ORGANOMETALLICS

Volume 2, Number 11, November 1983

Functionally Substituted Platinacyclobutanes. Conformation of $PtCl_2(CH_2C(CH_3)(CH_2OH)CH_2)(C_5H_5N)_2$ and Related Complexes in Solution and in the Solid State

J. Thomas Burton and Richard J. Puddephatt*

Department of Chemistry, The University of Western Ontario, London, Ontario, Canada N6A 5B7

Nancy L. Jones and James A. Ibers*

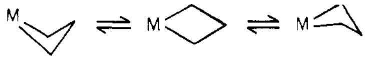
Department of Chemistry, Northwestern University, Evanston, Illinois, 60201

Received April 29, 1983

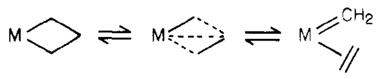
The platinacyclobutane complexes $PtCl_2(CH_2CR^1R^2CH_2)(C_5H_5N)_2$ (R^1 = H, R^2 = CH_2OH; R^1 = H, R^2 = CHMeOH; R^1 = H, R^2 = CMe_2OH; R^1 = Me, R^2 = CH_2OH) were synthesized from $[PtCl_2(C_2H_4)]_2$, the cyclopropane derivative, and pyridine. The lanthanide shift reagent $Eu(fod)_3$ was used to simplify the ^1H NMR spectra. An attempt has been made to study the conformation of the metallacyclobutane ring in solution on the basis of these NMR spectra. A single-crystal X-ray diffraction study of $PtCl_2(CH_2C(CH_3)(CH_2OH)CH_2)(C_5H_5N)_2$ was carried out. The compound crystallizes in the orthorhombic space group D_{2h}^{15}—*Pbca* with eight molecules in a cell of dimensions a = 19.596 (7) Å, b = 13.893 (5) Å, c = 13.108 (5) Å, and V = 3569 Å^3 (t = −151 °C). The final conventional and weighted agreement indices on F_o^2 are R = 0.056 and R_w = 0.086. The metallacyclobutane is puckered by 1.0° in the solid state and can be compared with a puckering of ~27° determined from solution studies on a series of related platinacycles. This difference may be of relevance to olefin metathesis reaction mechanisms.

The puckering of metallacyclobutanes has been discussed in detail as part of the mechanistic basis of selectivity of transition-metal complexes as catalysts for alkene metathesis.[1] Although metallacycles have been proposed as intermediates in alkene metathesis, it was only recently[2] that the titanacyclobutanes $Ti(C_5H_5)_2(CH_2CHRCH_2)$, R = t-Bu or Ph, and $Ti(C_5H_5)_2(CH_2CMe_2CH_2)$ were isolated from a well-defined metathesis system and structurally characterized. We assume that stable platinacyclobutanes, the subject of this paper, have structural features similar to those metallacyclobutanes involved in olefin metathesis. Platinacyclobutanes are much less strained than cyclobutane (≤5 kcal mol^{-1} in Pt(II) derivatives, ~12 kcal mol^{-1} in Pt(IV) derivatives, and 26 kcal mol^{-1} in cyclobutane).[3] Both ring puckering in solution and lack of appreciable ring strain may contribute to the importance of metallacycles as intermediates in transition-metal-catalyzed reactions.

Since there is a very low activation energy toward puckering of the metallacyclobutane ring (eq 1), the pucker angle found in an X-ray structure determination may depend on steric effects or crystal packing forces.[2,4-7] Thus, the degree of puckering of a metallacyclobutane ring in the solid state and in solution may differ. Moreover, for some electron configurations, but not for the 18-electron platinum(IV) complexes, there is the possibility of nonclassical structures (eq 2), intermediate between metallacyclobutanes and metal–carbene–alkene complexes.[8]



(1)



(2)

---

[1] For reviews see: Leconte, M.; Basset, J. M. *Ann. N.Y. Acad. Sci.* **1980**, *383*, 165–187. Calderon, N.; Lawrence, J. P.; Ofstead, E. A. *Adv. Organomet. Chem.* **1979**, *17*, 449–492. Grubbs, R. H. *Prog. Inorg. Chem.* **1979**, *24*, 1–50.

[2] Lee, J. B.; Gajda, G. J.; Schaefer, W. P.; Howard, T. R.; Ikariya, T.; Straus, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1981**, *103*, 7358–7361.

[3] Moore, S. S.; DiCosimo, R.; Sowinski, A. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1981**, *103*, 948–949.

[4] Rajaram, J.; Ibers, J. A. *J. Am. Chem. Soc.* **1978**, *100*, 829–838.

[5] Puddephatt, R. J. *Coord. Chem. Rev.* **1980**, *33*, 149–194.

[6] Rappe, A. K.; Goddard, W. A., III *J. Am. Chem. Soc.* **1982**, *104*, 297–299.

[7] Klingler, R. J.; Huffman, J. C.; Kochi, J. K. *J. Am. Chem. Soc.* **1982**, *104*, 2147–2157.

0276-7333/83/2302-1487$01.50/0

The complex $\overline{Pt(CH_2CH_2CH_2})(2,2'\text{-bipyridyl})$ shows a planar platinacyclobutane ring in the solid state, but in solution the large coupling constant $^3J(PtH)$ to the β-CH_2 protons was interpreted in terms of a very facile puckering (eq 1) and short Pt···H contacts.[7] However, it is surprising that there have been no previous attempts to estimate equilibrium pucker angles of metallacyclobutanes in solution, since standard NMR techniques have yielded pucker angles in cyclobutane derivatives that are consistent with those found by other methods.[9-11] Provided that there is negligible contribution to the bonding in metallacyclobutanes from nonclassical structures (eq 2), there is no reason why the same technique cannot be used to estimate the pucker angles in metallacyclobutanes, provided that the necessary coupling constants can be determined from the ^1H NMR spectra.

In this article the syntheses of some platinacyclobutane derivatives with hydroxymethyl substituents are reported. The presence of the donor hydroxyl group and the use of a lanthanide shift reagent aid analysis of the otherwise complex ^1H NMR spectra. From the vicinal $^3J(HH)$ coupling constants and an equation derived by Karplus[12] it is possible to estimate the conformation of the metallacyclobutane ring in solution. An X-ray structural study of $\overline{PtCl_2(CH_2C(CH_3)(CH_2OH)CH_2})(C_5H_5N)_2$ provides complementary data on the conformation in the solid state. Our results suggest that the puckering of the platinacyclobutane ring differs between the solid and solution states.

