

## Four Membered Chelate Aminoalkyl and Aminoalkenyl Complexes of Platinum(II). The Molecular and Crystal Structure of $[\text{PtCH}_2\text{CH}_2\text{NMe}_2\text{Cl}(\text{PPh}_3)]$ and $[\text{PtC}(\text{=CMe}_2)\text{CH}_2\text{NMe}_2\text{Cl}(\text{PPh}_3)]$

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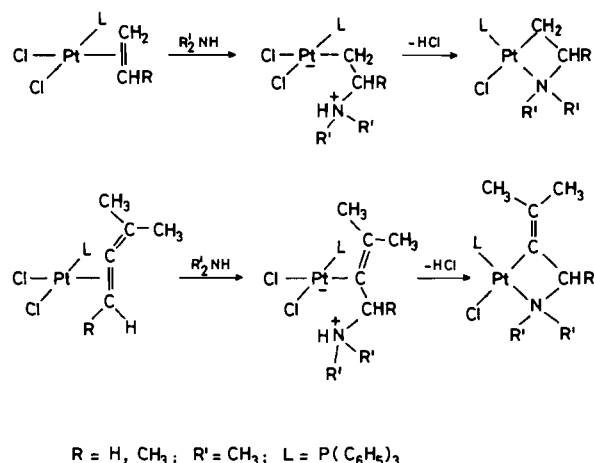
Single-crystal X-ray diffraction structure determinations have been performed on two platinum(II) complexes containing a cyclometallated four-membered ring:  $[\text{PtCH}_2\text{CH}_2\text{NMe}_2\text{Cl}(\text{PPh}_3)]$  (I) and  $[\text{PtC}(\text{=CMe}_2)\text{CH}_2\text{NMe}_2\text{Cl}(\text{PPh}_3)]$  (II). The crystal data are as follows: for complex I, space group monoclinic,  $P2_1/n$ ,  $a = 9.488(8)$  Å,  $b = 19.320(6)$  Å,  $c = 11.913(4)$  Å,  $\beta = 97.63(7)^\circ$ ,  $Z = 4$ ; for complex II, space group monoclinic,  $P2_1/a$ ,  $a = 19.231(6)$  Å,  $b = 12.023(5)$  Å,  $c = 10.256(4)$  Å,  $\beta = 95.60(6)^\circ$ ,  $Z = 4$ . The structures were solved by conventional Patterson, Fourier, and full matrix least-squares refinement techniques. The final consistency indices  $R$  and  $R_w$  are 0.049 and 0.062 (complex I, 2946 independent reflections), and 0.036 and 0.055 (complex II, 3437 independent reflections). Both compounds show the usual square-planar arrangement of the ligands, somewhat distorted by the presence of the four-membered ring which markedly deviates from planarity. The Pt–C bond length, the C–Pt–N bond angle and the puckering of the ring are 2.055(11) Å,  $70.6(4)^\circ$ , and  $8.3^\circ$  for complex I, and 2.002(7) Å,  $68.6(3)^\circ$ , and  $25.2^\circ$  for complex II respectively.

### Introduction

Cyclometallated compounds have been the object of several studies during the last years, and their preparation and properties have been recently reviewed [1, 2]. Much of the interest in this field arises since these complexes are often obtained as products of metallation reactions involving a C–H activation, and since they can be useful intermediates for non-conventional organic syntheses [1]. Within this class of compounds those containing a four-membered ring are rare [2]. Nevertheless they are an interesting object of investigation, owing to the

unusual structural and/or chemical properties that in principle could arise from the strained ring.

In previous papers [3, 4] we described the first example of platinum(II) complexes containing the four-membered Pt–C–C–N ring, obtained by amination of coordinated monoolefins [5], and allenes [6].



As a part of our work on C, N-chelate cycloplatinated compounds, we report now on the molecular and crystal structure of two such complexes:  $[\text{PtCH}_2\text{CH}_2\text{NMe}_2\text{Cl}(\text{PPh}_3)]$  (I) and  $[\text{PtC}(\text{=CMe}_2)\text{CH}_2\text{NMe}_2\text{Cl}(\text{PPh}_3)]$  (II). To our knowledge these are the first examples of platinum(II) complexes having the platinum atom inserted in an aliphatic four-membered ring without electron-withdrawing substituents.

### Experimental

#### Preparation of Complexes

Chloro [2-(dimethylamino)ethyl-C,N] (triphenylphosphine)platinum(II) (I) and chloro [1-(dimethylamino)-3-methyl-but-2-enyl-C,N] (triphenylphosphi-

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TABLE I. Crystal Data for  $[\text{Pt}(\overline{\text{C}}\text{H}_2\text{CH}_2\text{NMe}_2\text{Cl}(\text{PPh}_3))] \text{ (I)}$  and  $[\text{Pt}(\text{C}(\text{CMe}_2)\text{CH}_2\text{NMe}_2\text{Cl}(\text{PPh}_3))] \text{ (II)}$ .

|  | Complex I                                 | Complex II                                |
|--|---|---|
| mol formula                                | $\text{C}_{22}\text{H}_{25}\text{ClNPPt}$ | $\text{C}_{25}\text{H}_{29}\text{ClNPPt}$ |
| mol wt.                                    | 565.0                                     | 605.0                                     |
| cryst system                               | monoclinic                                | monoclinic                                |
| space group                                | $P2_1/n$                                  | $P2_1/a$                                  |
| <i>a</i> , Å                               | 9.488(8)                                  | 19.231(6)                                 |
| <i>b</i> , Å                               | 19.320(6)                                 | 12.023(5)                                 |
| <i>c</i> , Å                               | 11.913(4)                                 | 10.256(4)                                 |
| $\beta$ , deg                              | 97.63(7)                                  | 95.60(6)                                  |
| <i>V</i> , Å <sup>3</sup>                  | 2164.5                                    | 2360.0                                    |
| <i>Z</i>                                   | 4   | 4   |
| $\rho_{\text{calcd}}$ , g cm <sup>-3</sup> | 1.734                                     | 1.703                                     |
| $\rho_{\text{exptl}}$ , g cm <sup>-3</sup> | 1.74                                      | 1.71                                      |
| <i>F</i> (000)                             | 1096                                      | 1184                                      |
| $\mu(\text{MoK}\alpha, \text{cm}^{-1})$    | 70.2                                      | 64.5                                      |
| Crystal size (mm)                          | 0.2 × 0.3 × 0.5                           | 0.2 × 0.3 × 0.5                           |

ne)platinum(II) (II) were prepared as previously described [3, 4]. In both cases, crystals suitable for X-ray diffraction studies were obtained by slow crystallization from chloroform-*n*-heptane mixtures in the form of colorless regular prisms.

