiation	Mo-K_α (λ(Mo-K_{α_1}) 0.70930 Å), monochromatized from (002) face of mosaic graphite
Linear absorption coefficient	10.7 cm^{-1}
Transmission factors	0.837—0.868
Detector aperture	3.0 mm by 3.0 mm
Take-off angle	2.5°
Scan speed	2.0° in 2θ/min
2θ limits	3.0—55.0°
Background counts	10 sec at each end of scan with rescan option
Scan range	0.8° below K_{α_1} to 0.8° above K_{α_2}
Data collected	$h \geqslant 0$, $k \geqslant 0$, $\pm l$
p	0.04
Unique data, $F_0^2 > 3\sigma(F_0^2)$	4383
Final number of variables	226
Error in observation of unit weight, electrons	1.12 e^-
R	0.036
R_w	0.042

diffraction data set proceeded generally using methods described previously [3] except that a low temperature device closely based on the design of Huffman [4] was employed.

Details of data collection are given in Table 1. Although the crystal maintained its chemical integrity throughout data collection, as judged by stability of the standard reflections, the originally transparent colorless crystal changed to a clear yellow-brown within the 2 first days in the X-ray beam.

The structure was successfully solved by conventional Patterson and Fourier methods using procedures and computer programs described previously [3]. The positions of the atoms of the inner coordination sphere, Pd, Cl(1), Cl(2), P, and C(1), were obtained from a three-dimensional origin-removed Patterson function. The positions of all nonhydrogen atoms were found on a subsequent difference Fourier map. In the penultimate difference Fourier map the positions of all methyl and methylene hydrogen atoms were apparent. This outcome was undoubtedly aided by the diminished thermal motion at —160°C. These positions were idealized (C—H 0.95 Å). The fixed contributions from these hydrogen atoms were included in the final cycle of least-squares refinement. All nonhydrogen atoms were refined anisotropically. The final refinement converged to values of R and R_w of 0.036 and 0.042, respectively, and to an error in an observation of unit weight of 1.12 electrons for the 226 variables and 4383 observations. The largest residual peak is of height 0.9(1) $e^-/\text{Å}^3$ on the final difference Fourier map. No unusual trends were indicated from an analysis of $\Sigma w(|F_0| - |F_c|)^2$ as a function of $|F_0|$, setting angles, and Miller indices.

Final positional and thermal parameters are tabulated in Table 2. Root-mean-

TABLE 2

POSITION AND THERMAL PARAMETERS FOR *cis*-$PdCl_2[C((CH_3)_2NC)_2](P\text{-}n\text{-}Bu_3)$