Experimental Section

The ^1H and ^{13}C NMR spectra were recorded with a Varian XL100 spectrometer. Lanthanide shift studies were carried out by adding portions of a weighed sample of $Eu(fod)_3$ shift reagent (fod = 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dione) to a solution of a known weight of the platinacyclobutane in $CDCl_3$ solution. Molar ratios were calculated from each spectrum by comparison of the integration for the *tert*-butyl group of $Eu(fod)_3$ and the integration of an appropriate signal corresponding to the platinacyclobutane. Plots of δ (ppm) vs. $Eu(fod)_3$/substrate (where $Eu(fod)_3/\text{substrate} < 0.9$) are shown in Figure 1.[13]

Zeise's dimer $[PtCl_2(C_2H_4)]_2$ was prepared by a literature method.[14] Most cyclopropanes were commercial samples, but 2-cyclopropyl-2-propanol was prepared by reaction of cyclopropyl methyl ketone with methyl Grignard reagent[15] and 1-methyl-1-(hydroxymethyl)cyclopropane was prepared directly from the corresponding carboxylic acid by reduction with $LiAlH_4$.[16] For $\overline{CH_2CH_2C}(CH_3)(CH_2OH)$: $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 70.4 (CH_2OH), 20.6 (CH_3), 17.9 (CCH_3), 10.8 (CH_2CH_2).

Synthesis of Platinacyclobutanes. To a solution of $[PtCl_2(C_2H_4)]_2$ (0.15 g, 0.26 mmol) in dry, redistilled tetrahydrofuran (5 mL) was added the cyclopropane derivative (0.25 g, ~2.5 mmol). The mixture was allowed to stir for 1 day at room temperature in the dark. Then the solution was filtered to remove insoluble impurities and was evaporated to dryness. The dry pale yellow residue was suspended in dichloromethane (5 mL) and cooled in ice, and pyridine (~3 drops) was added until a clear solution was obtained. The solvent was evaporated and the residue washed with pentane and then recrystallized from dichloromethane–pentane at 0 °C. Complexes prepared in this way were the following: $\overline{PtCl_2(CH_2CH(CH_2OH)CH_2})(C_5H_5N)_2$, I: mp 93–95 °C dec. Anal. Calcd for $C_{14}H_{18}Cl_2N_2OPt$: C, 33.9; H, 3.7; N, 5.6. Found: C, 32.3; H, 3.6; N, 5.1. $\overline{PtCl_2(CH_2CH(CHMeOH)CH_2})(C_5H_5N)_2$, II: mp 120–127 °C dec. Anal. Calcd for $C_{15}H_{20}Cl_2N_2OPt$: C, 35.3; H, 3.9; N, 5.5. Found: C, 34.1; H, 3.5; N, 5.7. $\overline{PtCl_2(CH_2CH(CMe_2OH)CH_2})(C_5H_5N)_2$, III: mp 119–120 °C. Anal. Calcd for $C_{16}H_{22}Cl_2N_2OPt$: C, 36.6; H, 4.2; N, 5.3. Found: C, 36.4; H, 4.3; N, 5.2. $\overline{PtCl_2(CH_2CMe(CH_2OH)CH_2})(C_5H_5N)_2$, IV: mp 116–118 °C dec. Anal. Calcd for $C_{15}H_{20}Cl_2N_2OPt$: C, 35.3; H, 3.9; N, 5.5. Found: C, 35.2; H, 3.9; N, 5.4.

Crystallographic Study of $\overline{PtCl_2(CH_2C(CH_3)(CH_2OH)CH_2})(C_5H_5N)_2$, IV. Colorless crystals suitable for diffraction were grown from dichloromethane–pentane at 0 °C. Systematic extinctions ($0kl$, $k = 2n + 1$; $h0l$, $l = 2n + 1$; $hk0$, $h = 2n + 1$) characteristic of space group D_{2h}^{15}—$Pbca$ of the orthorhombic system were observed on X-ray photographs taken at room temperature from a crystal mounted in air. The absences observed at −151 °C on a Picker diffractometer are consistent with the room-temperature results. The density, 1.77 (2) g/cm^3, measured at room temperature by flotation of the crystals in aqueous $ZnCl_2$, is consistent with the density of 1.899 g/cm^3 calculated for eight molecules of $\overline{PtCl_2(CH_2C(CH_3)(CH_2OH)CH_2})(C_5H_5N)_2$ in the low-temperature cell.

A crystal, described by faces {210}, $(0\bar{1}6)$, and $(01\bar{6})$, cut from a larger crystal was mounted directly in a stream of cold dinitrogen gas[17] on a four-circle, computer-controlled Picker FACS-1 diffractometer.[18] Cell constants at −151 °C were obtained as described elsewhere[19] by a least-squares refinement of 25 centered reflections in the range $24° < 2\theta(\text{Mo K}\alpha_1) < 31°$. The cell constants are a = 19.596 (7) Å, b = 13.893 (5) Å, c = 13.108 (5) Å, and V = 3569 Å^3.

Data collection and reduction were carried out as described previously.[20] A total of 4550 unique reflections was collected in the range $3.5° \leq 2\theta(\text{Mo K}\alpha_1) \leq 57.0°$. Six strong reflections were remeasured every 100 reflections during the course of the data collection. Their intensities decreased from the initial measured intensities by an average of approximately 15% and the decrease varied from 5 to 25%. An approximate average correction for this decrease was made. Table I presents other parameters relevant to the data collection process.

Solution and refinement of the structure were carried out by standard procedures.[20] The position of the platinum atom was deduced from a sharpened, origin-removed Patterson synthesis. Full-matrix least-squares refinements and Fourier and difference Fourier syntheses were used to locate the positions for the remaining non-hydrogen atoms. The function minimized initially 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.[21] Anomalous dispersion terms for the Pt and two Cl atoms were included in F_c.[21,22] Isotropic refinement was continued until the conventional R index was 0.10. An absorption correction was applied, and the non-hydrogen atoms were allowed to vibrate anisotropically. An ensuing difference electron density map revealed most of the hydrogen atom positions. All hydrogen atom positions, except that of the hydroxy hydrogen, were

---

[8] Eisenstein, O.; Hoffmann, R.; Rossi, A. R. *J. Am. Chem. Soc.* **1981**, *103*, 5582–5584. McKinney, R. J.; Tulip, T. H.; Thorn, D. L.; Coolbaugh, T. S.; Tebbe, F. N. *Ibid.* **1981**, *103*, 5584–5586.

[9] Bothner-By, A. A. *Adv. Magn. Reson.* **1965**, *1*, 195–316.

[10] Wiberg, K. B.; Barth, D. E. *J. Am. Chem. Soc.* **1969**, *91*, 5124–5130.

[11] Abraham, R. J.; Cooper, M. A.; Indyk, H.; Siverns, T. M.; Whittaker, D. *Org. Magn. Reson.* **1973**, *5*, 373–377.

[12] Karplus, M. *J. Am. Chem. Soc.* **1963**, *85*, 2870–2871. The approximation $J = A + B\cos\theta + C\cos 2\theta$ was used, with coefficients A, B, and C from ref 9.

[13] See paragraph at end of paper regarding supplementary material.

[14] Chatt, J.; Searle, M. L. *Inorg. Synth.* **1957**, *5*, 210–215.

[15] Traas, P. C.; Boelans, H.; Takken, H. J. *Recl. Trav. Chim. Pays-Bas* **1976**, *95*, 57–66.

[16] Roberts, J. D.; Mazur, R. H. *J. Am. Chem. Soc.* **1951**, *73*, 2509–2520.

[17] Huffman, J. C. Ph.D. Thesis, Indiana University, 1974.

[18] The disk-oriented diffractometer control program is from: Lenhert, P. G. *J. Appl. Crystallogr.* **1975**, *8*, 568–570.

