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# The Structure of the Allylpalladium Chloride Complex $(C_3H_5PdCl)_2$ at −140 °C

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The crystal structure and molecular configuration of the allylpalladium chloride complex $(C_3H_5PdCl)_2$ have been determined from three-dimensional data taken at −140 °C. The unit cell is monoclinic, space group $P2_1/n$, $a=7{\cdot}46_2$, $b=7{\cdot}42_7$, $c=8{\cdot}60_5$ Å, $\beta=93{\cdot}5°$, two molecules of $(C_3H_5PdCl)_2$ per unit cell. The two Pd atoms are joined by chloride bridges in a planar arrangement and the allyl groups are bonded to the Pd atoms with their planes 111·5° to the plane of the Pd and Cl atoms. The C–C bonds are equal within the limit of experimental error, which along with the C–C–C bond angle of 119·8° indicates that the double bond in the allylic system is delocalized. The C atoms are all at the same distance from the Pd atoms within the limit of experimental error. The general configuration and the Pd · · · C, Pd–Cl and C ····· C distances indicate that the complex may be regarded as a half 'sandwich' complex similar in some respects to ferrocene rather than as an approximate square planar complex. After refinement by least squares, using the entire data ($R=0{\cdot}055$), the five H atoms were located approximately by a difference Fourier synthesis using limited data ($\sin\theta/\lambda<0{\cdot}6$, $R=0{\cdot}049$). The allylic system including the H atoms is planar within the limit of experimental error.

## Introduction

The reaction of allyl alcohol and PdCl at about 50 °C to form a greenish-yellow crystalline complex was first described by Smidt & Hafner (1959) and by Moiseev *et al.* (1959). Dehm & Chien (1960) investigated solutions of the allylpalladium chloride complex in deuterochloroform by nuclear magnetic resonance and infrared spectroscopy and concluded that the double bonds in the allyl groups were delocalized.

An X-ray investigation of the structure of the crystalline complex was therefore undertaken to determine the structural geometry and bond distances, in hope that information about the type of bonding might be obtained. As indicated by Cruickshank (1960), in order to determine bond distances involving relatively light atoms in the presence of moderately heavy atoms to an accuracy of ~ 0·02 Å the crystals must be essentially free of disorder and full three-dimensional data taken at low temperature must be used.

## Preliminary structure work

Single crystals of the $(C_3H_5PdCl)_2$ complex were grown slowly from toluene solutions of the purified complex. Crystals 0·30–0·33 mm in thickness and 0·40–0·47 mm in length were selected and mounted in thin walled glass capillaries. The linear absorption coefficient for Mo $K\alpha$ was ~ 46 $cm^{-1}$ and $\mu R$ for the crystals was ~ 0·70. Absorption corrections were not applied; however, separate scale factors for each layer were adjusted during the least-squares calculations.

The initial X-ray work was carried out with Buerger precession data for the [$hk0$] and [$h0l$] zones and Weissenberg data for the [$0kl$] zone. These data were taken at room temperature with Zr-filtered Mo $K\alpha$ radiation. The unit cell is monoclinic with

$$a=7{\cdot}46_2,\ b=7{\cdot}42_7,\ c=10{\cdot}8_7\ \text{Å};\ \beta=137{\cdot}0°,$$

two molecules of $(C_3H_5PdCl)_2$ per unit cell. From the extinctions, $hkl$ present in all orders, $h0l$ present with $l=2n$, and $0k0$ present with $k=2n$, the space group is $P2_1/c$. The unit cell is more conveniently described in terms of a different orientation with space group designation $P2_1/n$. The unit-cell dimensions are then

$$a=7{\cdot}46_2,\ b=7{\cdot}42_7,\ c=8{\cdot}60_5\ \text{Å};\ \beta=93{\cdot}5°.$$

The density calculated from X-ray data is $D_x \sim 2{\cdot}556$ $g.cm^{-3}$.

The Pd and Cl coordinates were determined from Patterson projections of the zonal data. The coordinates of the carbon atoms were then located approximately from electron density projections. It was decided to go directly to full three-dimensional data taken at low temperatures for refinement of the structure.

During the collection of the three-dimensional low temperature data for refinement, a note by Rowe (1962) on the structure of $(C_3H_5PdCl)_2$ appeared. The results were in general agreement with those obtained here. However, since Rowe used only two-dimensional data taken at room temperature, it was decided to continue the refinement with the three-dimensional low temperature data. Also after completion of this work a brief communication by Levdik & Porai-Koshits (1962) on the structure of $(C_3H_5PdCl)_2$ by two-dimensional methods became available.

### Refinement of the structure with the use of low temperature data

A modified Nonius Weissenberg camera with low temperature attachment was used for the low temperature work. The crystals were cooled by a stream of dry nitrogen which had been cooled by passing through a copper coil submerged in liquid nitrogen in a large Dewar vessel. The level of liquid nitrogen was kept constant by a constant level device connected to a large reservoir of the liquid. The temperature of the crystal was measured by a thermocouple adjacent to the crystal.

Eight layers $0kl$–$7kl$ of Weissenberg data were taken at $-140$ °C for the $(C_3H_5PdCl)_2$ complex, Zr-filtered Mo radiation being used. The multiple film technique was used with 0·0015″ Cu foil interleaved between the films. In addition four layers, $h0l$–$h3l$ were also taken with another crystal and used to place the $0kl$–$7kl$ layers on the same intensity scale. The intensities were measured visually using calibrated scales prepared with the same crystals used in obtaining the intensity data. A total of 1890 independent reflections were measured.

The approximate parameters obtained from the two-dimensional data were used to compute a three-dimensional difference Fourier synthesis to determine the coordinates of the carbon atoms more accurately. Refinement was then carried out by least-squares. Atomic form factors of McWeeny (1951) were used for C and H, Dawson's (1960) values were used for Cl and Thomas–Fermi values for Pd (*International Tables for X-ray Crystallography*, 1962). The form factors for Pd were corrected for the real contribution of anomalous dispersion (Dauben & Templeton, 1955). The least-squares calculations were carried out on the IBM 7090 computer with the Busing & Levy (1959*a*) IBM 704 program with a compatibility package. The function $(|F_o|-S|F_c|)^2$ was minimized, where $S$ is a scale factor for converting $F_o$ and $F_c$ to the same scale. A weighting scheme similar to that suggested by Hughes (1941) was used. The higher levels were given slightly less weight since these data were believed to be somewhat less accurate. Individual isotropic temperature factors for each atom were initially used.

The $R$ index dropped to 0·10 in a few cycles but was not appreciably lowered with additional cycles. Individual anisotropic temperature factors were then applied and $R$ dropped to 0·066 in two cycles. The inclusion of hydrogen atoms, at the positions expected for a planar molecule, improved only slightly the agreement between calculated and observed intensities. A few errors in the indexing of some of the high order reflections were corrected and a final least-squares calculation was run. At this point the corrections were all less than their standard deviations. The final $R$ value including only those reflections for which $F_o>0$ was 0·055.

Since the agreement between the calculated and observed data was quite good, it was decided to see if the hydrogen atoms in the allylic system could be located. Their coordinates would be useful for the interpretation of nuclear magnetic resonance and infrared data. In addition if there were some mixing of the $\pi$ and $\sigma$ bonds in the allylic system the hydrogen atoms would be expected to move back, away from the metal ion, and destroy the planarity of the allylic system. The $hkl$ data were then restricted to values for which $\sin\theta/\lambda<0{\cdot}6$ (827 reflections) and several cycles of least-squares were calculated keeping the positional and anisotropic temperature parameters for the Pd and Cl atoms constant at the values determined from the entire data. Contributions of hydrogen were included assuming the molecule was planar with a C–H distance of $\sim 1{\cdot}08$ Å and an H–C–H bond angle of $\sim 118°$. Anisotropic temperature factors for the hydrogen atoms were taken equal to those of the carbon atoms to which they were attached. The positional and temperature parameters of the hydrogen atoms were not varied during the least-squares calculations with limited data. Two sets of least-squares calculations using form factors for $Pd^{2+}$ and $Pd^{\circ}$ corrected for real part of the dispersion corrections were carried out; no significant difference was noted in the results. The final $R$ value for $Pd^{2+}$ was 0·049 for those reflections for which $F_o>0$ for the limited data. A three-dimensional difference Fourier synthesis was then computed with $[F_o-F_{(Pd^{2+}+Cl^-)}]$ as coefficients. Small peaks of about the expected magnitude occurred in the difference Fourier synthesis at, or very close to, the positions expected for hydrogen atoms in a planar molecule. A few additional peaks of similar but generally smaller magnitude also appeared in the difference Fourier synthesis. In addition, connecting rods of electron density between the C–C and C–H atoms were observed in the difference Fourier synthesis. A composite drawing of the three-dimensional electron density map of the carbon and hydrogen atoms with the sections taken through, or very close to, the center of maximum electron density of each atom is shown in Fig. 5.