#### X-Ray Data Collection and Reduction

Preliminary oscillation and Weissenberg photographs taken with MoK $\alpha$  radiation indicated a monoclinic lattice symmetry with  $P2_1/n$  and  $P2_1/a$  space groups for complexes I and II respectively.

Cell dimensions and reflection intensities were carried out at room temperature with a Zr-filtered MoK $\alpha$  radiation and pulse-height discrimination on a CAD-4 Enraf-Nonius diffractometer of the Centro di Metodologie Chimico-Fisiche of the University of Naples, equipped with PDP8/E and PDP11/34 digital computers. The refined unit cell parameters and orientation matrix for data collection were determined using a least-square procedure of the angular settings of 20 and 25 well-centered high-angle reflections [7] for the compounds I and II respectively. The standard deviations of the lattice parameters were obtained by comparison of the deviations from the integer values of the indices, calculated with the orientation matrix, for the setting values of the orientation reflections as determined by Duisenberg [8]. In Table I crystallographic data and some details of data collection are reported for the two compounds. The analysis of profiles of reflections for both samples gave a set of conditions reported as the following:

An  $\omega$ - $2\theta$  scan mode with a scan angle  $\Delta\omega = (1.1 + 0.35 \tan\theta)^\circ$  was chosen for the peak measurements; background counts were taken on an additional area of  $\Delta\omega/4^\circ$  of both sides of the main scan with the same scan speed for each reflection. A distance crystal-counter of 368 mm was used with a horizontal and vertical counter entrance aperture of 4 mm and  $(3.0 + 1.0 \tan\theta)$  mm respectively. The tube placed between the goniometer head and the detector was evacuated using a vacuum pump. Pre-scan runs were made at a speed of  $5^\circ/\text{min}$ . Reflections with a net intensity  $I \leq 0.5\sigma(I)$  were flagged as 'weak'; those having  $I > 0.5\sigma(I)$  were measured at lower speeds (in the range  $1$ – $5^\circ/\text{min}$ ), depending on the value of  $\sigma(I)/I$ . The maximum time allowed for the scan was set to 60 s. Two intensity-control reflections were used every 60 min of X-ray exposure time for monitoring the crystal and the electronic apparatus stability; no significant change in their intensities was observed during the data collections. Orientation matrix checks were made with respect to the scattering vectors of four well-centered reflections every 200 reflections; reorientation was made using 20 high-angle reflections if the displacement of measured scattering vectors exceeded the calculated value of  $0.15^\circ$ . A total of 4105 and 4611 reflections were collected in the range  $1$ – $50^\circ$  of  $2\theta$  for compound I and compound II. Of these reflections 2946 and 3437, respectively, had a net intensity\*, greater than  $3\sigma(I)$  and were used as such in all subsequent refinement calculations. All reflections were corrected for Lorentz and polarization effects; anomalous dispersion corrections for atomic scattering factors were applied to the Pt, Cl, C, P and N atom scattering curve [9]. No absorption corrections were applied, since the  $\mu\text{R}$ 's calculated for the two crystals used in the data collection, in the cylindrical approximation, presented values of 0.88 and 0.81 respectively.

#### Solution and Refinement

The structures of compounds I and II have been solved by direct application of the heavy-atom method. The position of the Pt and Cl atoms have been calculated from a Patterson synthesis and used in subsequent Fourier calculations that revealed the positions of all remaining lighter atoms in the independent unit for both complexes. The atomic coordinates were refined in the usual way with a full

\*The net intensity was  $I(\text{net}) = [s + 2(L + R)]/npi$ , where  $(L + R)$  is the total background count,  $s$  the scan count, and  $npi$  the ratio of the maximum possible scan speed to the applied scan speed. The standard deviation in the net intensity was calculated with  $\sigma(I) = (20.1166/npi) [s + 4(L + R)]^{1/2}$ . The  $\sigma(I)$ 's were converted to the estimated errors in the relative structure factors  $\sigma(F)$  by  $\sigma(F) = (\sigma(I)/LP)(1/2F_0)$ .

TABLE II. Atomic Fractional Coordinates ( $\times 10^4$ ) and Thermal Parameters ( $\times 10^4$ ) for  $[\text{Pt}(\overline{\text{CH}_2\text{CH}_2\text{NMe}_2\text{Cl}})(\text{PPh}_3)]$  (I).<sup>a,b</sup>