[19] Corfield, P. W.; Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 197–204.

[20] Jameson, G. B.; Ibers, J. A. *J. Am. Chem. Soc.* **1980**, *102*, 2823–2831. Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 204–210.

[21] 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.

[22] Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781–782.

Table I. Summary of Crystal Data and Intensity Collection for $\overline{PtCl_2(CH_2C(CH_3)(CH_2OH)CH_2})(C_5H_5N)_2$

compd	$\overline{PtCl_2(CH_2C(CH_3)(CH_2OH)CH_2})(C_5H_5N)_2$
formula	$C_{15}H_{20}Cl_2N_2OPt$
fw, amu	510.34
a, Å	19.596 (7)
b, Å	13.893 (5)
c, Å	13.108 (5)
V, Å^3	3569
Z	8
ρ_{calcd}, g/cm^3	1.899 (−151 °C)
ρ_{obsd}, g/cm^3	1.77 (2) (23 °C)
space group	D_{2h}^{15}–$Pbca$
cryst dimens, mm	0.19 × 0.26 × 0.80 along direct crystal axes
cryst shape	6-sided prism with major faces $\{\overline{2}10\}$, $(0\overline{1}6)$, $(01\overline{6})$
cryst vol, mm^3	0.018
t, °C	−151[a]
radiatn	graphite-monochromated Mo Kα, λ(Mo Kα_1) = 0.7093 Å
linear abs coeff, cm^{-1}	82.3
transmissn factors	0.272–0.409
receiving aperture	4.5 × 6.5 mm; 32 cm from crystal
takeoff angle, deg	3.3
scan speed, deg/min	2.0 in 2θ
2θ limits	3.5° ⩽ 2θ ⩽ 57.0°
scan range	1.0° below Kα_1 to 1.35° above Kα_2
background counts	10 s at each end of scan with rescan option[b]
unique data used in final refinement	4550, $+h,+k,+l$
unique data, $F_o^2 > 3\sigma(F_o^2)$	2962
final no. of variables	190
R (on F_o^2, all data)[c]	0.056
R_w (on F_o^2, all data)	0.086
R (on F_o for $F_o^2 > 3\sigma(F_o^2)$)	0.035
error in observn of unit weight	1.32 electrons^2

[a] See ref 17. [b] See ref 18. [c] This includes reflections with $F_o^2 < 0$.

Table II. Positional Parameters[a] for the Non-Hydrogen Atoms of $\overline{PtCl_2(CH_2C(CH_3)(CH_2OH)CH_2})(C_5H_5N)_2$

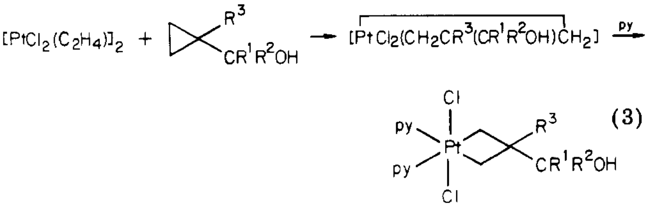
ATOM	X	Y	Z
PT	0.385642(13)	0.156614(15)	0.260867(16)
CL(1)	0.437354(95)	0.25472(12)	0.14146(12)
CL(2)	0.33670(10)	0.05924(12)	0.38440(13)
O	0.29023(34)	0.46354(42)	0.29995(65)
N(1)	0.48656(25)	0.12654(34)	0.32849(36)
N(2)	0.39922(29)	0.03017(38)	0.15906(39)
C(1)	0.29171(35)	0.20192(45)	0.21342(63)
C(2)	0.28686(35)	0.28697(51)	0.28871(66)
C(3)	0.35681(37)	0.27501(44)	0.34202(55)
C(4)	0.28285(39)	0.38081(45)	0.22727(59)
C(5)	0.22719(39)	0.27948(65)	0.36453(73)
C(6)	0.54074(31)	0.11088(41)	0.26977(47)
C(7)	0.60478(41)	0.09301(52)	0.30905(67)
C(8)	0.61301(44)	0.09314(57)	0.41380(66)
C(9)	0.55741(39)	0.11039(50)	0.47410(52)
C(10)	0.49573(38)	0.12642(44)	0.42997(47)
C(11)	0.42936(40)	−0.05164(47)	0.19097(63)
C(12)	0.43729(48)	−0.12984(49)	0.12814(57)
C(13)	0.41385(48)	−0.12383(49)	0.02838(54)
C(14)	0.38479(54)	−0.04143(59)	−0.00385(59)
C(15)	0.37796(46)	0.03454(56)	0.06214(47)

[a] Estimated standard deviation in the least significant figure(s) is given in parentheses in this and all subsequent tables.

idealized (C–H = 0.95 Å). The isotropic thermal parameter of a hydrogen atom was assigned to be 1.0 Å^2 greater than that of the carbon atom to which it is attached. These hydrogen atoms were included as fixed contributions in the final anisotropic refinements. The final cycle of least-squares refinement involved minimization of the function $\sum w(F_o^2 - F_c^2)^2$, where $w = 1/\sigma^2(F_o^2)$, and involved 190 variables and 4550 observations (including those for which $F_o^2 < 0$). This refinement converged to final agreement indices (on F_o^2) of R = 0.056 and R_w = 0.086. The error in an observation of unit weight is 1.32 e^2. The largest peaks in the final difference electron density map are approximately 1.65 (2) e Å^{-3} and are associated with the Pt position. The conventional R index on F_o for those 2962 reflections having $F_o^2 > 3\sigma(F_o^2)$ is 0.035. Analysis of $\sum w(F_o^2 - F_c^2)^2$ as a function of Miller indices, F_o^2, and setting angles revealed no unexpected trends. The final positional parameters of all non-hydrogen atoms are listed in Table II. Table III[13] presents thermal parameters for the non-hydrogen atoms, and Table IV[13] presents positional and thermal parameters for all hydrogen atoms. Table V lists values of $10|F_o|$ and $10|F_c|$;[13] a negative entry for $|F_o|$ indicates $F_o^2 < 0$. The root-mean-square amplitudes of vibration are presented in Table VI.[13]

Results

Syntheses. All known platinum(IV) metallacyclobutanes have either unsubstituted $\overline{PtCH_2CH_2CH_2}$ rings or have simple alkyl or aryl substituents on the ring. Our early attempts to prepare derivatives with amine functionality failed since reaction of Zeise's dimer with either 2-cyclopropylpyridine or (cyclopropylmethyl)dimethylamine gave only the simple amine complexes *trans*-[$PtCl_2(C_2H_4)L$]. However, we now find that oxygen functionality can be obtained as indicated by the high-yield syntheses of eq 3.