The final positional and temperature parameters along with their standard deviations for the Pd, Cl and C atoms are given in Table 2. The calculated and observed structure factors are listed in Table 1. The reflections that were unobserved or too faint to measure, are indicated by $F=0$. Reflections that could not be measured accurately were given zero or reduced weight in the least-squares calculations. They are marked with an asterisk in Table 1.

### Discussion of the structure

The configuration of the atoms in the $(C_3H_5PdCl)_2$ complex and the packing arrangement in the unit cell are shown in Figs. 1 and 2. The general arrangement of the atoms in the complex is more conveniently

## Table 1. *Observed and calculated structure factors*

The four columns within each group contain the values $k$, $l$, $10F_o$, an $10F_c$. Unobserved reflections and reflections too faint to measure are given by $F_o=0$. Reflections marked with an asterisk in addition to those with $F_o=0$ were given zero weight in the least-squares calculation

OKL

| | | | |
|---|---|---|---|
| 0 | 0 | 3360 | 3360 |
| 2 | 0 | 753 | -676 |
| 4 | 0 | 255 | -223 |
| 6 | 0 | 431 | 394 |
| 8 | 0 | 818 | -838 |
| 10 | 0 | 323 | 317 |
| 12 | 0 | 119 | 111 |
| 14 | 0 | 129 | -146 |
| 16 | 0 | 154 | 139 |
| 0 | 2 | 1457 | 1558 |
| 0 | 4 | 142 | 130 |
| 0 | 6 | 380 | -383 |
| 0 | 8 | 450 | -469 |
| 0 | 10 | 378 | -382 |
| 0 | 12 | 277 | -286 |
| 1 | 1 | 716 | 688 |
| 1 | 2 | 1201 | 1245 |
| 1 | 3 | 182 | 118 |
| 1 | 4 | 1162 | 1186 |
| 1 | 5 | 332 | -315 |
| 1 | 6 | 745 | 777 |
| 1 | 7 | 134 | -126 |
| 1 | 8 | 343 | 334 |
| 1 | 9 | 0 | -75 |
| 1 | 10 | 0 | 36 |
| 1 | 11* | 123 | -137 |
| 1 | 12 | 142 | -128 |
| 1 | 13 | 0 | -86 |
| 1 | 14* | 158 | -178 |
| 2 | 1 | 425 | 452 |
| 2 | 2 | 849 | -838 |
| 2 | 3 | 1015 | 1024 |
| 2 | 4 | 474 | -451 |
| 2 | 5 | 629 | 610 |
| 2 | 6 | 127 | 124 |
| 2 | 7 | 199 | 209 |
| 2 | 8 | 369 | 392 |
| 2 | 9 | 89 | 104 |
| 2 | 10 | 348 | 347 |
| 2 | 11 | 0 | -40 |
| 2 | 12 | 153 | 155 |
| 2 | 13 | 151 | -134 |
| 2 | 14 | 0 | 29 |
| 2 | 15* | 125 | -128 |
| 3 | 1 | 1084 | -1136 |
| 3 | 2 | 278 | 254 |
| 3 | 3 | 601 | -593 |
| 3 | 4 | 308 | -272 |
| 3 | 5 | 0 | 31 |
| 3 | 6 | 410 | -406 |
| 3 | 7 | 419 | 442 |
| 3 | 8 | 234 | -236 |
| 3 | 9 | 445 | 481 |
| 3 | 10 | 0 | 28 |
| 3 | 11 | 297 | 299 |
| 3 | 12 | 0 | 111 |
| 3 | 13 | 130 | 117 |
| 4 | 1 | 253 | -252 |
| 4 | 2 | 0 | -55 |
| 4 | 3 | 620 | -645 |
| 4 | 4* | 100 | 76 |
| 4 | 5 | 880 | -905 |
| 4 | 6* | 67 | 77 |
| 4 | 7 | 652 | -683 |
| 4 | 8 | 0 | 10 |
| 4 | 9* | 82 | -97 |
| 4 | 10 | 0 | -32 |
| 4 | 11 | 160 | 184 |
| 4 | 12 | 0 | 9 |
| 4 | 13* | 196 | 198 |
| 5 | 1 | 681 | 667 |
| 5 | 2* | 90 | -29 |
| 5 | 3 | 492 | 486 |
| 5 | 4 | 339 | -327 |
| 5 | 5 | 179 | 161 |
| 5 | 6 | 354 | -362 |
| 5 | 7 | 333 | -342 |
| 5 | 8 | 174 | -157 |
| 5 | 9 | 453 | -462 |
| 5 | 10 | 0 | 31 |
| 5 | 11 | 265 | -282 |
| 5 | 12 | 105 | 89 |
| 6 | 1 | 205 | 176 |
| 6 | 2 | 524 | 514 |
| 6 | 3 | 407 | 387 |
| 6 | 4 | 382 | 362 |
| 6 | 5 | 357 | 373 |
| 6 | 6 | 0 | -68 |
| 6 | 7 | 254 | 236 |
| 6 | 8 | 322 | -330 |
| 6 | 9 | 89 | 101 |
| 6 | 10 | 309 | -323 |
| 6 | 11 | 0 | -44 |
| 6 | 12 | 103 | -126 |
| 7 | 1 | 302 | -286 |
| 7 | 2 | 381 | 364 |
| 7 | 3 | 0 | -43 |
| 7 | 4 | 569 | 578 |
| 7 | 5 | 157 | 153 |
| 7 | 6 | 487 | 514 |

OKL

| | | | |
|---|---|---|---|
| 7 | 7 | 0 | 42 |
| 7 | 8 | 303 | 301 |
| 8 | 1 | 0 | -32 |
| 8 | 2 | 552 | -541 |
| 8 | 3* | 65 | -72 |
| 8 | 4 | 105 | -97 |
| 8 | 5* | 69 | 58 |
| 8 | 6 | 143 | 139 |
| 8 | 7* | 128 | 115 |
| 8 | 8 | 242 | 253 |
| 8 | 9 | 0 | 17 |
| 8 | 10 | 249 | 252 |
| 8 | 11 | 0 | -32 |
| 8 | 12 | 188 | 173 |
| 9 | 1 | 232 | -225 |
| 9 | 2 | 415 | -417 |
| 9 | 3 | 110 | -105 |
| 9 | 4 | 449 | -432 |
| 9 | 5 | 0 | 17 |
| 9 | 6 | 281 | -289 |
| 9 | 7 | 0 | 73 |
| 9 | 8 | 115 | -123 |
| 9 | 9 | 83 | 102 |
| 10 | 1 | 161 | -149 |
| 10 | 2 | 258 | 238 |
| 10 | 3 | 343 | -341 |
| 10 | 4* | 77 | 77 |
| 10 | 5 | 254 | -254 |
| 10 | 6* | 80 | -89 |
| 10 | 7* | 82 | -111 |
| 10 | 8 | 120 | -134 |
| 11 | 1 | 433 | 386 |
| 11 | 2 | 0 | -14 |
| 11 | 3 | 180 | 183 |
| 11 | 4 | 82 | 84 |
| 11 | 5 | 83 | -67 |
| 11 | 6 | 0 | 108 |
| 11 | 7 | 149 | -158 |
| 11 | 8 | 0 | 44 |
| 11 | 9 | 179 | -164 |
| 12 | 1* | 119 | 89 |
| 12 | 2 | 0 | 36 |
| 12 | 3 | 276 | 234 |
| 12 | 4 | 0 | -34 |
| 12 | 5 | 282 | 271 |
| 12 | 6 | 0 | -36 |
| 12 | 7 | 179 | 181 |