| Atom  | <i>x/a</i> | <i>y/b</i> | <i>z/c</i> | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|-------|------------|------------|------------|--------------|--------------|--------------|--------------|--------------|--------------|
| Pt    | 8214(4)    | 1257(2)    | 674(3)     | 89(5)        | 23(1)        | 45(3)        | 12(5)        | -1(6)        | 1(4)         |
| Cl    | 9484(4)    | 2326(2)    | 998(3)     | 145(4)       | 25(9)        | 120(3)       | -17(3)       | 36(6)        | 17(3)        |
| P     | 9197(3)    | 721(1)     | 2220(2)    | 65(3)        | 19(8)        | 50(2)        | -3(3)        | -2(4)        | 0(2)         |
| N     | 6853(12)   | 1616(7)    | -768(8)    | 155(11)      | 38(4)        | 64(8)        | 66(12)       | 27(21)       | 14(9)        |
| C(1)  | 6804(11)   | 489(8)     | 99(13)     | 149(22)      | 33(5)        | 129(14)      | 27(24)       | -187(22)     | -9(13)       |
| C(2)  | 5952(23)   | 924(10)    | -803(18)   | 277(31)      | 45(6)        | 198(22)      | 24(31)       | -191(43)     | -64(20)      |
| C(3)  | 7521(21)   | 1686(15)   | -1746(13)  | 187(23)      | 155(14)      | 57(12)       | 44(41)       | 40(33)       | 57(23)       |
| C(4)  | 5981(20)   | 2229(9)    | -551(16)   | 203(20)      | 45(5)        | 143(18)      | 111(22)      | -20(31)      | -14(16)      |
| C(5)  | 8588(13)   | -170(6)    | 2348(10)   | 75(13)       | 21(3)        | 69(9)        | -3(12)       | -19(24)      | 10(9)        |
| C(6)  | 8938(14)   | -639(6)    | 1514(11)   | 106(14)      | 24(4)        | 94(11)       | 16(14)       | -55(22)      | -17(11)      |
| C(7)  | 8505(22)   | -1311(7)   | 1513(13)   | 155(21)      | 27(4)        | 100(13)      | -21(20)      | -31(31)      | 5(12)        |
| C(8)  | 7669(14)   | -1566(7)   | 2358(13)   | 143(22)      | 23(4)        | 122(14)      | 23(11)       | -35(33)      | 6(12)        |
| C(9)  | 7334(11)   | -1068(6)   | 3201(12)   | 119(21)      | 25(4)        | 93(12)       | -6(12)       | -22(21)      | 9(11)        |
| C(10) | 7797(10)   | -379(6)    | 3165(10)   | 75(12)       | 28(4)        | 75(10)       | -6(13)       | -10(20)      | 16(10)       |
| C(11) | 8648(12)   | 1168(5)    | 3457(8)    | 66(14)       | 17(3)        | 39(7)        | -14(10)      | -18(10)      | 0(8)         |
| C(12) | 9497(12)   | 1154(6)    | 4484(10)   | 133(24)      | 26(4)        | 64(9)        | -32(17)      | 11(21)       | -1(10)       |
| C(13) | 9008(23)   | 1501(7)    | 5412(10)   | 166(25)      | 35(4)        | 43(9)        | -6(23)       | 4(22)        | -12(10)      |
| C(14) | 7689(16)   | 1822(7)    | 5295(11)   | 169(24)      | 24(4)        | 77(10)       | -5(10)       | 86(23)       | 1(10)        |
| C(15) | 6865(12)   | 1807(8)    | 4210(10)   | 108(13)      | 34(4)        | 74(10)       | -4(12)       | 34(20)       | 18(11)       |
| C(16) | 7358(11)   | 1490(6)    | 3315(10)   | 87(12)       | 20(3)        | 70(9)        | 24(15)       | 30(21)       | 8(9)         |
| C(17) | 11124(10)  | 645(6)     | 2514(9)    | 74(15)       | 25(3)        | 53(8)        | 2(16)        | -26(27)      | -11(9)       |
| C(18) | 11964(10)  | 1077(7)    | 1966(13)   | 72(13)       | 39(5)        | 121(14)      | -24(15)      | 0(24)        | -16(13)      |
| C(19) | 13489(21)  | 999(9)     | 2219(17)   | 105(21)      | 51(7)        | 182(20)      | 15(20)       | 33(31)       | -1(19)       |
| C(20) | 14076(14)  | 526(9)     | 2999(16)   | 113(24)      | 44(6)        | 178(19)      | 51(21)       | -40(36)      | -31(17)      |
| C(21) | 13195(12)  | 86(8)      | 3533(15)   | 90(22)       | 33(5)        | 155(16)      | 35(11)       | -30(35)      | 3(15)        |
| C(22) | 11737(13)  | 137(7)     | 3279(12)   | 102(18)      | 29(4)        | 96(12)       | 16(10)       | -13(24)      | -9(12)       |

<sup>a</sup>Standard deviations (in parentheses) are in units of the last significant figure. <sup>b</sup>The temperature factors are in the form  $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$ .

matrix least-squares procedure\*, using for all atoms isotropic thermal parameters. The *R* values were 0.095 and 0.085 for the complexes I and II respectively. The refinement of the two structures was carried out using the anisotropic thermal factors for all atoms until the maximum shifts on the atomic coordinates and the anisotropic thermal parameters were less than one-fifth and one-third of the corresponding standard deviations. The final unweighted and weighted *R* values were  $R(F) = 0.049$  and  $R_w(F) = 0.062$  for the complex I, and  $R(F) = 0.036$  and  $R_w(F) = 0.055$  for the complex II.

For both structures a weight factor  $w = 1/\sigma(F_o^2)$  on the basis of counting statistics was used for all reflections. The average deviation in the observations of unit weight defined by  $[\sum w(|F_o| - |F_c|)^2 / (m - n)]^{1/2}$  where *m* is the number of observations and *n* the number of variables, was 1.87 and 1.73 for both

structures respectively, as compared to the ideal value of 1.

## Results

The positional and thermal parameters for the two compounds are compiled in Tables II and III; bond distances and angles are given in Tables IV and V. A list of observed and calculated structure factors for the two compounds is available upon application to the Authors.

### $[\text{Pt}(\overline{\text{CH}_2\text{CH}_2\text{NMe}_2\text{Cl}})(\text{PPh}_3)]$ (I)

The compound crystallizes in the monoclinic space group  $P2_1/n$  with four molecules in the unit cell. The platinum atom displays the expected square-planar coordination, somewhat distorted by the strained four-membered ring. The nitrogen and phosphorus atoms are in *trans* positions. All the interatomic distances are in the expected range, the long Pt-Cl bond distance of 2.396(3) Å being consistent with the high *trans*-influence of the  $\sigma$ -bonded carbon

\*The function minimized was  $\Sigma(w(|F_o| - |F_c|))^2$ . The refinement was on *F*. The unweighted and weighted residuals are defined as follows:  $R_F = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|$ ;  $R_w(F) = (\Sigma w(|F_o| - |F_c|))^2 / (\Sigma w|F_o|^2)$ .