(3)

I, $R^1 = R^2 = R^3 = H$
II, $R^1 = R^3 = H$, $R^2 = Me$
III, $R^3 = H$, $R^1 = R^2 = Me$
IV, $R^1 = R^2 = H$, $R^3 = Me$

The complexes are most easily characterized by elemental analysis and by the $^{13}C\{^1H\}$ NMR spectra (Table VII). Compared with the free cyclopropane derivatives the directly bound carbon atoms (C^1, C^3) shift upfield by 11–14 ppm while the β-carbon atom (C^2) shifts downfield by 30–33 ppm in the platinacyclobutanes. The complexation shift of the β-carbon atom is similar to the difference in the ^{13}C chemical shifts of cyclopropane (−2.9 ppm) and cyclobutane (23.3 ppm),[23] as expected for the platinacy-

---

[23] Levy, G. C.; Lichter, R. L.; Nelson, G. L. "Carbon-13 NMR Spectroscopy"; Wiley-Interscience: New York, 1980.

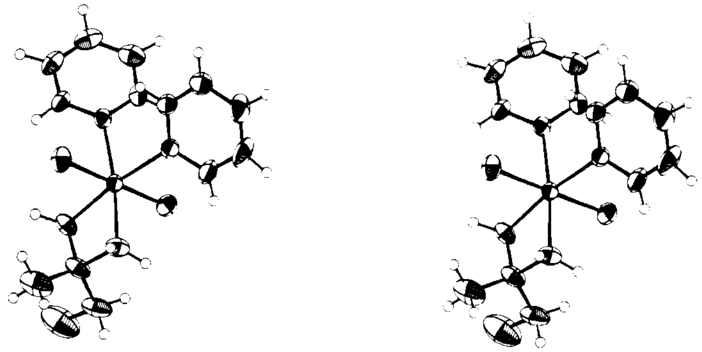
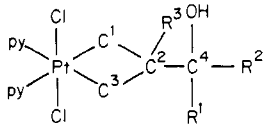


Figure 3. A stereoview of an individual molecule of $\overline{PtCl_2(CH_2C(CH_3)(CH_2OH)CH_2})(C_5H_5N)_2$. The 50% probability ellipsoids are shown, except for hydrogen atoms which have been drawn artifically small.

Table VII. ^{13}C **NMR Data for Platinacyclobutane Complexes**



	complex			
	I	II	III	IV
$R^1R^2R^3$	HHH	HMeH	MeMeH	HHMe
C^4 (ppm)	67.1	71.6	71.9	70.9
Δ^a (ppm)	−0.4	−0.8	+2.4	+0.5
$^3J(PtC^4)$, Hz	49.0	45.2	46.2	28.4
C^2 (ppm)	45.6	51.1	54.1	48.7
Δ^a (ppm)	+32.6	+32.6	+31.7	+30.8
$^2J(PtC^2)$, Hz	99.1	96.2	94.1	92.2
C^1 (ppm)	−11.3	−11.1[b]	−10.5	−3.0
Δ^a (ppm)	−14.0	−13.3[b]	−11.4	−13.9
$^1J(PtC^1)$, Hz	350.1	351.0[b]	352.3	355.7
C^3 (ppm)	−11.3	−10.5[b]	−10.5	−3.0
Δ^a (ppm)	−14.0	−13.7[b]	−11.4	−13.9
$^1J(PtC^3)$, Hz	350.1	349.2[b]	352.3	355.7
R^1 (ppm)		19.5	26.1	
Δ^a (ppm)		−3.1	−2.5	
R^2 (ppm)			26.1	
Δ^a (ppm)			−2.5	
R^3 (ppm)				24.7 (^3J = 26.6 Hz)
Δ^a (ppm)				+4.0

[a] Δ = complexation shift: [(chem shift)$_{\text{complex}}$ − (chem shift)$_{\text{free cyclopropane}}$]. [b] For the monomethylated derivative assignments based on C^1 and C^3 may be reversed.

clobutane formulations.[5] The coupling constants $^1J(PtC)$ and $^2J(PtC)$ between atoms of the PtC_3 ring are typical of complexes of this type and so provide useful characterization.[5] Even after 2 days there was no indication of the presence of a minor isomer, with the substituent(s) on the α-carbon atom, as found with methyl- or aryl-substituted platinacyclobutanes.[24] The substituents are presumably too bulky to give detectable amounts of such isomers, which would have been seen in abundance of 5% or more in the ^{13}C NMR spectra. For complex II, the presence of the chiral center C^4 (Table VII) leads to nonequivalence of the α-carbon atoms C^1 and C^3 so that separate resonances are observed.

Description of the Structure of $\overline{PtCl_2(CH_2C(CH_3)(CH_2OH)CH_2})(C_5H_5N)_2$, IV. The crystal structure of $\overline{PtCl_2(CH_2C(CH_3)(CH_2OH)CH_2})(C_5H_5N)_2$ consists of the packing of eight molecules in the unit cell, as shown in Figure 2.[13] The closest intermolecular interaction is calculated to be 2.27 Å between atoms O and HC(7). A stereoview of the molecule is depicted in Figure 3. Each molecule consists of a Pt center bound to two chloro ligands, two pyridine ligands, and the metallacyclic fragment. Pertinent bond lengths and angles are shown in Figure 4. Additional distances and angles are listed in Table VIII. Table IX presents results on least-squares planes.

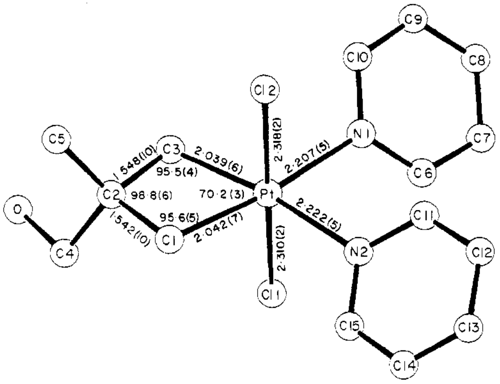


Figure 4. Drawing of $\overline{PtCl_2(CH_2C(CH_3)(CH_2OH)CH_2})(C_5H_5N)_2$. The hydrogen atoms have been omitted for clarity, and the atoms have been drawn as spheres with arbitrary radii.

The coordination geometry about the Pt atom is essentially octahedral. The average deviation from the best-weighted least-squares planes are as follows: Pt–C(1)–C(3)–N(1)–N(2), 0.002 Å; Pt–Cl(1)–Cl(2)–N(1)–C(1) 0.09 Å; Pt–Cl(1)–Cl(2)–N(2)–C(3), 0.07 Å. The Cl(1)–Pt–Cl(2) angle is 178.09 (6)°. Angles around the Pt atom in the equatorial plane are distorted from 90°: N(1)–Pt–N(2) = 89.10 (19)°, N(1)–Pt–C(3) = 101.04 (24)°, N(2)–Pt–C(1) = 99.71 (24)°, and C(1)–Pt–C(3) = 70.15 (28)°. The Pt–Cl(1) and Pt–Cl(2) bond distances, 2.310 (2) and 2.318 (2) Å, do not differ significantly nor do the Pt–N(1) and Pt–N(2) bond distances of 2.207 (5) and 2.222 (5) Å. The pyridine rings display typical bond lengths and angles.