1KL

| | | | |
|---|---|---|---|
| 1 | 0* | 683 | 592 |
| 2 | 0* | 69 | -88 |
| 3 | 0 | 1003 | -967 |
| 4 | 0 | 1185 | 1181 |
| 5 | 0 | 650 | 619 |
| 6 | 0 | 325 | -304 |
| 7 | 0 | 251 | -240 |
| 8 | 0 | 162 | -179 |
| 9 | 0 | 179 | -185 |
| 10 | 0 | 140 | 138 |
| 11 | 0 | 274 | 283 |
| 12 | 0 | 248 | -237 |
| 13 | 0 | 163 | -151 |
| 0 | 1 | 1487 | 1449 |
| 0 | 3 | 891 | 834 |
| 0 | 5 | 824 | 787 |
| 0 | 7 | 392 | 356 |
| 0 | 9 | 196 | -193 |
| 0 | 11 | 374 | -373 |
| 0 | 13 | 262 | -274 |
| 1 | 2 | 200 | 163 |
| 1 | 3 | 146 | 82 |
| 1 | 4 | 229 | 171 |
| 1 | 5 | 484 | 450 |
| 1 | 6 | 225 | 196 |
| 1 | 7 | 642 | 637 |
| 1 | 8 | 104 | 99 |
| 1 | 9 | 480 | 472 |
| 1 | 10 | 135 | -143 |
| 1 | 11 | 174 | 173 |
| 1 | 12* | 153 | -180 |
| 2 | 1 | 804 | -756 |
| 2 | 2 | 85 | 73 |
| 2 | 3 | 1067 | -1039 |
| 2 | 4 | 305 | 285 |
| 2 | 5 | 482 | -444 |
| 2 | 6 | 427 | 404 |
| 2 | 7 | 0 | 34 |
| 2 | 8 | 473 | 474 |
| 2 | 9 | 166 | 162 |
| 2 | 10 | 308 | 329 |
| 2 | 11 | 172 | 177 |
| 2 | 12 | 0 | 35 |
| 2 | 13 | 137 | 141 |
| 3 | 1 | 669 | 596 |
| 3 | 2 | 1262 | -1264 |
| 3 | 3 | 0 | -25 |
| 3 | 4 | 929 | -887 |
| 3 | 5 | 503 | -494 |
| 3 | 6 | 333 | -320 |

1KL

| | | | |
|---|---|---|---|
| 3 | 7 | 250 | -229 |
| 3 | 8 | 122 | 100 |
| 3 | 9* | 59 | -40 |
| 3 | 10 | 262 | 278 |
| 3 | 11 | 0 | -5 |
| 3 | 12 | 249 | 267 |
| 3 | 13 | 0 | -5 |
| 3 | 14 | 182 | 168 |
| 4 | 1* | 88 | -43 |
| 4 | 2 | 267 | 265 |
| 4 | 3 | 109 | 99 |
| 4 | 4 | 623 | -605 |
| 4 | 5 | 0 | -8 |
| 4 | 6 | 818 | -851 |
| 4 | 7 | 75 | -66 |
| 4 | 8 | 529 | -550 |
| 4 | 9 | 0 | -29 |
| 4 | 10 | 214 | -202 |
| 5 | 1 | 380 | 342 |
| 5 | 2 | 1013 | 1062 |
| 5 | 3* | 85 | -48 |
| 5 | 4 | 761 | 795 |
| 5 | 5 | 360 | -352 |
| 5 | 6 | 247 | 243 |
| 5 | 7 | 195 | -215 |
| 5 | 8 | 207 | -198 |
| 5 | 9* | 109 | -90 |
| 5 | 10 | 230 | -241 |
| 5 | 11 | 0 | -52 |
| 5 | 12 | 181 | -187 |
| 5 | 13 | 0 | -3 |
| 5 | 14 | 138 | -129 |
| 6 | 1 | 538 | 547 |
| 6 | 2 | 0 | -31 |
| 6 | 3 | 742 | 804 |
| 6 | 4 | 227 | 212 |
| 6 | 5 | 353 | 359 |
| 6 | 6 | 364 | 370 |
| 6 | 7* | 73 | -64 |
| 6 | 8 | 310 | 322 |
| 6 | 9 | 151 | -155 |
| 6 | 10 | 162 | 163 |
| 6 | 11* | 113 | -147 |
| 7 | 1 | 436 | -446 |
| 7 | 2* | 94 | -63 |
| 7 | 3 | 54 | 46 |
| 7 | 4 | 56 | -71 |
| 7 | 5 | 397 | 419 |
| 7 | 6 | 105 | -101 |
| 7 | 7 | 419 | 452 |
| 7 | 8 | 0 | -61 |
| 7 | 9 | 281 | 284 |
| 8 | 1 | 519 | -546 |
| 8 | 2* | 91 | -76 |
| 8 | 3 | 449 | -473 |
| 8 | 4 | 0 | 52 |
| 8 | 5 | 359 | -378 |
| 8 | 6 | 111 | 118 |
| 8 | 7 | 150 | -150 |
| 8 | 8 | 0 | 33 |
| 8 | 9 | 144 | 141 |
| 8 | 10 | 0 | -33 |
| 8 | 11 | 212 | 218 |
| 9 | 1 | 107 | 102 |
| 9 | 2 | 182 | -203 |
| 9 | 3 | 0 | -54 |
| 9 | 4 | 189 | -195 |
| 9 | 5 | 133 | -135 |
| 9 | 6* | 118 | -106 |
| 9 | 7 | 261 | -273 |
| 9 | 8 | 0 | 24 |
| 9 | 9 | 220 | -238 |
| 10 | 1 | 221 | 232 |
| 10 | 2 | 0 | 10 |
| 10 | 3 | 192 | 203 |
| 10 | 4 | 98 | -98 |
| 10 | 5 | 123 | 128 |
| 10 | 6 | 162 | -184 |
| 10 | 7 | 0 | 30 |
| 10 | 8 | 248 | -222 |
| 10 | 9 | 0 | -35 |
| 10 | 10 | 150 | -152 |
| 11 | 1* | 71 | -85 |
| 11 | 2 | 312 | 320 |
| 11 | 3 | 0 | 24 |
| 11 | 4 | 241 | 251 |
| 11 | 5 | 106 | 107 |
| 12 | 1 | 0 | 34 |
| 12 | 2 | 0 | -43 |
| 12 | 3 | 0 | -20 |
| 12 | 4 | 155 | 150 |
| 12 | 5 | 0 | 24 |
| 12 | 6 | 218 | 211 |
| 0 | -1 | 853 | 910 |
| 0 | -3 | 251 | -232 |
| 0 | -5 | 1063 | -1033 |
| 0 | -7 | 1027 | -1042 |
| 0 | -9 | 453 | -463 |
| 0 | -11 | 104 | -97 |
| 1 | -1 | 1256 | -1450 |

1KL

| | | | |
|---|---|---|---|
| 1 | -2 | 881 | 852 |
| 1 | -3 | 1368 | -1399 |
| 1 | -4 | 267 | -219 |
| 1 | -5 | 827 | -787 |
| 1 | -6 | 489 | -475 |
| 1 | -7* | 71 | -41 |
| 1 | -8 | 249 | -261 |
| 1 | -9 | 342 | 333 |
| 1 | -10* | 57 | -64 |
| 1 | -11 | 322 | 328 |
| 1 | -12 | 0 | 17 |
| 1 | -13 | 205 | 226 |
| 2 | -1 | 139 | -137 |
| 2 | -2 | 1056 | -1009 |
| 2 | -3 | 254 | 225 |
| 2 | -4 | 1051 | -1026 |
| 2 | -5 | 415 | 422 |
| 2 | -6 | 288 | -298 |
| 2 | -7 | 427 | 439 |
| 2 | -8 | 149 | 156 |
| 2 | -9 | 369 | 395 |
| 2 | -10 | 262 | 267 |
| 2 | -11 | 162 | 169 |
| 2 | -12 | 190 | 185 |
| 3 | -1 | 432 | 418 |
| 3 | -2 | 223 | -193 |
| 3 | -3 | 223 | 180 |
| 3 | -4 | 406 | 385 |
| 3 | -5 | 0 | 49 |
| 3 | -6 | 650 | 641 |
| 3 | -7 | 163 | 144 |
| 3 | -8 | 540 | 569 |
| 3 | -9 | 0 | 53 |
| 3 | -10 | 279 | 282 |
| 3 | -11 | 132 | -141 |
| 3 | -12 | 0 | 22 |
| 3 | -13 | 121 | -125 |
| 4 | -1 | 117 | -125 |
| 4 | -2 | 1069 | 1013 |
| 4 | -3 | 107 | -74 |
| 4 | -4 | 584 | 562 |
| 4 | -5* | 44 | 68 |
| 4 | -6 | 390 | 366 |
| 4 | -7 | 146 | 118 |
| 4 | -8 | 0 | 8 |
| 4 | -9 | 0 | 12 |
| 4 | -10 | 264 | -260 |
| 4 | -11 | 0 | -28 |
| 4 | -12 | 303 | -302 |
| 4 | -13 | 0 | -17 |
| 4 | -14 | 148 | -177 |
| 5 | -1 | 388 | 383 |
| 5 | -2 | 87 | -72 |
| 5 | -3 | 283 | 279 |
| 5 | -4 | 288 | -281 |
| 5 | -5 | 184 | 173 |
| 5 | -6 | 369 | -393 |
| 5 | -7 | 105 | 97 |
| 5 | -8 | 381 | -404 |
| 5 | -9 | 0 | -37 |
| 5 | -10 | 261 | -267 |
| 5 | -11 | 148 | -160 |
| 6 | -1* | 45 | 79 |
| 6 | -2 | 505 | -523 |
| 6 | -3 | 226 | -219 |
| 6 | -4 | 474 | -464 |
| 6 | -5 | 306 | -295 |
| 6 | -6 | 171 | -163 |
| 6 | -7 | 287 | -281 |
| 6 | -8 | 0 | 48 |
| 6 | -9 | 299 | -317 |
| 6 | -10 | 130 | 113 |
| 6 | -11 | 137 | -153 |
| 6 | -12* | 87 | 135 |
| 7 | -1 | 699 | -706 |
| 7 | -2 | 288 | -287 |
| 7 | -3 | 645 | -638 |
| 7 | -4* | 53 | 83 |
| 7 | -5 | 295 | -310 |
| 7 | -6 | 249 | 235 |
| 7 | -7 | 0 | -49 |
| 7 | -8 | 124 | 116 |
| 7 | -9 | 156 | 138 |
| 7 | -10 | 0 | 29 |
| 7 | -11 | 209 | 217 |
| 7 | -12 | 0 | -1 |
| 7 | -13 | 185 | 178 |
| 8 | -1 | 336 | -332 |
| 8 | -2 | 0 | -32 |
| 8 | -3 | 124 | 122 |
| 8 | -4* | 70 | 75 |
| 8 | -5 | 459 | 455 |
| 8 | -6 | 0 | 12 |
| 8 | -7 | 459 | 474 |
| 9 | -1 | 385 | 403 |
| 9 | -2 | 0 | -70 |
| 9 | -3 | 495 | 508 |
| 9 | -4 | 122 | 127 |
| 9 | -5 | 330 | 355 |
| 9 | -6 | 188 | 193 |