TABLE III. Atomic Fractional Coordinates ( $\times 10^4$ ) and Thermal Parameters ( $\times 10^4$ ) for  $[\text{Pt}(\overline{\text{C}(\text{=CMe}_2)\text{CH}_2\text{NMe}_2\text{Cl}})(\text{PPh}_3)]$  (II).<sup>a,b</sup>

| Atom  | $x/a$   | $y/b$    | $z/c$    | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|-------|---------|----------|----------|--------------|--------------|--------------|--------------|--------------|--------------|
| Pt    | 2010(2) | 1261(3)  | 2449(3)  | 18(1)        | 40(2)        | 64(3)        | 6(3)         | 13(3)        | 15(5)        |
| Cl    | 2293(2) | 2333(3)  | 634(3)   | 45(9)        | 92(2)        | 145(3)       | 46(3)        | 88(3)        | 125(4)       |
| P     | 1092(1) | 2311(2)  | 2760(2)  | 17(6)        | 40(2)        | 69(2)        | -7(2)        | 7(2)         | -13(3)       |
| N     | 2910(4) | 261(6)   | 2369(7)  | 20(2)        | 51(6)        | 74(7)        | 15(6)        | 21(7)        | 5(14)        |
| C(1)  | 2004(5) | -42(8)   | 3665(8)  | 21(2)        | 60(7)        | 62(8)        | 7(8)         | 9(8)         | 14(12)       |
| C(2)  | 2837(5) | -316(9)  | 3657(9)  | 23(3)        | 69(8)        | 93(10)       | 30(8)        | 24(9)        | 75(12)       |
| C(3)  | 1547(5) | -731(8)  | 4143(9)  | 30(3)        | 46(6)        | 60(9)        | -2(8)        | 14(9)        | 10(10)       |
| C(4)  | 761(5)  | -488(8)  | 4098(11) | 17(3)        | 49(7)        | 163(14)      | -19(7)       | 14(10)       | 13(21)       |
| C(5)  | 1748(7) | -1857(8) | 4804(10) | 52(4)        | 44(7)        | 99(11)       | 7(10)        | 24(12)       | 67(12)       |
| C(6)  | 2837(5) | -532(9)  | 1270(10) | 28(3)        | 62(8)        | 102(11)      | 22(9)        | -2(10)       | -42(21)      |
| C(7)  | 3585(5) | 858(9)   | 2416(12) | 19(3)        | 69(8)        | 163(14)      | -6(8)        | 15(11)       | -38(23)      |
| C(8)  | 873(5)  | 2487(7)  | 4445(9)  | 22(3)        | 41(6)        | 85(9)        | -9(7)        | 13(8)        | -4(11)       |
| C(9)  | 1217(5) | 1959(8)  | 5463(9)  | 29(3)        | 59(8)        | 72(9)        | -17(8)       | 9(9)         | 16(15)       |
| C(10) | 1066(6) | 2143(9)  | 6731(10) | 38(4)        | 62(8)        | 84(10)       | -20(9)       | 16(10)       | -11(24)      |
| C(11) | 536(6)  | 2892(9)  | 6979(11) | 37(3)        | 58(8)        | 129(12)      | -29(9)       | 55(10)       | -14(21)      |
| C(12) | 177(6)  | 3453(9)  | 5974(10) | 33(3)        | 71(9)        | 101(11)      | -17(9)       | 50(9)        | -27(22)      |
| C(13) | 334(5)  | 3265(9)  | 4682(10) | 28(3)        | 55(7)        | 104(11)      | 6(8)         | 44(9)        | 2(20)        |
| C(14) | 1201(5) | 3775(8)  | 2279(8)  | 31(3)        | 60(7)        | 38(7)        | 2(8)         | 21(8)        | 7(11)        |
| C(15) | 665(6)  | 4364(9)  | 1574(10) | 35(3)        | 50(7)        | 88(10)       | 14(9)        | 9(10)        | 26(24)       |
| C(16) | 800(6)  | 5479(9)  | 1310(10) | 43(4)        | 70(8)        | 91(11)       | 36(10)       | 16(11)       | 22(22)       |
| C(17) | 1408(7) | 6009(9)  | 1781(12) | 47(4)        | 62(9)        | 122(13)      | -15(10)      | 29(13)       | 2(21)        |
| C(18) | 1930(6) | 5417(10) | 2438(11) | 48(5)        | 62(9)        | 130(14)      | -16(11)      | -10(14)      | 26(26)       |
| C(19) | 1835(6) | 4279(9)  | 2755(12) | 38(4)        | 48(8)        | 156(15)      | 8(10)        | 7(13)        | 11(21)       |
| C(20) | 292(5)  | 1866(8)  | 1787(9)  | 24(3)        | 41(6)        | 82(9)        | 20(7)        | -5(9)        | 12(11)       |
| C(21) | -338(5) | 1650(10) | 2256(10) | 24(3)        | 75(8)        | 105(11)      | -11(9)       | 5(10)        | -20(24)      |
| C(22) | -915(6) | 1255(10) | 1460(15) | 26(3)        | 90(11)       | 221(20)      | -13(11)      | -33(14)      | -12(22)      |
| C(23) | -839(7) | 1102(10) | 132(13)  | 41(4)        | 80(10)       | 154(15)      | -4(11)       | -71(13)      | -26(25)      |
| C(24) | -216(7) | 1308(10) | -387(13) | 45(5)        | 89(11)       | 154(16)      | -39(12)      | -47(14)      | 23(20)       |
| C(25) | 361(6)  | 1703(10) | 435(10)  | 39(4)        | 81(9)        | 68(10)       | -12(10)      | -29(11)      | 7(20)        |

<sup>a</sup>Standard deviations (in parentheses) are in units of the last significant figure. <sup>b</sup>The temperature factors are in the form  $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$ .