ATOM	X[A]	Y	Z	B11[B]	B22	B33	B12	B13	B23
PD	0.040566(31)	0.162941(16)	0.312631(12)	52.66(41)	13.13(11)	6.93(7)	-0.41(17)	5.50(11)	0.31(7)
CL(1)	0.26739(11)	0.059703(58)	0.331861(47)	93.8(15)	22.49(37)	16.87(24)	14.57(60)	14.33(48)	3.42(24)
CL(2)	0.13956(11)	0.225201(56)	0.217562(44)	95.4(15)	22.35(36)	11.94(22)	-0.28(59)	16.16(46)	2.69(22)
P	-0.16981(11)	0.261147(55)	0.295213(42)	68.0(14)	16.80(34)	10.10(21)	2.22(55)	5.12(42)	0.92(21)
C(1)	-0.05572(41)	0.11869(21)	0.38796(16)	59.7(52)	15.2(13)	7.77(80)	7.2(21)	1.5(16)	1.03(81)
C(2)	-0.15752(43)	0.04686(23)	0.40836(17)	58.9(55)	14.8(14)	10.85(88)	8.0(23)	10.2(18)	2.24(91)
C(3)	-0.08540(41)	0.10963(22)	0.45516(17)	50.3(50)	19.2(15)	9.02(84)	9.1(22)	5.4(17)	3.38(88)
N(1)	-0.25369(36)	-0.02186(18)	0.39157(15)	74.9(46)	17.4(12)	12.22(83)	-5.6(19)	9.2(16)	-0.35(80)
N(2)	-0.06124(38)	0.14623(19)	0.51738(14)	89.0(52)	17.8(14)	7.92(74)	3.0(21)	7.1(16)	0.52(78)
C(4)	-0.35570(49)	-0.05921(24)	0.43846(21)	79.7(67)	22.7(15)	20.6(12)	-4.0(26)	14.6(22)	3.8(11)
C(5)	-0.29621(52)	-0.04803(25)	0.31894(21)	98.6(74)	19.5(17)	16.3(11)	-7.7(29)	7.4(23)	-4.8(11)
C(6)	0.02093(52)	0.23063(26)	0.52675(20)	114.4(73)	26.9(18)	10.8(11)	-10.4(38)	1.1(23)	-2.3(11)
C(7)	-0.14832(49)	0.11622(26)	0.57201(19)	109.6(65)	28.3(18)	9.50(97)	3.8(28)	12.9(21)	1.0(11)
C(11)	-0.31895(45)	0.24829(25)	0.21074(18)	73.0(57)	23.7(17)	9.93(88)	0.9(26)	-0.3(18)	1.8(10)
C(12)	-0.40613(46)	0.16262(22)	0.20062(18)	78.3(61)	19.4(14)	13.29(92)	3.1(24)	6.9(19)	-0.68(93)
C(13)	-0.52417(46)	0.15825(24)	0.12983(20)	70.2(58)	26.1(16)	14.7(10)	1.6(25)	2.2(19)	-3.3(10)
C(14)	-0.61980(57)	0.07382(30)	0.11752(24)	131.1(81)	35.1(22)	27.4(14)	-15.5(35)	4.4(27)	-12.2(14)
C(21)	-0.09216(45)	0.37155(22)	0.29333(17)	81.7(62)	17.0(13)	10.41(90)	2.0(23)	6.4(19)	-0.21(88)
C(22)	-0.01511(46)	0.40984(23)	0.36459(19)	68.4(63)	15.8(14)	12.7(10)	1.8(24)	3.5(20)	0.18(95)
C(23)	0.07075(48)	0.49653(23)	0.35718(19)	80.6(67)	16.1(14)	15.9(11)	-1.8(25)	11.0(21)	1.10(96)
C(24)	0.13679(53)	0.54103(25)	0.42600(21)	120.4(73)	21.0(17)	17.0(12)	-12.3(29)	13.7(23)	-3.9(12)
C(31)	-0.30987(45)	0.26170(23)	0.35736(19)	79.7(59)	19.6(15)	10.8(10)	5.4(24)	2.4(19)	0.19(97)
C(32)	-0.45796(47)	0.32594(25)	0.34514(21)	77.0(60)	25.2(17)	20.8(11)	6.8(27)	6.1(21)	2.4(11)
C(33)	-0.52294(52)	0.34382(27)	0.41422(23)	101.8(69)	32.2(19)	28.0(14)	10.7(38)	5.1(25)	-5.8(13)
C(34)	-0.58565(57)	0.26514(30)	0.44433(24)	128.3(78)	42.4(22)	24.3(14)	-13.6(35)	21.9(27)	-10.0(14)

[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.

TABLE 3

ROOT-MEAN-SQUARE AMPLITUDE OF VIBRATION (Å) FOR *cis*-$PdCl_2[C(Me_2NC)_2](P\text{-}n\text{-}Bu_3)$