1KL

| | | | |
|---|---|---|---|
| 9 | -7 | 0 | 10 |
| 9 | -8 | 109 | 107 |
| 9 | -9 | 181 | -175 |
| 9 | -10 | 0 | 57 |
| 9 | -11 | 150 | -151 |
| 10 | -1 | 148 | 144 |
| 10 | -2 | 338 | 362 |
| 10 | -3 | 0 | 5 |
| 10 | -4 | 342 | 366 |
| 10 | -5 | 149 | -156 |
| 10 | -6* | 84 | 97 |
| 10 | -7 | 211 | -225 |
| 10 | -8 | 0 | -82 |
| *10 | -9 | 138 | -149 |
| 10 | -10 | 120 | -126 |
| 11 | -1* | 83 | -76 |
| 11 | -2* | 96 | 121 |
| 11 | -3 | 0 | -50 |
| 11 | -4 | 148 | -146 |
| 11 | -5 | 0 | -47 |
| 11 | -6 | 289 | -276 |
| 11 | -7 | 0 | -51 |
| 11 | -8 | 259 | -239 |
| 12 | -1 | 0 | 57 |
| 12 | -2 | 299 | -288 |
| 12 | -3 | 0 | 15 |
| 12 | -4 | 270 | -226 |

2KL

| | | | |
|---|---|---|---|
| 2 | 0 | 264 | -276 |
| 3 | 0 | 585 | 603 |
| 4 | 0 | 184 | 127 |
| 5 | 0 | 487 | 494 |
| 6 | 0 | 149 | 146 |
| 7 | 0 | 684 | -693 |
| 8 | 0* | 117 | 86 |
| 9 | 0 | 370 | 358 |
| 10 | 0 | 0 | 9 |
| 11 | 0 | 136 | -120 |
| 12 | 0 | 0 | -59 |
| 13 | 0* | 107 | -124 |
| 0 | 2* | 455 | 323 |
| 0 | 4 | 1017 | 999 |
| 0 | 6 | 984 | 1040 |
| 0 | 8 | 395 | 371 |
| 0 | 10 | 122 | -128 |
| 0 | 12 | 215 | -198 |
| 0 | 14 | 195 | -163 |
| 1 | 2 | 1003 | -971 |
| 1 | 3 | 355 | 346 |
| 1 | 4 | 484 | -446 |
| 1 | 5 | 621 | 613 |
| 1 | 6 | 254 | 236 |
| 1 | 7 | 343 | 315 |
| 1 | 8 | 536 | 551 |
| 1 | 9* | 72 | 18 |
| 1 | 10 | 405 | 406 |
| 1 | 11* | 96 | -102 |
| 1 | 12 | 209 | 188 |
| 2 | 1 | 870 | -850 |
| 2 | 2 | 758 | -714 |
| 2 | 3 | 891 | -867 |
| 2 | 4 | 667 | -644 |
| 2 | 5 | 140 | -101 |
| 2 | 6 | 356 | -356 |
| 2 | 7 | 408 | 378 |
| 2 | 8 | 222 | -203 |
| 2 | 9 | 401 | 419 |
| 2 | 10 | 0 | -43 |
| 2 | 11 | 221 | 227 |
| 2 | 12 | 125 | 120 |
| 3 | 1 | 379 | -316 |
| 3 | 2 | 152 | 128 |
| 3 | 3 | 791 | -812 |
| 3 | 4 | 239 | -224 |
| 3 | 5 | 765 | -818 |
| 3 | 6 | 157 | -144 |
| 3 | 7 | 532 | -553 |
| 3 | 8 | 0 | 2 |
| 3 | 9 | 198 | -188 |
| 3 | 10 | 123 | -120 |
| 3 | 11* | 70 | 83 |
| 3 | 12* | 90 | -121 |
| 3 | 13* | 156 | 165 |
| 4 | 1 | 1189 | 1233 |
| 4 | 2 | 106 | 81 |
| 4 | 3 | 368 | 387 |
| 4 | 4* | 46 | -18 |
| 4 | 5* | 49 | 11 |
| 4 | 6 | 125 | -128 |
| 4 | 7 | 216 | -224 |
| 4 | 8* | 73 | -44 |
| 4 | 9 | 332 | -352 |
| 4 | 10 | 0 | 25 |
| 4 | 11 | 318 | -317 |
| 4 | 12 | 0 | 22 |
| 4 | 13 | 184 | -164 |
| 5 | 1 | 480 | 485 |
| 5 | 2 | 254 | 236 |

Table 1 (*cont.*)

2KL

| | | | |
|---|---|---|---|
| 5 | 3 | 687 | 702 |
| 5 | 4 | 0 | -21 |
| 5 | 5 | 520 | 533 |
| 5 | 6 | 96 | -85 |
| 5 | 7 | 343 | 357 |
| 5 | 8 | 0 | -77 |
| 5 | 9 | 174 | 149 |
| 5 | 10 | 159 | -153 |
| 5 | 11 | 0 | -12 |
| 5 | 12 | 94 | -117 |
| 5 | 13* | 113 | -132 |
| 6 | 1 | 508 | -513 |
| 6 | 2 | 478 | 498 |
| 6 | 3 | 335 | -324 |
| 6 | 4 | 467 | 474 |
| 6 | 5* | 56 | 17 |
| 6 | 6 | 225 | 222 |
| 6 | 7 | 227 | 229 |
| 6 | 8 | 146 | 164 |
| 6 | 9 | 201 | 212 |
| 6 | 10 | 0 | 70 |
| 6 | 11* | 131 | 142 |
| 7 | 1 | 109 | 84 |
| 7 | 2 | 489 | -504 |
| 7 | 3 | 159 | -135 |
| 7 | 4 | 124 | -115 |
| 7 | 5 | 303 | -300 |
| 7 | 6 | 179 | 168 |
| 7 | 7 | 143 | -143 |
| 7 | 8 | 258 | 260 |
| 7 | 9 | 0 | 10 |
| 7 | 10 | 249 | 247 |
| 7 | 11 | 0 | 63 |
| 7 | 12 | 152 | 151 |
| 8 | 1* | 59 | -94 |
| 8 | 2 | 242 | -250 |
| 8 | 3* | 61 | 70 |
| 8 | 4 | 452 | -491 |
| 8 | 5 | 0 | 35 |
| 8 | 6 | 434 | -470 |
| 8 | 7 | 0 | -14 |
| 8 | 8 | 196 | -181 |
| 9 | 1 | 0 | -44 |
| 9 | 2 | 346 | 363 |
| 9 | 3 | 187 | -187 |
| 9 | 4 | 203 | 201 |
| 9 | 5 | 230 | -235 |
| 9 | 6* | 72 | -103 |
| 9 | 7* | 90 | -121 |
| 9 | 8 | 323 | -286 |
| 9 | 9 | 0 | -20 |
| 9 | 10 | 232 | -200 |
| 10 | 1 | 308 | 310 |
| 10 | 2 | 131 | 145 |
| 10 | 3 | 287 | 299 |
| 10 | 4 | 204 | 208 |
| 10 | 5 | 0 | 36 |
| 10 | 6 | 201 | 200 |
| 10 | 7 | 164 | -167 |
| 10 | 8* | 80 | 92 |
| 10 | 9 | 186 | -187 |
| 11 | 1 | 0 | 35 |
| 11 | 2 | 0 | -30 |
| 11 | 3 | 227 | 242 |
| 11 | 4 | 0 | 40 |
| 11 | 5 | 345 | 323 |
| 11 | 6 | 0 | 34 |
| 11 | 7 | 243 | 229 |
| 12 | 1 | 289 | -305 |
| 12 | 2 | 0 | -33 |
| 12 | 3 | 139 | -159 |
| 13 | 3 | 167 | -177 |
| 0 | -2 | 592 | -668 |
| 0 | -4 | 715 | -702 |
| 0 | -6 | 879 | -906 |
| 0 | -8 | 440 | -468 |
| 0 | -10 | 0 | 52 |
| 0 | -12 | 241 | 252 |
| 0 | -14 | 249 | 220 |
| 1 | -2 | 636 | -627 |
| 1 | -3 | 104 | -90 |
| 1 | -4 | 339 | -312 |
| 1 | -5 | 384 | -379 |
| 1 | -6 | 208 | 187 |
| 1 | -7 | 402 | -390 |
| 1 | -8 | 511 | 519 |
| 1 | -9 | 178 | -168 |
| 1 | -10 | 425 | 460 |
| 1 | -11* | 70 | 90 |
| 1 | -12 | 237 | 236 |
| 1 | -13* | 97 | 114 |
| 2 | -1 | 689 | -685 |
| 2 | -2 | 512 | 506 |
| 2 | -3 | 607 | -641 |
| 2 | -4 | 845 | 856 |
| 2 | -5 | 203 | -205 |
| 2 | -6 | 469 | 469 |
| 2 | -7 | 194 | 213 |
| 2 | -8 | 186 | 174 |
| 2 | -9 | 423 | 443 |
| 2 | -10 | 0 | 9 |
| 2 | -11 | 324 | 321 |
| 2 | -12* | 92 | -109 |
| 2 | -13* | 80 | 89 |
| 3 | -1 | 495 | 468 |
| 3 | -2 | 746 | 705 |
| 3 | -3 | 958 | 938 |