TABLE IV. Bond Distances (Å) and Bond Angles (Deg) for  $[\text{PtCH}_2\text{CH}_2\text{NMe}_2\text{Cl}(\text{PPh}_3)]$  (I).<sup>a</sup>

| Bond Distances |           |               |           |
|----------------|-----------|---------------|-----------|
| Pt-Cl          | 2.396(3)  | C(9)-C(10)    | 1.405(12) |
| Pt-P           | 2.210(2)  | C(10)-C(5)    | 1.367(12) |
| Pt-N           | 2.123(7)  | C(11)-C(12)   | 1.374(12) |
| Pt-C(1)        | 2.055(11) | C(12)-C(13)   | 1.422(13) |
| P-C(5)         | 1.828(8)  | C(13)-C(14)   | 1.388(14) |
| P-C(11)        | 1.842(7)  | C(14)-C(15)   | 1.419(13) |
| P-C(17)        | 1.820(8)  | C(15)-C(16)   | 1.364(12) |
| N-C(2)         | 1.584(19) | C(16)-C(11)   | 1.363(11) |
| N-C(3)         | 1.405(13) | C(17)-C(18)   | 1.377(13) |
| N-C(4)         | 1.487(14) | C(18)-C(19)   | 1.447(14) |
| C(1)-C(2)      | 1.512(18) | C(19)-C(20)   | 1.367(18) |
| C(5)-C(6)      | 1.416(13) | C(20)-C(21)   | 1.403(17) |
| C(6)-C(7)      | 1.361(13) | C(21)-C(22)   | 1.379(13) |
| C(7)-C(8)      | 1.447(16) | C(22)-C(17)   | 1.411(12) |
| C(8)-C(9)      | 1.456(16) |               |           |
| Bond Angles    |           |               |           |
| Cl-Pt-P        | 97.0(1)   | C(12)-C(11)-P | 120.6(6)  |
| Cl-Pt-N        | 95.0(3)   | C(16)-C(11)-P | 117.4(6)  |

(continued overleaf)

TABLE IV. (continued)

|               |           |                   |           |
|---------------|-----------|-------------------|-----------|
| Cl–Pt–C(1)    | 165.5(3)  | C(18)–C(17)–P     | 119.3(7)  |
| P–Pt–N        | 166.3(3)  | C(22)–C(17)–P     | 119.8(7)  |
| P–Pt–C(1)     | 97.1(3)   | C(5)–C(6)–C(7)    | 120.8(10) |
| N–Pt–C(1)     | 70.6(4)   | C(6)–C(7)–C(8)    | 121.1(10) |
| Pt–P–C(5)     | 114.1(3)  | C(7)–C(8)–C(9)    | 116.4(10) |
| Pt–P–C(11)    | 108.3(2)  | C(8)–C(9)–C(10)   | 120.5(10) |
| Pt–P–C(17)    | 120.0(3)  | C(9)–C(10)–C(5)   | 120.3(9)  |
| Pt–C(1)–C(2)  | 95.6(8)   | C(10)–C(5)–C(6)   | 120.8(9)  |
| Pt–N–C(2)     | 90.8(7)   | C(11)–C(12)–C(13) | 118.0(9)  |
| Pt–N–C(3)     | 114.2(7)  | C(12)–C(13)–C(14) | 121.0(9)  |
| Pt–N–C(4)     | 114.3(7)  | C(13)–C(14)–C(15) | 117.6(9)  |
| C(5)–P–C(11)  | 104.4(4)  | C(14)–C(15)–C(16) | 121.0(9)  |
| C(5)–P–C(17)  | 103.2(4)  | C(15)–C(16)–C(11) | 120.2(8)  |
| C(11)–P–C(17) | 105.5(4)  | C(16)–C(11)–C(12) | 122.0(8)  |
| C(1)–C(2)–N   | 102.4(10) | C(17)–C(18)–C(19) | 117.6(11) |
| C(2)–N–C(3)   | 111.2(12) | C(18)–C(19)–C(20) | 121.2(12) |
| C(2)–N–C(4)   | 111.4(10) | C(19)–C(20)–C(21) | 120.0(11) |
| C(3)–N–C(4)   | 113.0(11) | C(20)–C(21)–C(22) | 119.8(11) |
| C(6)–C(5)–P   | 116.0(7)  | C(21)–C(22)–C(17) | 120.5(10) |
| C(10)–C(5)–P  | 123.1(7)  | C(22)–C(17)–C(18) | 120.9(8)  |

<sup>a</sup>The standard error (in parentheses) after each parameter refers to the last decimal place given.

TABLE V. Bond Distances (Å) and Bond Angles (Deg) for  $[\text{Pt}(\text{C}(\text{CMe}_2)\text{CH}_2\text{NMe}_2\text{Cl}(\text{PPh}_3))] (\text{II})$ .<sup>a</sup>