Atom	Minimum	Intermediate	Maximum
Pd	0.1097(6)	0.1268(5)	0.1204(5)
Cl(1)	0.138(2)	0.161(1)	0.202(1)
Cl(2)	0.121(2)	0.167(1)	0.183(1)
P	0.134(2)	0.141(1)	0.149(2)
C(1)	0.111(7)	0.130(6)	0.152(6)
C(2)	0.113(7)	0.126(7)	0.162(6)
C(3)	0.111(7)	0.123(6)	0.167(5)
N(1)	0.133(6)	0.147(5)	0.163(5)
N(2)	0.119(6)	0.146(6)	0.167(5)
C(4)	0.137(7)	0.170(6)	0.203(6)
C(5)	0.136(7)	0.175(6)	0.189(6)
C(6)	0.135(7)	0.175(7)	0.203(6)
C(7)	0.123(7)	0.179(6)	0.192(6)
C(11)	0.127(7)	0.160(6)	0.173(6)
C(12)	0.146(6)	0.158(6)	0.161(6)
C(13)	0.144(6)	0.159(6)	0.190(5)
C(14)	0.155(7)	0.216(6)	0.257(6)
C(21)	0.138(6)	0.144(6)	0.159(6)
C(22)	0.137(6)	0.145(7)	0.158(6)
C(23)	0.137(6)	0.153(7)	0.176(6)
C(24)	0.145(7)	0.170(6)	0.207(6)
C(31)	0.138(6)	0.149(6)	0.168(6)
C(32)	0.147(7)	0.179(6)	0.201(5)
C(33)	0.165(6)	0.195(6)	0.243(6)
C(34)	0.175(7)	0.189(6)	0.259(6)

square amplitudes of vibration are given in Table 3. A table representing the values of 10 $|F_0|$ and 10 $|F_c|$ for the reflections used in the refinement is available *.

Results and discussion

As illustrated by the packing diagram of Fig. 1, the crystal structure of *cis*-$PdCl_2[C(Me_2NC)_2](P\text{-}n\text{-}Bu_3)$ consists of discrete molecular units with no unusual intermolecular constants. Intramolecular distances and angles are given in Table 4.

The molecular structure of the complex, along with the numbering scheme used, is shown in Fig. 2. Fig. 3 displays the carbocyclic backbone and coordination sphere about the metal atom along with some important distances and angles. The overall geometry of the complex is as anticipated [1], with a square-planar geometry about the metal, *cis*-chloro ligands, and an unopened cyclopropenylidene ring bonded only through the unique carbon atom C(1). Also, as has been observed in similar platinum-group metal compounds containing

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* The Table of structure amplitudes has been deposited as NAPS Document No. 03417 (30 pages). Order from NAPS ℅ Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10017. Remit in advance, in U.S. funds only $ 7.50 for photocopies or $ 3.00 for microfiche. Outside the U.S. and Canada add postage of $ 3.00 for photocopy and $ 1.00 for microfiche.

TABLE 4

SELECTED DISTANCES (Å) AND ANGLES (deg) IN *cis*-$PdCl_2[C(Me_2NC)_2](P\text{-}n\text{-}Bu_3)$

Bond distance (Å)

Pd—Cl(1)	2.385(1)	P—C(11)	1.821(4)
Pd—Cl(2)	2.361(1)	P—C(21)	1.824(4)
Pd—P	2.238(1)	P—C(31)	1.798(4)
Pd—C(1)	1.961(3)	C(11)—C(12)	1.523(5)
C(1)—C(2)	1.385(5)	C(21)—C(22)	1.531(5)
C(1)—C(3)	1.380(4)	C(31)—C(32)	1.525(5)
C(2)—C(3)	1.384(5)	C(12)—C(13)	1.518(5)
C(2)—N(1)	1.316(4)	C(22)—C(23)	1.528(5)
C(3)—N(2)	1.324(4)	C(32)—C(33)	1.561(6)
N(1)—C(4)	1.455(5)	C(13)—C(14)	1.510(6)
N(1)—C(5)	1.455(5)	C(23)—C(24)	1.516(5)
N(2)—C(6)	1.459(5)	C(33)—C(34)	1.483(6)
N(2)—C(7)	1.456(4)		

Bond angle (deg)