2KL

| | | | |
|---|---|---|---|
| 3 | -4 | 0 | 17 |
| 3 | -5 | 800 | 852 |
| 3 | -6 | 283 | -263 |
| 3 | -7 | 509 | 529 |
| 3 | -8 | 122 | -113 |
| 3 | -9 | 183 | 164 |
| 3 | -10* | 68 | -78 |
| 3 | -11* | 95 | -89 |
| 3 | -12* | 94 | -76 |
| 3 | -13 | 167 | -182 |
| 3 | -14 | 0 | -46 |
| 3 | -15* | 107 | -151 |
| 4 | -1 | 1344 | 1384 |
| 4 | -2* | 52 | -7 |
| 4 | -3 | 567 | 547 |
| 4 | -4* | 75 | -65 |
| 4 | -5 | 183 | -165 |
| 4 | -6* | 66 | 43 |
| 4 | -7 | 450 | -459 |
| 4 | -8* | 50 | 54 |
| 4 | -9 | 371 | -384 |
| 4 | -10 | 0 | 10 |
| 4 | -11 | 273 | -270 |
| 4 | -12 | 0 | -30 |
| 4 | -13* | 148 | -159 |
| 4 | -14 | 0 | -26 |
| 5 | -1 | 352 | -336 |
| 5 | -2 | 466 | 442 |
| 5 | -3 | 806 | -828 |
| 5 | -4 | 0 | 24 |
| 5 | -5 | 765 | -765 |
| 5 | -6 | 224 | -201 |
| 5 | -7 | 362 | -379 |
| 5 | -8 | 121 | -139 |
| 5 | -9 | 0 | -61 |
| 5 | -10 | 115 | -127 |
| 5 | -11 | 0 | 50 |
| 5 | -12 | 98 | -99 |
| 5 | -13 | 119 | 123 |
| 6 | -1 | 529 | -538 |
| 6 | -2 | 473 | -467 |
| 6 | -3 | 433 | -406 |
| 6 | -4 | 713 | -706 |
| 6 | -5 | 115 | -83 |
| 6 | -6 | 339 | -344 |
| 6 | -7 | 225 | 215 |
| 6 | -8* | 68 | -86 |
| 6 | -9 | 264 | 267 |
| 6 | -10 | 0 | 20 |
| 6 | -11* | 168 | 181 |
| 7 | -1 | 0 | -32 |
| 7 | -2 | 530 | -560 |
| 7 | -3 | 0 | 6 |
| 7 | -4 | 122 | -119 |
| 7 | -5 | 201 | 178 |
| 7 | -6 | 246 | 241 |
| 7 | -7 | 222 | 221 |
| 7 | -8 | 352 | 354 |
| 7 | -9 | 92 | 111 |
| 7 | -10 | 270 | 274 |
| 8 | -1 | 183 | -164 |
| 8 | -2 | 322 | 302 |
| 8 | -3 | 0 | -29 |
| 8 | -4 | 432 | 420 |
| 8 | -5* | 69 | 83 |
| 8 | -6 | 443 | 461 |
| 8 | -7* | 73 | 108 |
| 8 | -8 | 225 | 233 |
| 8 | -9 | 0 | 5 |
| 8 | -12 | 150 | -138 |
| 9 | -1 | 0 | 57 |
| 9 | -2 | 230 | 229 |
| 9 | -3 | 188 | 170 |
| 9 | -4 | 159 | 169 |
| 9 | -5 | 241 | 248 |
| 9 | -6 | 0 | -19 |
| 9 | -7 | 164 | 153 |
| 9 | -8 | 229 | -237 |
| 9 | -9 | 0 | 15 |
| 9 | -10 | 247 | -239 |
| 10 | -1 | 238 | 241 |
| 10 | -2 | 91 | -113 |
| 10 | -3 | 212 | 206 |
| 10 | -4 | 186 | -174 |
| 10 | -5 | 0 | 50 |
| 10 | -6 | 192 | -182 |
| 10 | -7* | 141 | -123 |
| 10 | -8 | 103 | -117 |
| 10 | -9 | 212 | -214 |
| 11 | -1* | 142 | -125 |
| 11 | -2* | 143 | -129 |
| 11 | -3 | 252 | -248 |
| 11 | -4 | 0 | -17 |
| 11 | -5 | 274 | -268 |
| 11 | -6 | 0 | 37 |
| 11 | -7 | 226 | -218 |
| 12 | -1 | 322 | -312 |
| 12 | -2 | 0 | -16 |
| 12 | -3* | 169 | -147 |
| 13 | -3 | 228 | 198 |
| 13 | -4 | 0 | -17 |
| 13 | -5 | 217 | 190 |