|                       |           |                   |           |
|-----------------------|-----------|-------------------|-----------|
| <b>Bond Distances</b> |           |                   |           |
| Pt–Cl                 | 2.370(2)  | C(9)–C(10)        | 1.378(10) |
| Pt–P                  | 2.219(2)  | C(10)–C(11)       | 1.402(12) |
| Pt–N                  | 2.115(5)  | C(11)–C(12)       | 1.362(12) |
| Pt–C(1)               | 2.002(7)  | C(12)–C(13)       | 1.406(11) |
| P–C(8)                | 1.831(7)  | C(14)–C(15)       | 1.394(10) |
| P–C(14)               | 1.845(7)  | C(14)–C(19)       | 1.406(12) |
| P–C(20)               | 1.829(8)  | C(15)–C(16)       | 1.397(12) |
| N–C(6)                | 1.473(9)  | C(16)–C(17)       | 1.378(13) |
| N–C(7)                | 1.479(9)  | C(17)–C(18)       | 1.355(13) |
| N–C(2)                | 1.538(8)  | C(18)–C(19)       | 1.422(12) |
| C(1)–C(2)             | 1.515(10) | C(20)–C(21)       | 1.371(11) |
| C(2)–C(3)             | 1.336(10) | C(20)–C(25)       | 1.420(11) |
| C(3)–C(5)             | 1.546(10) | C(21)–C(22)       | 1.395(12) |
| C(3)–C(4)             | 1.536(10) | C(22)–C(23)       | 1.396(15) |
| C(8)–C(9)             | 1.340(10) | C(23)–C(24)       | 1.381(15) |
| C(8)–C(13)            | 1.434(10) | C(24)–C(25)       | 1.408(12) |
| <b>Bond Angles</b>    |           |                   |           |
| Cl–Pt–P               | 92.8(1)   | C(9)–C(8)–P       | 122.7(6)  |
| Cl–Pt–N               | 91.6(2)   | C(13)–C(8)–P      | 118.2(6)  |
| Cl–Pt–C(1)            | 158.4(2)  | C(15)–C(14)–P     | 121.7(6)  |
| P–Pt–N                | 174.0(2)  | C(19)–C(14)–P     | 115.9(6)  |
| P–Pt–C(1)             | 107.6(2)  | C(21)–C(20)–P     | 126.1(6)  |
| N–Pt–C(1)             | 68.6(3)   | C(25)–C(20)–P     | 114.8(6)  |
| Pt–P–C(8)             | 117.4(3)  | C(8)–C(9)–C(10)   | 121.8(8)  |
| Pt–P–C(14)            | 113.1(2)  | C(9)–C(10)–C(11)  | 119.9(8)  |
| Pt–P–C(20)            | 113.2(2)  | C(10)–C(11)–C(12) | 120.3(8)  |
| Pt–C(1)–C(2)          | 95.9(4)   | C(11)–C(12)–C(13) | 119.6(8)  |
| Pt–C(1)–C(3)          | 139.2(6)  | C(12)–C(13)–C(8)  | 119.4(8)  |

(continued on facing page)

TABLE V. (continued)

|                |          |                   |           |
|----------------|----------|-------------------|-----------|
| Pt–N–C(2)      | 90.8(4)  | C(13)–C(8)–C(9)   | 119.1(7)  |
| Pt–N–C(7)      | 116.1(5) | C(14)–C(15)–C(16) | 116.5(8)  |
| Pt–N–C(6)      | 112.4(4) | C(15)–C(16)–C(17) | 122.9(8)  |
| C(8)–P–C(14)   | 100.6(3) | C(16)–C(17)–C(18) | 119.7(9)  |
| C(8)–P–C(20)   | 106.9(3) | C(17)–C(18)–C(19) | 120.9(9)  |
| C(14)–P–C(20)  | 104.2(3) | C(18)–C(19)–C(14) | 117.5(8)  |
| C(1)–C(2)–N    | 99.0(5)  | C(19)–C(14)–C(15) | 122.2(8)  |
| C(2)–N–C(7)    | 114.4(6) | C(20)–C(21)–C(22) | 122.6(9)  |
| C(2)–N–C(6)    | 110.8(6) | C(21)–C(22)–C(23) | 117.6(10) |
| C(6)–N–C(7)    | 110.9(6) | C(22)–C(23)–C(24) | 121.9(9)  |
| C(1)–C(3)–C(5) | 124.0(7) | C(23)–C(24)–C(25) | 119.5(10) |
| C(1)–C(3)–C(4) | 123.6(7) | C(24)–C(25)–C(20) | 119.2(9)  |
| C(5)–C(3)–C(4) | 112.5(6) | C(25)–C(20)–C(21) | 119.1(7)  |
| C(2)–C(1)–C(3) | 123.0(7) |                   |           |

<sup>a</sup>The standard error (in parentheses) after each parameter refers to the last decimal place given.

atom [1, 2]. A view of the molecule is given in Fig. 1 with the atom numbering scheme.

#### $[PtCl(=CMe_2)CH_2NMe_2Cl(PPh_3)]$ (II).

The compound crystallizes in the monoclinic space group  $P2_1/a$  with four molecules in the unit cell. The structure is similar to that of I, with all the interatomic distances in the expected range. However II displays a distortion greater than I from the square planar geometry of the coordinates ligands. A view of the molecule is given in Fig. 2 with the atom numbering scheme.

### Discussion

Table VI shows a comparison of some geometrical parameters involving the coordination sphere and the four-membered ring in compounds I and II and in some cyclometallated platinum(II) complexes whose structures have been determined [11–14].

#### Bond Lengths

The Pt–C(1) bond lengths of 2.05 and 2.00 Å in I and II respectively are the shortest among those reported in Table VI. The Pt–C  $\sigma$ -bond distance of 2.00 Å in I is actually the shortest observed even for non-cyclic platinum(II) alkyl or alkenyl complexes [10, 14]. The difference in length of 0.05 Å between Pt–C(alkyl) and Pt–C(alkenyl) bonds in I and II respectively is in full agreement with the mean contraction (0.06 Å) that is observed upon a change of the hybridization state of the  $\sigma$ -bonded carbon atom [15]. As has been pointed out with detailed arguments [15], this contraction is explained sufficiently by the difference in covalent radii between  $sp^2$  and  $sp^3$  carbon atoms, thus confirming the previous conclusion that  $\sigma$ -alkenyl ligands

do not display appreciable  $\pi$ -acidity in their platinum(II) complexes [15]. This conclusion is substantiated by the finding that the C=C bond length in II (1.34 Å) has nearly the same value as in ethylene. Were a back-donation involved in the Pt–alkenyl linkage, an increase of the C=C bond length would be expected.