Cl(1)—Pd—Cl(2)	92.55(4)	C(2)—N(1)—C(5)	119.0(3)
Cl(1)—Pd—P	179.25(3)	C(3)—N(2)—C(6)	118.9(3)
Cl(1)—Pd—C(1)	89.7(1)	C(4)—N(1)—C(5)	116.9(3)
Cl(2)—Pd—P	87.25(4)	C(6)—N(2)—C(7)	117.3(3)
Cl(2)—Pd—C(1)	176.5(1)	Pd—P—C(11)	112.0(1)
P—Pd—C(1)	90.6(1)	Pd—P—C(21)	113.5(1)
Pd—C(1)—C(2)	147.7(3)	Pd—P—C(31)	116.1(1)
Pd—C(1)—C(3)	152.1(3)	C(11)—P—C(21)	103.6(2)
C(2)—C(1)—C(3)	60.1(2)	C(11)—P—C(31)	105.2(2)
C(1)—C(2)—C(3)	59.8(2)	C(21)—P—C(31)	105.3(2)
C(1)—C(3)—C(2)	60.1(2)	P—C(11)—C(12)	114.6(3)
C(1)—C(2)—N(1)	148.3(3)	P—C(21)—C(22)	115.1(2)
C(1)—C(3)—N(2)	148.3(3)	P—C(31)—C(32)	117.0(3)
N(1)—C(2)—C(3)	151.9(3)	C(11)—C(12)—C(13)	111.2(3)
N(2)—C(3)—C(2)	151.6(3)	C(21)—C(22)—C(23)	111.2(3)
C(2)—N(1)—C(4)	122.1(3)	C(31)—C(32)—C(33)	110.7(3)
C(3)—N(2)—C(7)	122.2(3)	C(12)—C(13)—C(14)	112.8(3)
C(22)—C(23)—C(24)	113.6(3)		
C(32)—C(33)—C(34)	112.9(3)		

Torsion angle (deg)

C(1)—Pd—P—C(11)	—113.7(2)
C(1)—Pd—P—C(21)	129.4(2)
C(1)—Pd—P—C(31)	7.1(2)

Average deviation (Å) from least-squares plane: $Ax + By + Cz = D$

	Dev.	*A*	*B*	*C*	*D*
Plane 1 (Pd, Cl(1), Cl(2), P, C(1))	0.025	3.657	9.793	10.261	4.953
Plane 2 (C(1), C(2), C(3), N(1), N(2))	0.006	6.049	—8.972	2.727	—0.267
Plane 3 (C(1), C(2), C(3), N(1), N(2), (C(4), C(5), C(6), C(7))	0.076	5.922	—9.164	3.099	—0.154
Plane 4 (P, C(11), C(12), C(13), C(14))	0.008	6.648	—6.164	—10.333	—5.788
Plane 5 (P, C(21), C(22), C(23), C(24))	0.047	7.324	—5.887	—4.671	—4.163

Interplanar angle (deg)

Plane 1—Plane 2	80.3

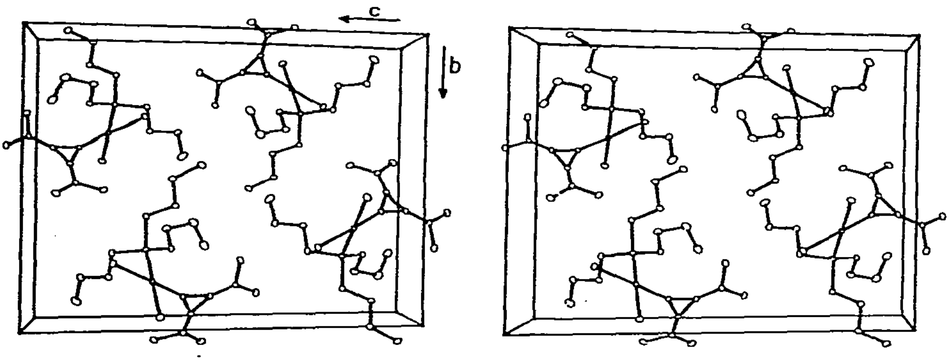


Fig. 1. A stereo view of the unit cell of *cis*-$PdCl_2[C(Me_2NC)_2](P\text{-}n\text{-}Bu_3)$. Twenty percent probability ellipsoids are plotted.

a cyclic carbenoid ligand [5], the plane of the 3-membered ring is nearly perpendicular to the metal square-plane; the dihedral angle between the C(1), C(2), C(3), N(1), N(2) best plane and the Pd, Cl(1), Cl(2), P, C(1) best plane is 80.3°.