3KL

| | | | |
|---|---|---|---|
| 2 | 0 | 614 | -638 |
| 3 | 0 | 786 | 795 |
| 4 | 0 | 583 | 582 |
| 5 | 0 | 449 | -436 |
| 6 | 0 | 365 | -364 |
| 7 | 0 | 279 | 259 |
| 8 | 0 | 0 | 1 |
| 9 | 0 | 221 | 224 |
| 10 | 0 | 228 | 215 |
| 11 | 0 | 292 | -305 |
| 12 | 0 | 205 | -197 |
| 0 | 1 | 876 | -822 |
| 0 | 3 | 478 | 434 |
| 0 | 5 | 830 | 820 |
| 0 | 7 | 627 | 661 |
| 0 | 9 | 331 | 328 |
| 0 | 11 | 176 | 152 |
| 1 | 2* | 199 | -144 |
| 1 | 3 | 1104 | -1106 |
| 1 | 4 | 492 | 478 |
| 1 | 5 | 532 | -536 |
| 1 | 6 | 362 | 343 |
| 1 | 7 | 0 | -24 |
| 1 | 8* | 78 | 74 |
| 1 | 9 | 201 | 211 |
| 1 | 10 | 0 | 64 |
| 1 | 11 | 255 | 234 |
| 1 | 12 | 0 | 42 |
| 1 | 13 | 197 | 198 |
| 2 | 1 | 219 | 174 |
| 2 | 2 | 1046 | -1108 |
| 2 | 3* | 80 | -79 |
| 2 | 4 | 703 | -711 |
| 2 | 5 | 385 | -399 |
| 2 | 6* | 68 | -55 |
| 2 | 7 | 480 | -493 |
| 2 | 8 | 122 | 109 |
| 2 | 9 | 363 | -358 |
| 2 | 10 | 150 | 130 |
| 2 | 11 | 92 | -105 |
| 2 | 12 | 147 | 145 |
| 3 | 1 | 128 | 109 |
| 3 | 2 | 273 | 257 |
| 3 | 3 | 221 | 204 |
| 3 | 4 | 283 | -273 |
| 3 | 5 | 286 | 277 |
| 3 | 6 | 546 | -531 |
| 3 | 7 | 166 | 148 |
| 3 | 8 | 498 | -479 |
| 3 | 9* | 72 | -78 |
| 3 | 10 | 227 | -230 |
| 3 | 11 | 190 | -183 |
| 4 | 1* | 160 | 119 |
| 4 | 2 | 629 | 642 |
| 4 | 3* | 94 | -53 |
| 4 | 4 | 599 | 634 |
| 4 | 5* | 65 | -76 |
| 4 | 6 | 487 | 505 |
| 4 | 7* | 92 | -34 |
| 4 | 8 | 0 | -6 |
| 4 | 9 | 0 | 33 |
| 4 | 10 | 273 | -291 |
| 4 | 11 | 0 | 5 |
| 4 | 12 | 255 | -248 |
| 5 | 1 | 227 | 230 |
| 5 | 2 | 141 | -116 |
| 5 | 3 | 309 | 290 |
| 5 | 4* | 58 | 73 |
| 5 | 5 | 297 | 275 |
| 5 | 6 | 375 | 371 |
| 5 | 7 | 97 | 93 |
| 5 | 8 | 436 | 453 |
| 5 | 9 | 0 | -87 |
| 5 | 10 | 231 | 231 |
| 5 | 11 | 136 | -145 |
| 6 | 1 | 163 | -142 |
| 6 | 2 | 467 | -501 |
| 6 | 3* | 61 | -47 |
| 6 | 4 | 370 | -354 |
| 6 | 5 | 228 | 227 |
| 6 | 6 | 119 | -103 |
| 6 | 7 | 377 | 374 |
| 6 | 8 | 0 | 42 |
| 6 | 9 | 322 | 332 |
| 6 | 10 | 103 | 109 |
| 7 | 1 | 494 | -505 |
| 7 | 2* | 65 | 26 |
| 7 | 3 | 514 | -540 |
| 7 | 4 | 272 | -261 |
| 7 | 5 | 370 | -362 |
| 7 | 6 | 199 | -173 |
| 7 | 7 | 94 | -117 |
| 7 | 8 | 0 | -9 |
| 7 | 11 | 193 | 211 |
| 8 | 1 | 310 | 309 |
| 8 | 2 | 0 | 52 |
| 8 | 3 | 168 | -156 |
| 8 | 4 | 0 | -19 |
| 8 | 5 | 344 | -361 |
| 8 | 6 | 124 | -121 |
| 8 | 7 | 332 | -338 |
| 8 | 8 | 0 | -48 |
| 8 | 9 | 215 | -219 |
| 9 | 1 | 500 | 510 |
| 9 | 2 | 0 | 72 |
| 9 | 3 | 446 | 458 |
| 9 | 4 | 97 | -94 |

3KL

| | | | |
|---|---|---|---|
| 9 | 5 | 212 | 200 |
| 9 | 6 | 156 | -135 |
| 10 | 1 | 98 | -94 |
| 10 | 2 | 377 | 394 |
| 10 | 3* | 83 | 89 |
| 10 | 4 | 285 | 289 |
| 10 | 5 | 193 | 198 |
| 10 | 6 | 0 | 53 |
| 10 | 7 | 192 | 192 |
| 11 | 1 | 0 | -63 |
| 11 | 2* | 88 | -91 |
| 11 | 3 | 0 | -64 |
| 11 | 4* | 141 | 155 |
| 11 | 5 | 0 | -65 |
| 11 | 6 | 235 | 226 |
| 12 | 1 | 0 | -73 |
| 12 | 2 | 275 | -251 |
| 12 | 3 | 0 | 16 |
| 12 | 4 | 239 | -221 |
| 0 | -1 | 1380 | -1644 |
| 0 | -3 | 849 | -882 |
| 0 | -5 | 409 | -408 |
| 0 | -7 | 105 | -101 |
| 0 | -9 | 143 | 143 |
| 0 | -11 | 273 | 282 |
| 0 | -13 | 294 | 273 |
| 0 | -15* | 102 | 122 |
| 1 | -1 | 490 | -480 |
| 1 | -2 | 688 | -697 |
| 1 | -3 | 267 | 259 |
| 1 | -4 | 240 | -251 |
| 1 | -5 | 551 | 550 |
| 1 | -6 | 0 | -3 |
| 1 | -7 | 523 | 558 |
| 1 | -8 | 0 | -41 |
| 1 | -9 | 377 | 386 |
| 1 | -10 | 0 | 78 |
| 1 | -11 | 170 | 170 |
| 1 | -12* | 108 | 149 |
| 2 | -1 | 489 | 522 |
| 2 | -2 | 191 | 127 |
| 2 | -3 | 857 | 915 |
| 2 | -4 | 561 | 591 |
| 2 | -5 | 583 | 591 |
| 2 | -6 | 439 | 457 |
| 2 | -7* | 63 | 80 |
| 2 | -8 | 366 | 356 |
| 2 | -9 | 207 | -199 |
| 2 | -10 | 260 | 265 |
| 2 | -11 | 237 | -229 |
| 2 | -12 | 0 | 62 |
| 2 | -13* | 94 | -144 |
| 3 | -1 | 521 | 516 |
| 3 | -2 | 1006 | 1064 |
| 3 | -3 | 313 | 296 |
| 3 | -4 | 748 | 773 |
| 3 | -5 | 264 | -256 |
| 3 | -6 | 292 | 275 |
| 3 | -7 | 351 | -361 |
| 3 | -8 | 160 | -148 |
| 3 | -9 | 219 | -201 |
| 3 | -10 | 305 | -301 |
| 3 | -11 | 0 | -0 |
| 3 | -12 | 256 | -263 |
| 3 | -13 | 0 | 32 |
| 3 | -14 | 157 | -163 |
| 4 | -1 | 185 | 179 |
| 4 | -2 | 204 | 197 |
| 4 | -3 | 0 | 3 |
| 4 | -4 | 347 | -339 |
| 4 | -5* | 73 | -70 |
| 4 | -6 | 738 | -778 |
| 4 | -7* | 68 | -63 |
| 4 | -8 | 588 | -626 |
| 4 | -9 | 0 | 1 |
| 4 | -10 | 210 | -221 |
| 5 | -1 | 325 | 300 |
| 5 | -2 | 666 | -682 |
| 5 | -3* | 93 | 62 |
| 5 | -4 | 717 | -721 |
| 5 | -5 | 337 | -311 |
| 5 | -6 | 370 | -366 |
| 5 | -7 | 329 | -318 |
| 5 | -8 | 144 | 136 |
| 5 | -9 | 157 | -147 |
| 5 | -10 | 296 | 293 |
| 5 | -11 | 0 | -12 |
| 5 | -12 | 232 | 234 |
| 5 | -13 | 0 | 35 |
| 5 | -14* | 145 | 126 |
| 6 | -2* | 81 | -67 |
| 6 | -3 | 633 | -642 |
| 6 | -4 | 195 | 188 |
| 6 | -5 | 453 | -456 |
| 6 | -6 | 341 | 323 |
| 6 | -7 | 0 | -46 |
| 6 | -8 | 325 | 312 |
| 6 | -9 | 207 | 213 |
| 6 | -10 | 227 | 202 |
| 6 | -11 | 228 | 225 |
| 7 | -1 | 308 | -304 |
| 7 | -2 | 278 | 263 |
| 7 | -3 | 0 | 41 |
| 7 | -4* | 126 | 91 |
| 7 | -5 | 344 | 334 |
| 7 | -6 | 0 | 15 |
| 7 | -7 | 427 | 431 |