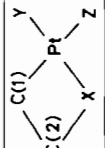
The Pt–Cl bond lengths of 2.396(3) Å in I and 2.370(2) Å in II suggest that the *trans*-influence of the alkenyl carbon atom is slightly weaker than that of the alkyl carbon atom, in agreement with the results reported for other alkyl and alkenyl complexes of platinum(II) [10, 15]. This conclusion is confirmed by the Pt–Cl stretching frequencies in the IR spectra of the two compounds: 270  $cm^{-1}$  for I and 280  $cm^{-1}$  for II, the former indicating a slightly weaker bond than the latter.

The Pt–N bond lengths in I and II are nearly equal (2.123(7) Å and 2.115(5) Å respectively). We have found no reported structure of platinum(II) complexes in which an aliphatic amine is *trans* to a phosphine ligand. However, since typical values for Pt–N distances *trans* to a ligand of weak *trans*-influence are in the range 2.02–2.10 Å [16], the values found in I and II are as expected with a *trans*-ligand of intermediate *trans*-influence such as triphenylphosphine [17].

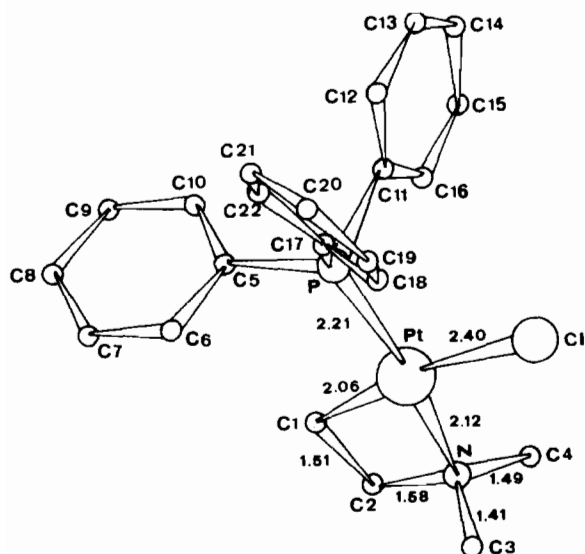
#### Bond Angles and Conformations

The inspection of Table VI shows that the bond angle C(1)–Pt–X is almost invariant (mean value 68°), while some differences are observed in the puckering of the four-membered ring and in the distortion from the square-planar arrangement of the ligands. For the compounds III–VII reported in Table VI these distortions were ascribed to non-bonded interactions between the side groups and the ring atoms [12, 14]. Our results are in agreement

TABLE VI. Comparison of Geometries of Aliphatic Four-Membered Ring Pt(II) Metallocycles.

|  | I <sup>a</sup> | II <sup>b</sup> | III <sup>c</sup> | IV <sup>d</sup> | V <sup>e</sup> | VI <sup>f</sup> | VII <sup>g</sup> |
|---|----------------|-----------------|------------------|-----------------|----------------|-----------------|------------------|
|   | X=N, Y=P, Z=Cl | X=N, Y=P, Z=Cl  | X=C, Y=Z=P       | X=C, Y=Z=P      | X=C, Y=Z=P     | X=O, Y=Z=As     | X=O, Y=Z=P       |
| Intramolecular Distances, Å   |                |                 |                  |                 |                |                 |                  |
| Pt-C(1)   | 2.055(11)      | 2.002(7)        | 2.137(6)         | 2.137(6)        | 2.158(14)      | 2.103(7)        | 2.13(2)          |
| Pt...C(2)   | 2.667          | 2.631           | 2.712            | 2.694           | 2.687          | 2.576           | 2.61             |
| Pt-X  | 2.123(7)       | 2.115(5)        | 2.139(6)         | 2.159(6)        | 2.200(14)      | 2.050(5)        | 2.06(2)          |
| Pt-Y  | 2.210(2)       | 2.219(2)        | 2.314(2)         | 2.302(2)        | 2.303(4)       | 2.341(1)        | 2.247(6)         |
| Pt-Z  | 2.396(3)       | 2.370(2)        | 2.291(2)         | 2.332(2)        | 2.339(4)       | 2.402(1)        | 2.311(6)         |
| C(1)-C(2)   | 1.512(18)      | 1.515(10)       | 1.545(9)         | 1.557(9)        | 1.556(19)      | 1.580(10)       | 1.56(3)          |
| C(2)-X  | 1.584(19)      | 1.538(8)        | 1.584(9)         | 1.548(10)       | 1.509(19)      | 1.361(9)        | 1.38(3)          |
| C(1)...X  | 2.414          | 2.321           | 2.404            | 2.394           | 2.403          | 2.335           | 2.26             |
| Bond Angles, deg  |                |                 |                  |                 |                |                 |                  |
| C(1)-Pt-X   | 70.6(4)        | 68.6(3)         | 68.4(2)          | 67.7(2)         | 66.9(5)        | 68.4(3)         | 65.4(7)          |
| C(1)-C(2)-X   | 102.4(10)      | 99.0(5)         | 100.4(5)         | 100.9(6)        | 103.2(11)      | 105.1(5)        | 100(2)           |
| Pt-C(1)-C(2)  | 95.6(8)        | 95.9(4)         | 93.5(4)          | 92.3(4)         | 91.2(8)        | 87.7(4)         | 89(1)            |
| Pt-X-C(2)   | 90.8(7)        | 90.8(4)         | 92.3(4)          | 91.7(4)         | 90.8(8)        | 96.0(4)         | 97(1)            |
| Y-Pt-Z  | 97.0(1)        | 92.8(1)         | 97.0(1)          | 97.1(1)         | 94.6(1)        | 95.5(1)         | 98.2(2)          |
| Y-Pt-C(1)   | 97.1(3)        | 107.6(2)        | 97.1(2)          | 98.6(2)         | 97.5(4)        | 102.8(2)        | 105.9(5)         |
| Z-Pt-X  | 95.0(3)        | 91.6(2)         | 99.8(2)          | 97.3(2)         | 101.1(4)       | 93.2(2)         | 90.8(4)          |
| Torsion Angles (abs values), deg  |                |                 |                  |                 |                |                 |                  |
| Pt-C(1)-C(2)-X  | 6.9            | 21.3            | 20.1             | 23.6            | 24.6           | 14.8            | 24.4             |
| C(1)-C(2)-X-Pt  | 6.6            | 20.0            | 20.0             | 23.3            | 24.1           | 15.2            | 25.5             |
| C(2)-X-Pt-C(1)  | 5.0            | 16.0            | 15.2             | 17.8            | 18.2           | 11.8            | 20.0             |
| X-Pt-C(1)-C(2)  | 5.3            | 16.3            | 15.6             | 17.7            | 17.6           | 10.1            | 17.4             |
| Dihedral Angles (abs values), deg   |                |                 |                  |                 |                |                 |                  |
| C(1)-Pt-X   | 6.6            | 9.6             | 18.0             | 10.5            | 6.4            | 4.5             | 6.8              |
| Y-Pt-Z  |                |                 |                  |                 |                |                 |                  |
| C(1)-Pt-X   | 8.3            | 25.2            | 24.4             | 28.6            | 29.7           | 18.2            | 30.0             |
| C(1)-C(2)-X   |                |                 |                  |                 |                |                 |                  |