In the structure there is a high degree of equivalence in the metric parameters of the chemically equivalent bonds in the cyclopropenylidene ligands. This result derives certainly in part from the low temperature of data collection.

Coordination about the palladium atom. The metal geometry is square-planar with the average deviation of the plane-defining atoms [Pd, Cl(1), Cl(2), P, and C(1)] from their best plane of only 0.025 Å. This plane is additionally a rough molecular mirror plane. However, in contrast to the related molecule *cis*-$PtCl_2(\overline{-CNPh(CH_2)_2NPh})(PEt_3)$ [5], in which the analogous plane is exact and coincides with a crystallographic mirror plane, in the present compound the symmetry is broken by the "slipped" carbenoid ligand (vide infra) and one

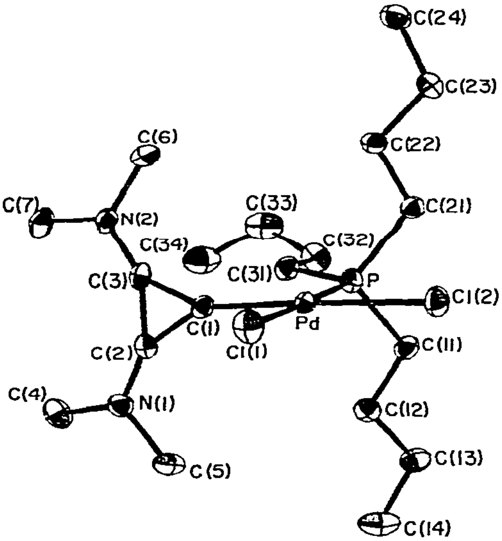


Fig. 2. Molecular structure of *cis*-$PdCl_2[C(Me_2NC)_2](P\text{-}n\text{-}Bu_3)$. The thermal ellipsoids correspond to 50% probability enclosures. Hydrogen atoms have been omitted.

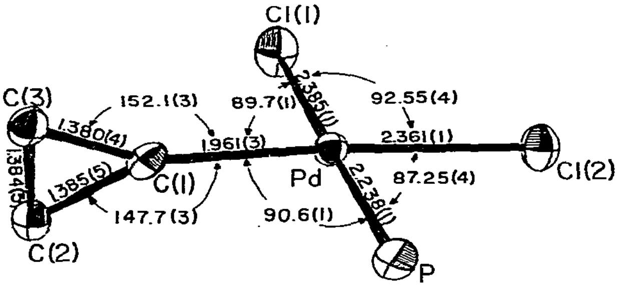


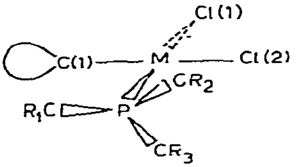
Fig. 3. A perspective view of the inner coordination sphere of *cis*-$PdCl_2[C(Me_2NC)_2](P\text{-}n\text{-}Bu_3)$ with important distances and angles. The thermal ellipsoids are drawn at the 50% probability level.

butyl group (C(31) through C(34)) of the phosphine ligand. Deviations from right angles in the PdL_4 plane are generally small, the chloro ligands forming the largest *cis* angle (92.55(4)°) presumably reflecting the dominance of their mutual electron cloud repulsions over the many other factors involved.