3KL

| | | | |
|---|---|---|---|
| 7 | -8 | 0 | 70 |
| 7 | -9 | 315 | 317 |
| 8 | -1 | 578 | 590 |
| 8 | -2 | 0 | -50 |
| 8 | -3 | 451 | 440 |
| 8 | -4 | 0 | -35 |
| 8 | -5 | 267 | 255 |
| 8 | -6 | 118 | 102 |
| 8 | -7* | 121 | 93 |
| 8 | -8* | 89 | 88 |
| 8 | -9* | 131 | -101 |
| 8 | -10 | 0 | -4 |
| 8 | -11 | 186 | -193 |
| 9 | -1 | 189 | 159 |
| 9 | -2 | 234 | 236 |
| 9 | -3 | 130 | -135 |
| 9 | -4 | 188 | 170 |
| 9 | -5 | 197 | -209 |
| 9 | -6 | 0 | 71 |
| 9 | -7 | 242 | -226 |
| 9 | -8 | 0 | -19 |
| 9 | -9 | 194 | -180 |
| 10 | -1 | 260 | -249 |
| 10 | -2 | 0 | -49 |
| 10 | -3 | 262 | -268 |
| 10 | -4 | 220 | -219 |
| 10 | -5 | 184 | -166 |
| 10 | -6 | 199 | -197 |
| 10 | -7 | 0 | -19 |
| 10 | -8 | 170 | -168 |
| 11 | -1 | 131 | -126 |
| 11 | -2 | 396 | -372 |
| 11 | -3 | 0 | -74 |
| 11 | -4 | 286 | -232 |
| 12 | -4 | 141 | 140 |
| 12 | -5 | 0 | 34 |
| 12 | -6 | 229 | 224 |
| 12 | -7 | 0 | 32 |
| 12 | -8 | 181 | 186 |

4KL

| | | | |
|---|---|---|---|
| 2 | 0 | 724 | 774 |
| 3 | 0 | 262 | -256 |
| 4 | 0 | 88 | 84 |
| 5 | 0 | 180 | -165 |
| 6 | 0 | 512 | -506 |
| 7 | 0* | 87 | 96 |
| 8 | 0 | 584 | 601 |
| 9 | 0 | 114 | 110 |
| 10 | 0 | 270 | -266 |
| 0 | 2 | 621 | -572 |
| 0 | 4 | 204 | -169 |
| 0 | 6 | 0 | -12 |
| 0 | 8 | 296 | 290 |
| 0 | 10 | 369 | 381 |
| 0 | 12 | 248 | 255 |
| 1 | 1 | 319 | -308 |
| 1 | 2 | 680 | -665 |
| 1 | 3 | 0 | -48 |
| 1 | 4 | 700 | -664 |
| 1 | 5 | 0 | 31 |
| 1 | 6 | 575 | -566 |
| 1 | 7 | 0 | 1 |
| 1 | 8 | 325 | -338 |
| 1 | 9 | 136 | 122 |
| 1 | 10 | 0 | -59 |
| 1 | 11 | 179 | 181 |
| 1 | 12* | 88 | 115 |
| 1 | 13 | 0 | 64 |
| 1 | 14 | 158 | 148 |
| 2 | 1 | 453 | -395 |
| 2 | 2 | 846 | 809 |
| 2 | 3 | 534 | -500 |
| 2 | 4 | 349 | 311 |
| 2 | 5 | 375 | -378 |
| 2 | 6 | 249 | -228 |
| 2 | 7 | 290 | -279 |
| 2 | 8 | 326 | -318 |
| 2 | 9 | 196 | -190 |
| 2 | 10 | 223 | -221 |
| 2 | 11 | 0 | 38 |
| 2 | 12* | 89 | -110 |
| 2 | 13 | 142 | 142 |
| 3 | 1 | 832 | 807 |
| 3 | 2 | 73 | 57 |
| 3 | 3 | 471 | 464 |
| 3 | 4 | 550 | 542 |
| 3 | 5 | 0 | -18 |
| 3 | 6 | 357 | 343 |
| 3 | 7 | 301 | -308 |
| 3 | 8 | 0 | 27 |
| 3 | 9 | 338 | -348 |
| 3 | 10* | 66 | -68 |
| 3 | 11 | 218 | -237 |
| 4 | 1 | 98 | 71 |
| 4 | 2* | 65 | -54 |
| 4 | 3 | 654 | 633 |
| 4 | 4 | 0 | -29 |
| 4 | 5 | 742 | 756 |
| 4 | 6 | 0 | 52 |
| 4 | 7 | 387 | 426 |
| 5 | 1 | 690 | -728 |
| 5 | 2 | 112 | 106 |
| 5 | 3 | 451 | -455 |
| 5 | 4 | 409 | 418 |
| 5 | 5* | 44 | 6 |

Table 1 (*cont.*)

4KL

| | | | |
|---|---|---|---|
| 5 | 6 | 309 | 302 |
| 5 | 7 | 350 | 370 |
| 5 | 8 | 0 | 76 |
| 5 | 9 | 338 | 340 |
| 5 | 10 | 0 | -7 |
| 5 | 11 | 172 | 166 |
| 6 | 1 | 225 | -203 |
| 6 | 2 | 619 | -662 |
| 6 | 3 | 340 | -359 |
| 6 | 4 | 290 | -302 |
| 6 | 5 | 335 | -342 |
| 6 | 6 | 197 | 186 |
| 6 | 7 | 233 | -218 |
| 6 | 8 | 280 | 278 |
| 6 | 9 | 0 | -58 |
| 6 | 10 | 204 | 193 |
| 7 | 1* | 67 | 97 |
| 7 | 2 | 268 | -276 |
| 7 | 3 | 0 | -41 |
| 7 | 4 | 471 | -510 |
| 7 | 5 | 0 | -55 |
| 7 | 6 | 410 | -440 |
| 7 | 7 | 0 | -11 |
| 7 | 8 | 228 | -216 |
| 8 | 1 | 111 | 114 |
| 8 | 2 | 325 | 344 |
| 8 | 3 | 0 | -24 |
| 8 | 4* | 109 | 119 |
| 8 | 5* | 121 | -110 |
| 8 | 6 | 0 | -29 |
| 8 | 7 | 0 | -72 |
| 8 | 8 | 204 | -201 |
| 8 | 9 | 0 | 20 |
| 8 | 10 | 250 | -234 |
| 9 | 1 | 232 | 228 |
| 9 | 2 | 290 | 304 |
| 9 | 3* | 137 | 142 |
| 9 | 4 | 255 | 245 |
| 9 | 5 | 0 | 42 |
| 9 | 6 | 237 | 225 |
| 9 | 7 | 0 | -53 |
| 9 | 8* | 161 | 159 |
| 10 | 1 | 130 | 116 |
| 10 | 2 | 184 | -167 |
| 10 | 3 | 169 | 188 |
| 10 | 4 | 0 | -33 |
| 10 | 5* | 179 | 182 |
| 10 | 6 | 0 | 66 |
| 10 | 7* | 172 | 152 |
| 0 | -2 | 1107 | -1158 |
| 0 | -4 | 333 | -352 |
| 0 | -6 | 380 | 377 |
| 0 | -8 | 532 | 550 |
| 0 | -10 | 336 | 352 |
| 0 | -12 | 223 | 210 |
| 1 | -1 | 714 | -697 |
| 1 | -2 | 645 | 661 |
| 1 | -3 | 431 | -449 |
| 1 | -4 | 921 | 967 |
| 1 | -5 | 195 | 200 |
| 1 | -6 | 707 | 746 |
| 1 | -7 | 317 | 305 |
| 1 | -8 | 295 | 280 |
| 1 | -9 | 191 | 179 |
| 1 | -10 | 0 | -20 |
| 1 | -11* | 74 | 88 |
| 1 | -12* | 148 | -141 |
| 1 | -13 | 0 | 42 |
| 1 | -14 | 158 | -161 |
| 2 | -1* | 88 | 61 |
| 2 | -2 | 523 | 543 |
| 2 | -3 | 737 | 812 |
| 2 | -4 | 249 | 237 |
| 2 | -5 | 744 | 755 |
| 2 | -6 | 100 | -82 |
| 2 | -7 | 308 | 297 |
| 2 | -8 | 310 | -303 |
| 2 | -9 | 0 | 3 |
| 2 | -10 | 350 | -344 |
| 2 | -11* | 91 | -116 |
| 2 | -12 | 178 | -182 |
| 2 | -13* | 157 | -125 |
| 3 | -1 | 726 | 782 |
| 3 | -2 | 192 | -193 |
| 3 | -3 | 397 | 405 |
| 3 | -4 | 167 | -174 |
| 3 | -5 | 0 | -22 |
| 3 | -6 | 222 | -204 |
| 3 | -7 | 370 | -365 |
| 3 | -8 | 270 | -249 |
| 3 | -9 | 442 | -443 |
| 3 | -10* | 72 | -66 |
| 3 | -11 | 275 | -287 |
| 4 | -1 | 442 | -431 |
| 4 | -2 | 147 | 97 |
| 4 | -3 | 438 | -440 |
| 4 | -4 | 0 | 37 |
| 4 | -5 | 501 | -521 |
| 4 | -6* | 100 | -95 |
| 4 | -7 | 505 | -500 |
| 4 | -8* | 68 | -83 |
| 4 | -9 | 184 | -166 |
| 4 | -10 | 0 | 2 |
| 4 | -11 | 136 | 120 |
| 4 | -12 | 0 | 19 |
| 4 | -13 | 193 | 209 |
| 5 | -1 | 508 | -506 |