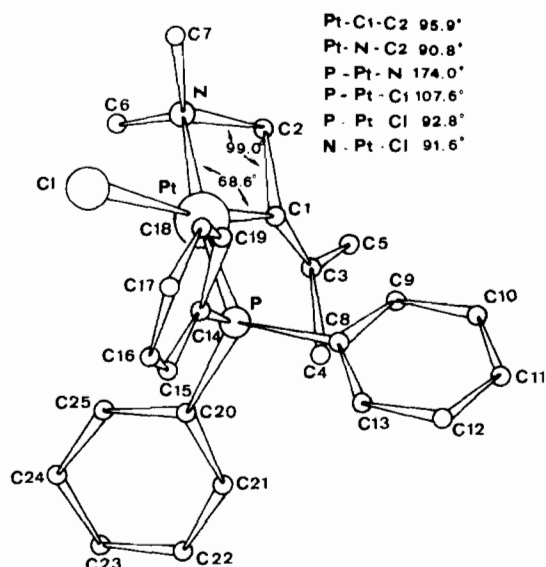
<sup>a</sup> [Pt(CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>Cl)(PPh<sub>3</sub>)<sub>2</sub>], this work. <sup>b</sup> [Pt(C(=O)Me<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>Cl)(PPh<sub>3</sub>)<sub>2</sub>], this work. <sup>c</sup> [Pt(CN)<sub>2</sub>CH<sub>2</sub>C(CN)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>], ref. 13. <sup>d</sup> [Pt(CN)<sub>2</sub>CH(Ph)C(CN)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] ref. 12. <sup>e</sup> [Pt(CN)<sub>2</sub>CH(Ph)C(CN)(COOPh)(PPh<sub>3</sub>)<sub>2</sub>], ref. 12. <sup>f</sup> [Pt(CN)<sub>2</sub>C(CN)<sub>2</sub>O(AsPh<sub>3</sub>)<sub>2</sub>], ref. 11. <sup>g</sup> [Pt(CN)<sub>2</sub>CH(CN)O(PPh<sub>3</sub>)<sub>2</sub>], ref. 14.



Pt-C1-C2 95.6°  
 Pt-N-C2 90.8°  
 P-Pt-N 166.3°

Fig. 1. Perspective view of the molecular structure of  $[\text{Pt}(\text{CH}_2\text{CH}_2\text{NMe}_2)\text{Cl}(\text{PPh}_3)]$  showing the atomic numbering scheme and some relevant bond distances and angles.

with those conclusions. Complex I, which has no bulky substituents on the organic moiety of the ring, shows a moderate deviation from planarity of the coordination sphere, and, more significantly, only a little puckering of the four-membered ring. The dihedral angle between the planes  $\text{C}(1)\text{-Pt-N}$  and  $\text{C}(1)\text{-C}(2)\text{-N}$  is in fact  $8.3^\circ$  in I, whereas the mean value for complexes III–VII is  $26^\circ$ . On the other hand complex II shows a deviation from planarity of the



Pt-C1-C2 95.9°  
 Pt-N-C2 90.8°  
 P-Pt-N 174.0°  
 P-Pt-C1 107.6°  
 P-Pt-Cl 92.8°  
 N-Pt-Cl 91.6°

Fig. 2. Perspective view of the molecular structure of  $[\text{PtC}(\text{=CMe}_2)\text{CH}_2\text{NMe}_2\text{Cl}(\text{PPh}_3)]$  showing the atomic numbering scheme and some relevant bond distances and angles.

coordination sphere greater than I and a puckering of the ring ( $25.2^\circ$ ) comparable with that observed in compounds III–VII. Moreover three other significant distortions from an ideal geometry are observable in complex II: a) A rather high bond angle  $\text{P-Pt-C}(1)$  ( $107.6^\circ$  in II *versus*  $97.1^\circ$  in I), that is actually the greatest among the analogous angles reported in Table VI. b) A remarkable high bond angle  $\text{Pt-C}(1)\text{-C}(2)$  ( $139.2^\circ$ ), that is actually the



greatest observed for platinum-alkenyl complexes [18]. c) A significantly non-zero angle ( $10.6^\circ$ ) between the mean plane of the atoms C(2), C(1), C(3), C(4), C(5), that are almost coplanar within 0.03 Å, and the Pt-C(1) vector. All these distortions can be to a large extent ascribed to the steric interactions between the C(4) methyl and the C(8)-C(13) phenyl groups (non-bonded contact C(4)-C(9) = 3.34 Å). Although these distortions probably require little energy [12], it is not unlikely that they can contribute in significant extent to the higher reactivity of complex II that has been observed in the insertion reaction of carbon monoxide [4].

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