The platinacyclobutane moiety is essentially planar, the largest deviation being that of atom C(2) (0.008 (8) Å); the dihedral angle between the C(1)–Pt–C(3) and C(1)–C(2)–C(3) planes (or pucker angle) is 1.0°. The Pt–C(1) and Pt–C(3) bond distances are 2.042 (7) and 2.039 (6) Å, respectively, and are typical for Pt–C bonds. The C–C bond lengths within the metallacycle (C(1)–C(2) = 1.542 (10) Å and C(2)–C(3) = 1.548 (10) Å) are normal and do not differ from the exocyclic C–C bond lengths (C(2)–C(4) = 1.534 (10) Å, C(2)–C(5) = 1.538 (10) Å).

Results from previous structural investigations on other platinacyclobutane complexes are summarized in Table X.[4,7,25-30] The first five compounds are six-coordinate

---

[24] Al-Essa, R. J.; Puddephatt, R. J.; Perkins, D. C. L.; Rendle, M. C.; Tipper, C. F. H. *J. Chem. Soc., Dalton Trans.* **1981**, 1738–1745.

[25] Gillard, R. D.; Keeton, M.; Mason, R.; Pilbrow, M. F.; Russell, D. R. *J. Organomet. Chem.* **1971**, *33*, 247–258.

Table VIII. Selected Distances (Å) and Angles (deg) in $PtCl_2(CH_2C(CH_3)(CH_2OH)CH_2)(C_5H_5N)_2$

Bond Distances					
Pt-Cl(1)	2.310 (2)	Pt-C(2)	2.676 (7)	C(8)-C(9)	1.367 (11)
Pt-Cl(2)	2.318 (2)	C(1)-C(2)	1.542 (10)	C(9)-C(10)	1.358 (10)
av	2.314 (6)[a]	C(2)-C(3)	1.548 (10)	C(10)-N(1)	1.342 (8)
Pt-N(1)	2.207 (5)	C(2)-C(4)	1.534 (10)	N(2)-C(11)	1.347 (8)
Pt-N(2)	2.222 (5)	C(2)-C(5)	1.538 (10)	C(11)-C(12)	1.372 (9)
av	2.214 (11)	C(4)-O	1.500 (10)	C(12)-C(13)	1.388 (10)
Pt-C(1)	2.042 (7)	N(1)-C(6)[b]	1.329 (8)	C(13)-C(14)	1.347 (10)
Pt-C(3)	2.039 (6)	C(6)-C(7)	1.379 (10)	C(14)-C(15)	1.371 (11)
av	2.040 (6)	C(7)-C(8)	1.383 (11)	C(15)-N(2)	1.338 (8)

Bond Angles					
Cl(1)-Pt-Cl(2)	178.09 (6)	N(1)-Pt-N(2)	89.10 (19)	Pt-N(2)-C(15)	119.79 (47)
Cl(1)-Pt-C(1)	90.41 (22)	Pt-C(1)-C(2)	95.55 (46)	C(6)-N(1)-C(10)	117.82 (57)
Cl(1)-Pt-C(3)	89.94 (20)	Pt-C(3)-C(2)	95.54 (44)	N(1)-C(6)-C(7)	122.70 (64)
Cl(1)-Pt-N(1)	89.47 (13)	C(1)-C(2)-C(3)	98.75 (55)	C(6)-C(7)-C(8)	118.47 (79)
Cl(1)-Pt-N(2)	90.40 (15)	C(1)-C(2)-C(4)	108.55 (68)	C(7)-C(8)-C(9)	118.78 (80)
Cl(2)-Pt-C(1)	91.13 (22)	C(1)-C(2)-C(5)	114.10 (63)	C(8)-C(9)-C(10)	119.45 (69)
Cl(2)-Pt-C(3)	89.52 (21)	C(5)-C(2)-C(3)	111.98 (69)	C(9)-C(10)-N(1)	122.77 (69)
Cl(2)-Pt-N(1)	88.84 (14)	C(3)-C(2)-C(4)	111.94 (56)	C(11)-N(2)-C(15)	117.99 (63)
Cl(2)-Pt-N(2)	90.44 (15)	C(5)-C(2)-C(4)	110.96 (62)	N(2)-C(11)-C(12)	122.09 (74)
C(1)-Pt-C(3)	70.15 (28)	C(2)-C(4)-O	108.23 (66)	C(11)-C(12)-C(13)	118.70 (73)
C(1)-Pt-N(1)	171.19 (23)	Pt-N(1)-C(6)	120.94 (40)	C(12)-C(13)-C(14)	119.11 (71)
C(1)-Pt-N(2)	99.71 (24)	Pt-N(1)-C(10)	121.21 (47)	C(13)-C(14)-C(15)	119.85 (72)
C(3)-Pt-N(1)	101.04 (24)	Pt-N(2)-C(11)	122.20 (47)	C(14)-C(15)-N(2)	122.24 (74)
C(3)-Pt-N(2)	169.86 (24)				

[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 least-squares matrix. [b] Atoms C(6)-C(10) off N(1) and C(11)-C(15) off N(2) constitute the pyridine carbon atoms.

Table IX. Best Weighted Least Squares Planes in $PtCl_2(CH_2C(CH_3)(CH_2OH)CH_2)(C_5H_5N)_2$

	coeff ($Ax + By + Cz - D = 0$[a])			
plane no.	A	B	C	D
1	8.450	8.159	-8.979	2.194
2	8.413	8.224	-8.942	2.200
3	-8.469	-8.192	8.943	-2.216
4	-8.221	-8.357	8.911	-2.184
5	8.417	8.183	-8.973	2.187

	deviations (Å) from planes				
	1	2	3	4	5
Pt	0.0000 (2)	0.0000 (2)	0		0.0000 (2)
N(1)	0.000 (5)				-0.003 (5)
N(2)	-0.003 (5)				-0.007 (5)
C(1)	0.002 (8)	0.007 (8)	0	0	0.006 (8)
C(2)		-0.008 (8)		0	-0.014 (8)
C(3)	-0.006 (7)	0.006 (7)	0	0	-0.002 (7)

Dihedral Angles (deg) between Planes

plane	angle	plane	angle
1-2	0.3	3-4	1.0
1-3	179.8	3-5	179.8
1-4	178.9	4-5	179.0
1-5	0.1		
2-3	179.8		
2-4	179.2		
2-5	0.2		

[a] The plane is in crystal coordinates as defined by: Hamilton, W. C. *Acta Crystallogr.* **1961**, *14*, 185-189.

octahedral Pt(IV) complexes with trans apical Cl ligands while the last six are four-coordinate square-planar Pt(II) complexes. The Pt–C bond lengths are typical for Pt–C σ bonds and appear to increase as the degree of substitution on the metallacycle increases. The C–C bond lengths in the metallacycles (C(1)–C(2) and C(2)–C(3) here) do not

---

(26) McGinnety, J. A. *J. Organomet. Chem.* **1973**, *59*, 429–441.

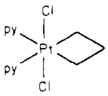
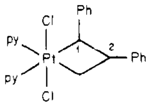
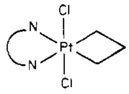
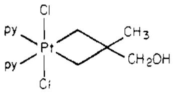
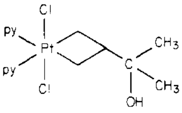
(27) At the present time we are unable to account for the difference in the C(1)–C(2) and C(2)–C(3) bond lengths. Decomposition of the crystal during data collection (decrease in intensity of standard reflections by an average of 17% from initial measured intensities) may have given rise to these anomalous bond lengths although all other aspects of the structure determination are normal. Sabat, M.; Jones, N. L.; Ibers, J. A., unpublished results.