The Pd—Cl bond lengths are 2.385(1) and 2.361(1) Å for Cl(1) and Cl(2), respectively. These values fall within the range of 2.24 to 2.45 Å observed for other Pd^{II}—Cl bonds [6]. The two Pd—Cl bonds differ significantly by 0.024(2) Å. In view of the experimentally identical set of Pt—Cl distances in *cis*-$PtCl_2$-$(\overbrace{—CNPh(CH_2)_2N}Ph)(PEt_3)$ (see Table 5) the *trans* influence ascribed to that compound [5] should apply equally well here. The Pd—P bond distance of 2.238(1) Å is not unusual. In palladium(II) compounds having chloro ligands *trans* to P, Pd—P bond lengths have been observed between 2.219(4) [7] and 2.260(2) Å [8]. Two of the three butyl groups of the $P(C_4H_9)_3$ ligand are in a planar zig-zag configuration in which the steric repulsion between hydrogen

TABLE 5

COMPARATIVE BOND DISTANCES AND ANGLES IN RELATED METAL—CARBOCYCLIC CARBENOID COMPLEXES

 Cl(1) C(1) M Cl(2) CR_2 R_1C P CR_3	*cis*-$PdCl_2[C(Me_2NC)_2]$-$(P\text{-}n\text{-}Bu_3)$[a]	*cis*-$PtCl_2(\overbrace{-C-NPh-(CH_2)_2-N}Ph)$-$(PEt_3)$[b]
M—P	2.238(1) Å	2.234(3) Å
M—Cl(1)	2.385(1) Å	2.381(3) Å
M—Cl(2)	2.361(1) Å	2.362(3) Å
P—CR(2,3) [c]	1.824(4) and 1.821(4) Å	1.823(13) Å
P—CR(1)	1.798(4) Å	1.796(16) Å
M—P—CR(2,3)	112.0(1) and 113.5(1)°	112.0(4)°
M—P—CR(1)	116.1(1)°	116.3(5)°
C(1)—M—P—CR(1)	7.1(2)°	0° [d]

[a] This work. [b] Ref. 5. [c] Refer to sketch in upper left of table for notation. [d] Constrained by crystallographic mirror symmetry.

atoms on adjacent carbon atoms is minimized [9]. The third alkyl chain, which is eclipsed with respect to the Pd—C(1) bond when viewed down the Pd—P vector, takes on a helical conformation. The P—C bonds and angles also reflect the disparate nature of this third butyl group. These P—C distances and M—P—C angles are close to analogous values observed in *cis*-$PtCl_2(\overline{—CNPh(CH_2)_2N}Ph)(PEt_3)$ [5] in which no mention was made of this disparity, possibly owing to the higher estimated standard deviations for that structure (Table 5).

The 1.961(3) Å Pd—C(1) bond distance is somewhat shorter than an ordinary Pd—C single bond length, even when account is taken of hybridization. For example the Pd—C(sp^2) distances of the metal—σ-vinyl bonds in *cis*-bis[1,2-bis-(trifluoromethyl)-3-acetyl-4-oxopent-1-enyl-*O,C*]palladium(II) average 1.993 Å [10].

The bis(dimethylamino)cyclopropenylidene ligand. An approximate molecular mirror plane is defined by the metal and four bound atoms with the largest deviation from this symmetry found in the "slipped" carbocyclic ligand. Atom C(2) is 0.880 Å from the plane 1 (Table 4) while atom C(3) is only 0.479 Å out of the plane on the opposite side. No unusual nonbonding contacts which would account for this tilt were seen between the two distal methyl groups of the bis(dimethylamino)cyclopropenylidene ligand. Furthermore, if steric crowding were the cause of the displacement, then a significant asymmetry in the bond angles C(1)—C(2)—N(1) [148.3(3)°] and C(1)—C(3)—N(2) [148.3(3)°] would have been expected. This tilt is reminiscent of that of 5.9° of the π-bound ethylene group from the normal to the platinum square plane in Zeise's salt [11]. No such symmetry was reported for the 2,3-diphenylcyclopropenylidene ligand in $Cr(CO)_5[C(CPh)_2]$ [2]. The N atoms are sp^2 hybridized, are coplanar with the C_3 ring, and are bonded at a 1.320(4) Å distance from the ring carbon atoms. This distance is markedly shorter than a C—N single bond distance of 1.474(5) Å observed in CH_3NH_2 [12].

The infrared spectrum of *cis*-$PdCl_2[C(Me_2NC)_2](P\text{-n-}Bu_3)$ (II) shows two strong characteristic bands at 1903 and 1557 cm^{-1} These we assign to the ring deformation of the C_3 core and to the stretching vibration of the C_{ring}—N bond, respectively. When the alkyl group of the peripheral amino substituent is changed from CH_3 to $CH(CH_3)_2$, the latter absorption band shifts to 1487 cm^{-1}. Presumably nonbonded interactions between the bulky isopropyl groups destroy the C_3N_2 planarity and lead to a decrease in the double-bond character of the C_{ring}—N bond. The corresponding band positions in the dimer I occur at 1887 and 1567 cm^{-1}.

Figure 4 displays the ^{13}C NMR spectrum of the NMe_2 groups in II. The two methyl signals occur at δ 39.9 and 42.3 ppm at −28°C. These two signals arise because hindered rotation about the C_{ring}—N bond places the methyl groups in different magnetic environments. The two signals broaden at elevated temperature and coalesce at 35.5°C. From these NMR measurements the free energy of activation to rotation about the C_{ring}—N bond was determined to be 15.4 kcal/mole, using the formulation of Stewart and Siddall [13]. This energy for the analogous complex in which isopropyl groups are substituted for methyl groups is less than 8.4 kcal/mole. These results are consistent with the trend from the infrared spectra. The ^{13}C chemical shifts of the C_3 ring in these two compounds are virtually identical, and this suggests little structural change of the Pd—C_3 portion.

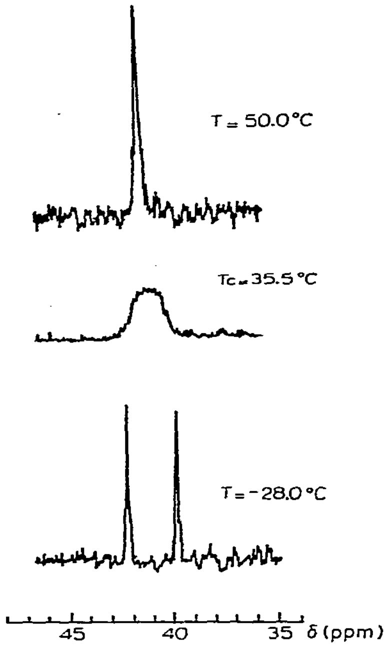


Fig. 4. ^{13}C chemical shift data for the NMe_2 groups of *cis*-$PdCl_2[C(Me_2NC)_2](P\text{-}n\text{-}Bu_3)$ in CD_2Cl_2.

Judging from the high symmetry of the C_3 ring, with its unimodal bond distribution, the π-back donation from the Pd atom would appear to be comparable with that of the amino groups. Participation of the metal d_{xy} orbital in this back bonding would explain the orientation of the metal-square plane at a dihedral angle of 80.3° with the least-squares plane of the ligand. On the other hand, this dihedral angle could be a manifestation of steric factors. There are considerable differences in the average C—C and C_{ring}—N bond distances between the aromatic tris(dimethylamino)cyclopropenium cation (C—C 1.363(7), C—N 1.333(7) Å) [14] and those here (C—C 1.383(2), C—N 1.320(4) Å). The N—Me distances are the same in the two structures.

Preferred canonical forms. No simple description of the present structure in terms of canonical forms A—D appears possible. Form D (a carbene) is favored by the short Pd—C bond and the orientation of the C_3 ring relative to the metal—ligand plane. It is also favored by the relatively low values of the C_{ring}—N stretching vibrational frequencies. But the C—N bond lengths, which are short, and the planarity of the C_3N_2 portion of the molecule favor the forms B, C. The equivalence of the distances within the C_3 ring suggests contributions to the bonding of forms B, C, and D, since form A is not compatible with the other observations.

Acknowledgments

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