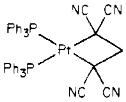
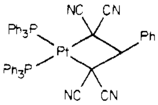
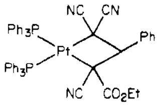
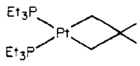
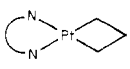
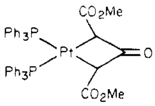
(28) Yarrow, D. J.; Ibers, J. A.; Lenarda, M.; Graziani, M. *J. Organomet. Chem.* **1974**, *70*, 133–145.

(29) Ibers, J. A.; DiCosimo, R.; Whitesides, G. M. *Organometallics* **1982**, *1*, 13–20.

(30) Clarke, D. A.; Kemmitt, R. D. W.; Mazid, M. A.; Schilling, M. D.; Russell, D. R. *J. Chem. Soc., Chem. Commun.* **1978**, 744–745.

Table X. Comparison of Intramolecular Distances, Bond Angles, and Pucker Angles in Platinacyclobutanes

	compound					
						
Intramolecular Distances (Å)						
Pt-C(1)	2.04 (5)	2.06 (3)	2.05 (3)	2.07 (4)	2.042 (7)	2.064 (10)
Pt-C(2)	2.69 (5)	2.60 (4)	2.62 (3)	2.76 (4)	2.676 (7)	2.670 (9)
Pt-C(3)	2.19 (5)	2.11 (5)	2.17 (3)	2.07 (4)	2.039 (6)	2.061 (9)
C(1)-C(2)	1.48 (8)	1.59 (7)	1.59 (4)	1.63 (6)	1.542 (10)	1.597 (12)
C(2)-C(3)	1.82 (9)	1.48 (5)	1.71 (4)	1.63 (6)	1.548 (10)	1.492 (14)
C(1)-C(3)	2.55 (10)	2.39 (7)	2.60 (4)		2.345 (10)	2.375 (12)
Bond Angles (Deg)						
C(1)-Pt-C(3)	74 (2)	70 (2)	76 (1)	71.9 (23)	70.15 (28)	70.50 (36)
C(1)-C(2)-C(3)	101 (4)	102 (3)	104 (2)	96.2 (51)	98.75 (55)	100.42 (64)
Pt-C(1)-C(2)	99 (4)	90 (2)	91 (2)	96.0 (30)	95.55 (46)	92.71 (54)
Pt-C(3)-C(2)	84 (3)	91 (3)	84 (2)	96.0 (30)	95.54 (44)	96.15 (53)
Pucker Angle[a]						
[C(1)-Pt-C(3)]-[C(1)-C(2)-C(3)]	12	28	22	0	1.0	5
ref	25	26		7[b]	this work[b]	27[b]

	compound					
						
Intramolecular Distances (Å)						
Pt-C(1)	2.137 (6)	2.137 (6)	2.158 (14)	2.080 (6)	2.030 (10)	2.149 (6)
Pt-C(2)	2.712 (6)	2.694 (6)	2.687 (14)	2.696 (6)	2.665 (10)	2.42
Pt-C(3)	2.139 (6)	2.159 (6)	2.200 (14)	2.086 (6)	2.037 (10)	2.128 (6)
C(1)-C(2)	1.545 (9)	1.557 (9)	1.556 (19)	1.535 (9)	1.534 (14)	1.496
C(2)-C(3)	1.584 (9)	1.548 (10)	1.509 (19)	1.536 (9)	1.534 (13)	1.496
C(1)-C(3)	2.404 (9)	2.394 (9)	2.403 (20)	2.308 (9)		
Bond Angles (Deg)						
C(1)-Pt-C(3)	68.4 (2)	67.7	66.9	67.3 (3)	69.9 (4)	
C(1)-C(2)-C(3)	100.4 (5)	100.9	103.2	97.5 (5)	98.8 (8)	
Pt-C(1)-C(2)	93.5 (4)	92.3	91.2	95.4 (4)	95.8 (6)	
Pt-C(3)-C(3)	92.3 (4)			95.1 (4)	95.5 (6)	
Pucker Angle[a]						
[(C(1)-Pt-C(3)]-[C(1)-C(2)-C(3)]	24	29	30	22	3	50
ref	28	4	4	29[b]	7[b]	30

[a] The unsigned acute angle is given. [b] A low-temperature structure determination (−70 °C or below).

vary much from an average value of 1.56 Å when account is taken of the limits of accuracy of some of these structure determinations. The degree of puckering of the metallacyclic ring varies widely (0–50°) and generally increases as the ring becomes more substituted.

NMR Spectra. The ^1H NMR data for the complexes are given in Table XI. For complex IV the analysis of the spectrum was simple, but for complexes I–III the spectra were very complex with many overlapping multiplets (Figure 5[13]). Thus, use of the lanthanide shift reagent $Eu(fod)_3$ was necessary for simplifying the spectra. The resultant shift parameters *S* are given in Table XI. For complex I the ^1H NMR spectrum was simulated by means of parameters obtained by extrapolation from the observed spectra in the presence of varying amounts of shift reagent. These parameters were refined with the program LAOCN3[31] (Figure 6[13]). The coupling constants (and chemical shifts) obtained by direct measurement from the first-order spectra with shift reagent present were in good agreement with those obtained from the NMR simulation. Thus, coordination of the hydroxyl function to the shift reagent does not appear to change to any significant degree the geometry of the complex. There was only one problem in assignment, namely to distinguish between the hydrogen atoms H^c and H^d (Table XI). We assign H^c as the proton cis to the substituent CR^1R^2OH on the basis of the larger shift parameter *S*. There are fairly good precedents for this assignment from lanthanide shift studies on a number of cycloalkyl alcohol and ketone derivatives.[32]

Puckering of the Platinacyclobutane Ring. For complexes III[33] and IV in the solid state, the puckering angles (Table X) are only 5° and 1°, respectively. This

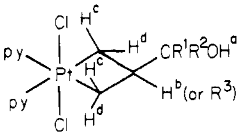
---

[31] Bothner-By, A. A.; Castellano, S. M. In "Computer Programs for Chemistry"; DeTar, D. F., Ed.; W. A. Benjamin: New York, 1968; Vol. I, Chapter 3.

[32] Cockerill, A. F.; Davies, G. L. O.; Harden, R. C.; Rackham, D. M. *Chem. Rev.* **1973**, *73*, 553–588. Mayo, G. C. *Chem. Soc. Rev.* **1973**, *2*, 49–74 and references therein.

[33] Although we cannot explain the anomaly in the structure of III at the present time,[27] we are confident that the pucker angle is 5° ± 1°.

Table XI. ^1H NMR Data for



compd	$R^1R^2R^3$	$\delta(H^a)$,[a] S,[b] ppm	$\delta(H^b)$,[a] S,[b] ppm	$\delta(H^c)$,[a] S,[b] ppm	$\delta(H^d)$,[a] S,[b] ppm	$J(H^bH^c)$, Hz	$J(H^bH^d)$, Hz	$J(H^cH^d)$, Hz
I[c]	HHH	1.83, 42.5	(3.06), 6.4	(2.47), 5.9	(2.61), 3.7	6.9	9.1	−4.8
I[d]				2.46	2.61	7.6	8.9	−4.8
II[e]	HMeH	1.87, 41.2	(3.63), 5.4	(2.74), 4.0	(2.64), 3.1	8.9	9.3	4.8[h]
III[f]	MeMeH	2.10, 38.3	(2.75), 5.7	(2.87), 7.0	(2.57), 3.7	8.3	9.4	4.8[h]
IV[g]	HHMe	1.64	...	2.39	2.74	...	...	4.84[h]

[a] δ values ($CDCl_3$ solution) either measured directly or, for complex signals, extrapolated. [b] S is defined by δ(complexed) = δ(uncomplexed) + $S[Eu(fod)_3]/[substrate]$. The assignments for H^c and H^d are made on the basis of the expected larger S for H^c. S values are given immediately below δ values. [c] $\delta(CH_2OH)$ 3.51 (d), S 11.64; from shift reagent study (molar ratio = 0.494), $^2J(^{195}Pt-^1H^c) = 82.5$ Hz, $^2J(^{195}Pt-^1H^d) = 84.0$ Hz. [d] Values obtained from LAOCN3 simulation. [e] $\delta(CHOH)$ 3.66 (q), S 12.30; $\delta(CMeOH)$ 1.03 (d), S 6.64, from SR study (molar ratio = 1.3), $^2J(^{195}Pt-^1H^c) = 85.0$ Hz, $^2J(^{195}Pt-^1H^d) = 84.8$ Hz. [f] $\delta(CMe_2)$ 1.18 (s), S 6.22; from SR study (molar ratio = 0.495), $^2J(^{195}Pt-^1H^c) = 84.6$ Hz, $^2J(^{195}Pt-^1H^d) = 80.8$ Hz. [g] $\delta(CH_2OH)$ 3.45 (s); $\delta(CMe)$ 1.16 (s), assignments for H^c and H^d may be reversed. $^2J(^{195}Pt-^1H^c) = 84.73$ Hz, $^2J(^{195}Pt-^1H^a) = 84.47$ Hz, $^4J(^{195}Pt-^1H^{R3}) = 3.9$ Hz. [h] Sign was not measured but is presumably negative by analogy with I.

Table XII. Torsion Angles (deg) in the Platinacyclobutanes

complex	$R^1R^2R^3$	coupling const, Hz	torsion angle,[a] (soln)	pucker angle, deg soln	pucker angle, deg solid state
I	HHH	$^3J(H^bH^c) = 7.6$	(37)[b] 134	15	
		$^3J(H^bH^d) = 8.9$	(141) 28	39	
II	HMeH	$^3J(H^bH^c) = 8.9$	(28) 141	23	
		$^3J(H^bH^d) = 9.3$	(144) 25	34	
III	MeMeH	$^3J(H^bH^c) = 8.3$	(32) 138	19	5
		$^3J(H^bH^d) = 9.4$	(144) 24	33	
IV	HHMe				1

[a] From the two solutions of the equation $J = 7 - \cos\theta + 5\cos 2\theta$ in ref 9, where θ is the torsion angle. [b] Torsion angles in parentheses were not used in the calculation of the pucker angle. See ref 36.

is surprising since the parent compound $PtCl_2(CH_2CH_2CH_2)py_2$ has a pucker angle of 12° (Table X)[25] and all precedents would suggest that the bulky CMe_2OH substituent in III would induce a larger puckering angle.[34] In cyclobutanes it has proved possible to use an equation derived by Karplus,[12] which relates the magnitude of the vicinal $^3J(HH)$ coupling constant to the HCCH torsion angle, to estimate the HCCH torsion angles and hence the extent of ring puckering.[9-11] The geometry of compound IV, as derived from the X-ray results, may be used to obtain a plot of pucker angle vs. torsion angle[35,36] (Figure 7[13]), and, if the equation derived by Karplus is valid for these compounds, it should then be possible to estimate pucker angles in solution for this series of platinacyclobutanes.

As it is not possible to prove the validity of the equation, the results must be regarded as tentative. We note that the platinacyclobutanes $Cl_2L_2PtCH^aPhCH^bPhCH^cH^d$ where L = pyridine, V, or 4-*tert*-butylpyridine, give $^3J(H^bH^c) \simeq J(H^bH^d) = 9.0 \pm 1.0$ or 8.6 ± 1.0 Hz, respectively.[37,38] On the basis of the constants given in Table XII, these coupling constants imply a pucker angle of 25–30° while in the solid state the two independent molecules of V have pucker angles of 22° and 28°, as determined by X-ray studies. The agreement here is satisfactory.[39]

If the same calculation is carried out for complexes I–III, Table XII, the pucker angles are 27 ± 8° in solution, with no significant differences between the individual molecules. These angles are in the range that might have been expected by comparison with related molecules given in Table X but are very different from those determined in

---

(34) For example, *tert*-butyl substituents are often used to induce alicyclic compounds to adopt a preferred conformation with this substituent in an equatorial position.

(35) For a chain of atoms 1, 2, 3, and 4, the torsion angle is defined as the angle between the directions 2–1 and 3–4 in projection down 2–3 or as the angle between the normals to the planes 1–2–3 and 2–3–4. By convention, the angle is considered positive if when looking from 2 to 3 a clockwise motion of atom 1 would superimpose it on atom 4. Busing, W. R.; Martin, K. O.; Levy, H. A. "ORFFE, A Fortran Crystallographic Function and Error Program"; Oak Ridge National Laboratory; Oak Ridge, TN, 1964.

(36) We have used Pt–C bond lengths of 2.040 Å, metallacyclic C–C bond lengths of 1.545 Å, a C(1)–C(2)–C(3) bond angle of 98.68°, and at planarity (pucker angle 0°) a Pt–C–C bond angle of 95.60°. Hydrogen atom positions of CH_2 groups were idealized so that the H–C–H angle is 109.5° and the CH_2 plane is perpendicular to the CXY plane, where X and Y are the other atoms attached to C. If an H–C–H bond angle of 114° is assumed (Dunitz, J. D.; Schomaker, V. *J. Chem. Phys.* **1952**, *20*, 1703–1707), the values of the derived torsion angles change by not more than 2°. We have used the smaller set of torsion angles to obtain the pucker angles from Figure 7. Larger pucker angles (~36°) were obtained from the larger set of torsion angles, but they were less consistent internally.

(37) McQuillin, F. G.; Powell, K. G. *J. Chem. Soc., Dalton Trans.* **1972**, 2123–2126.

(38) Al-Essa, R. J.; Puddephatt, R. J.; Thompson, P. J.; Tipper, C. F. H. *J. Am. Chem. Soc.* **1980**, *102*, 7546–7553.

(39) Examination of space-filling molecular models based on the X-ray structure[26] indicates very significant steric hindrance to a planar platinacyclobutane ring in V, so that it is probable that the conformation in the solid state and in solution will be similar in this case. Al-Essa, R. J.; Puddephatt, R. J.; Quyser, M. A.; Tipper, C. F. H. *J. Am. Chem. Soc.* **1979**, *101*, 364–370.

the solid state for complexes III[33] and IV. There are two possible explanations for this discrepancy. The first is that the equation derived by Karplus does not apply and that the calculated solution pucker angles in Table XII are wrong. The second explanation is that the puckering angles are different in the solid state and in solution. We favor the latter explanation, especially in view of agreement between pucker angles in solution and in the solid state for V.[39]

How does one explain possible differences between solution and solid state? It seems unlikely that solvent coordination ($CDCl_3$ in this instance) is inducing puckering in solution. Rather, it seems more likely that puckering in solution is close to that of the hypothetical, unconstrained gaseous species and that the differences between solution and solid state are the results of packing effects in the solid state. Although this suggestion is hardly surprising, it is hard to substantiate. Some support results from the wide variation of pucker angles among the compounds of Table X, as we presume that the packing forces differ widely among the various compounds. It is interesting that compounds III and IV, though they crystallize in different space groups (*P*2$_1$/*c* and *Pbca*), show similar pucker angles (1° and 5°) and show similar intermolecular interactions that could be indicative of similar packing forces.

Although the results are tentative, owing to the assumptions involved, we believe that the puckering differs in these metallacyclobutanes in solution and the solid state. Such a difference is important, since metallacycle puckering is often invoked in the mechanism of olefin metathesis reactions catalyzed in solution by transition-metal systems and except for rather specially tailored metallacycles, such as those synthesized here, information on the pucker angles is limited to results from solid-state studies.

Acknowledgment. This research was supported by the National Science Foundation (Grant CHE80-09671) at Northwestern University and NSERC (Canada) at U.W.O. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

Registry No. I, 86854-27-5; II, 86854-28-6; III, 86854-29-7; IV, 86854-30-0; $[PtCl_2(C_2H_4)]_2$, 12073-36-8; cyclopropanemethanol, 2516-33-8; α-methylcyclopropanemethanol, 765-42-4; α,α-dimethylcyclopropanemethanol, 930-39-2; 1-methylcyclopropanemethanol, 2746-14-7.

Supplementary Material Available: Table III, thermal parameters for the non-hydrogen atoms, Table IV, positional and thermal parameters for the hydrogen atoms, Table V, root-mean-square amplitudes of vibration, Table VI, $10|F_o|$ vs. $10|F_c|$, Figure 1, δ vs. concentration of shift reagent, Figure 2, stereoview of the unit cell, Figure 5, ^1H spectrum of III, Figure 6, ^1H NMR spectra of I, and Figure 7, torsion angle vs. pucker angle (24 pages). Ordering information is given on any current masthead page.

Photoreactivity of (η^3-Allyl)palladium Complexes in the Presence of Organic Halides

Bertha De Poorter,[1] Jacques Muzart,* and Jean-Pierre Pete

Laboratoire de Photochimie, Equipe de Recherche Associée au CNRS No. 688, U.E.R. Sciences, B.P. 347, 51062 Reims Cedex, France

Received December 28, 1982

Depending on the medium, bis(μ-chloro)bis(η^3-allyl)dipalladium complexes react photochemically with organic halides to yield either halogen-exchanged complexes or alkylated olefins.

Introduction

The reactivity of (η^3-allyl)palladium chloride complexes toward nucleophiles and even organometallics is well-known and has been applied frequently to alkylate olefinic compounds at the allylic position.[2] On the other hand, (η^3-allyl)nickel bromide complexes can be alkylated directly by organic halides.[3] These nickel complexes are generally prepared from allylic derivatives contrary to their palladium analogues that can be synthesized from olefins.[4]

Table I. Irradiation of 1 at λ = 366 nm in the Presence of Organic Halides

RX	RX/1 mole/mole	solv	conversn, %	yield of 2,[a] %
none[7]	0	CH_2Cl_2	0	
$BrCH(CO_2Et)_2$	10	CH_2Cl_2	30	28[b]
PhBr	used as solvent	PhBr	30	20
Cl_3CBr	100	CH_2Cl_2	76	40[c]
PhI	10	CH_2Cl_2	37	36
$PhCH_2Br$	25	CH_2Cl_2	80	79

[a] Isolated yield of 2 based on the amount of converted 1. [b] Also observed was a trace of 3. [c] Also isolated was 5 (15%) and a 1/2 mixture of 3 + 4 (15%).

In relation to a general study of the photoreactivity of (η^3-allyl)palladium complexes,[5,6] we have examined if these

---

(1) Postdoctoral Fellow 1981–1982.

(2) For example, see: (a) Tsuji, J.; Takahashi, H.; Morikawa, M. *Tetrahedron Lett.* **1965**, 4387. (b) Collins, D. J.; Jackson, W. R.; Timms, R. N. *Aust. J. Chem.* **1977**, *30*, 2167. (c) Trost, B. M. *Tetrahedron* **1977**, *33*, 2615. (d) Trost, B. M.; Weber, L.; Strege, P. E.; Fullerton, T. J.; Dietsche, T. J. *J. Am. Chem. soc.* **1978**, *100*, 3416, 3426. (e) Trost, B. M.; Verhoeven, T. R. *Ibid.* **1978**, *100*, 3435. (f) Manchand, P. S.; Wong, H. S.; Blount, J. F. *J. Org. Chem.* **1978**, *43*, 4769. (g) Castanet, Y.; Petit, F. *Tetrahedron Lett.* **1979**, 3221. (h) Tsuji, J.; "Organic Synthesis with Palladium Compounds"; Springer-Verlag: New York, 1980. (i) Chiusoli, G. P.; Costa, M.; Terenghi, G.; Mari, A. *Transition Met. Chem. (Weinheim, Ger.)* **1980**, *5*, 379. (j) Åkermark, B.; Jutand, A. *J. Organomet. Chem.* **1981**, *217*, C41. (k) Temple, J. S.; Riediker, M.; Schwartz, J. *J. Am. Chem. Soc.* **1982**, *104*, 1310. (l) Hegedus, L. S.; Tamura, R. *Organometallics* **1982**, *1*, 1188.

(3) (a) Corey, E. J.; Semmelhack, M. F. *J. Am. Chem. Soc.* **1967**, *89*, 2755. (b) Semmelhack, M. F. *Org. React. (N.Y.)* **1972**, *19*, 115. (c) Hegedus, L. S.; Miller, L. L. *J. Am. Chem. Soc.* **1975**, *97*, 459. (d) Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organotransition Metal Chemistry; University Science Books: Mill Valley, CA, 1980.

(4) (a) Trost, B. M.; Strege, P. E.; Weber, L.; Fullerton, T. J.; Dietsche, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 3407 and cited references therein. (b) Trost, B. M.; Metzner, P. J. *Ibid.* **1980**, *102*, 3572.

(5) Muzart, J.; Pete, J. P. *J. Chem. Soc., Chem. Commun.* **1980**, 257.