4KL

| | | | |
|---|---|---|---|
| 5 | -2 | 230 | -221 |
| 5 | -3 | 236 | -221 |
| 5 | -4 | 289 | -270 |
| 5 | -5 | 53 | -71 |
| 5 | -6 | 262 | -256 |
| 5 | -7 | 211 | 197 |
| 5 | -8 | 168 | -163 |
| 5 | -9 | 338 | 335 |
| 5 | -10 | 0 | 11 |
| 5 | -11 | 291 | 283 |
| 6 | -1 | 112 | 108 |
| 6 | -2 | 313 | -293 |
| 6 | -3 | 382 | 380 |
| 6 | -4* | 85 | -95 |
| 6 | -5 | 396 | 386 |
| 6 | -6* | 54 | 54 |
| 6 | -7 | 201 | 206 |
| 6 | -8 | 211 | 222 |
| 6 | -9 | 0 | 77 |
| 6 | -10 | 304 | 295 |
| 6 | -11 | 0 | -26 |
| 6 | -12 | 150 | 153 |
| 7 | -1 | 332 | 332 |
| 7 | -2 | 405 | 402 |
| 7 | -3 | 271 | 255 |
| 7 | -4 | 476 | 479 |
| 7 | -5 | 0 | -67 |
| 7 | -6 | 363 | 371 |
| 7 | -7 | 0 | -121 |
| 7 | -8 | 219 | 225 |
| 8 | -1 | 188 | 160 |
| 8 | -2 | 477 | 496 |
| 8 | -3 | 0 | 11 |
| 8 | -4 | 136 | 132 |
| 8 | -5 | 0 | -22 |
| 8 | -6 | 183 | -168 |
| 8 | -7 | 0 | 18 |
| 8 | -8 | 271 | -269 |
| 8 | -9 | 0 | 15 |
| 8 | -10 | 211 | -211 |
| 8 | -11 | 0 | -12 |
| 8 | -12 | 158 | -141 |
| 9 | -1 | 240 | 227 |
| 9 | -2 | 253 | -243 |
| 9 | -3 | 117 | 85 |
| 9 | -4 | 416 | -429 |
| 9 | -5* | 109 | -99 |
| 9 | -6 | 370 | -359 |
| 9 | -7* | 159 | -139 |
| 9 | -8* | 120 | -117 |
| 10 | -1 | 0 | -79 |
| 10 | -2 | 277 | -255 |
| 10 | -3 | 318 | -335 |
| 10 | -4 | 161 | -145 |
| 10 | -5 | 318 | -314 |
| 10 | -6 | 0 | 51 |
| 10 | -7 | 149 | -116 |
| 10 | -8 | 175 | 148 |
| 12 | -1 | 0 | 80 |
| 12 | -2 | 0 | -50 |
| 12 | -3 | 266 | 179 |
| 12 | -4 | 0 | 8 |
| 12 | -5 | 248 | 220 |
| 12 | -6 | 0 | 73 |
| 12 | -7 | 212 | 182 |

5KL

| | | | |
|---|---|---|---|
| 2 | 0 | 282 | 315 |
| 3 | 0 | 569 | 594 |
| 4 | 0 | 700 | -701 |
| 5 | 0 | 647 | -645 |
| 6 | 0 | 278 | 254 |
| 7 | 0* | 102 | 63 |
| 8 | 0* | 158 | 143 |
| 9 | 0* | 76 | 96 |
| 10 | 0* | 174 | -157 |
| 11 | 0* | 164 | -158 |
| 12 | 0* | 184 | 185 |
| 13 | 0* | 202 | 176 |
| 0 | 1 | 554 | -549 |
| 0 | 3 | 646 | -679 |
| 0 | 5 | 652 | -670 |
| 0 | 7 | 213 | -208 |
| 0 | 9 | 266 | 252 |
| 0 | 11 | 258 | 271 |
| 0 | 13 | 150 | 155 |
| 1 | 2 | 207 | -184 |
| 1 | 3* | 53 | 48 |
| 1 | 4 | 447 | -443 |
| 1 | 5 | 340 | -330 |
| 1 | 6 | 279 | -256 |
| 1 | 7 | 517 | -514 |
| 1 | 8 | 0 | 23 |
| 1 | 9 | 333 | -336 |
| 1 | 10 | 166 | 160 |
| 2 | 1 | 639 | 662 |
| 2 | 2 | 344 | 305 |
| 2 | 3 | 606 | 609 |
| 2 | 4 | 121 | -101 |
| 2 | 5 | 262 | 237 |
| 2 | 6 | 441 | -445 |
| 2 | 7 | 0 | 5 |
| 2 | 8 | 417 | -427 |
| 2 | 9 | 0 | -58 |
| 2 | 10 | 210 | -203 |
| 2 | 11* | 165 | -133 |

5KL

| | | | |
|---|---|---|---|
| 3 | 1 | 194 | -181 |
| 3 | 2 | 754 | 779 |
| 3 | 3 | 241 | 218 |
| 3 | 4 | 573 | 582 |
| 3 | 5 | 283 | 275 |
| 3 | 6 | 247 | 249 |
| 3 | 7 | 0 | 31 |
| 3 | 8 | 0 | -39 |
| 3 | 9 | 0 | 34 |
| 3 | 10 | 197 | -197 |
| 4 | 1* | 49 | -47 |
| 4 | 2 | 102 | 83 |
| 4 | 3 | 0 | 16 |
| 4 | 4 | 466 | 459 |
| 4 | 5 | 127 | 117 |
| 4 | 6 | 405 | 431 |
| 4 | 7* | 57 | 77 |
| 4 | 8 | 310 | 325 |
| 4 | 9 | 0 | -12 |
| 4 | 10 | 215 | 200 |
| 5 | 1 | 252 | -258 |
| 5 | 2 | 730 | -765 |
| 5 | 3* | 59 | 58 |
| 5 | 4 | 401 | -402 |
| 5 | 5 | 184 | 181 |
| 5 | 6 | 102 | -104 |
| 5 | 7 | 133 | 104 |
| 5 | 8* | 63 | 73 |
| 5 | 9* | 81 | 104 |
| 5 | 10* | 130 | 125 |
| 6 | 1 | 541 | -529 |
| 6 | 2* | 51 | 46 |
| 6 | 3 | 489 | -503 |
| 6 | 4 | 195 | -190 |
| 6 | 5 | 180 | -173 |
| 6 | 6 | 316 | -310 |
| 6 | 7 | 0 | -9 |
| 6 | 8 | 241 | -234 |
| 7 | 1 | 277 | 272 |
| 7 | 2* | 68 | 78 |
| 7 | 3* | 57 | -62 |
| 7 | 4 | 215 | 210 |
| 7 | 5 | 267 | -277 |
| 7 | 6 | 134 | 110 |
| 7 | 7 | 267 | -274 |
| 7 | 8 | 0 | -41 |
| 7 | 9 | 190 | -190 |
| 8 | 1 | 324 | 339 |
| 8 | 2 | 0 | -16 |
| 8 | 3 | 369 | 381 |
| 8 | 4 | 0 | -48 |
| 8 | 5 | 308 | 314 |
| 8 | 6 | 0 | -3 |
| 8 | 7* | 70 | 78 |
| 8 | 8 | 0 | 15 |
| 8 | 9* | 91 | -134 |
| 8 | 10 | 0 | -5 |
| 8 | 11 | 111 | -148 |
| 9 | 1 | 177 | -156 |
| 9 | 2 | 172 | 170 |
| 9 | 3 | 0 | -21 |
| 9 | 4 | 200 | 194 |
| 9 | 5 | 151 | 150 |
| 9 | 6* | 87 | 101 |
| 9 | 7 | 263 | 272 |
| 9 | 8 | 0 | -14 |
| 9 | 9 | 189 | 175 |
| 10 | 1 | 169 | -183 |
| 10 | 2 | 126 | -132 |
| 10 | 3 | 186 | -185 |
| 10 | 4 | 0 | 35 |
| 10 | 5* | 103 | -119 |
| 10 | 6 | 183 | 194 |
| 10 | 7 | 0 | -18 |
| 10 | 8 | 191 | 194 |
| 11 | 2 | 222 | -237 |
| 11 | 3 | 0 | -74 |
| 11 | 4 | 227 | -246 |
| 13 | 2 | 211 | 208 |
| 0 | -1 | 301 | -286 |
| 0 | -3 | 0 | -37 |
| 0 | -5 | 450 | 467 |
| 0 | -7 | 724 | 772 |
| 0 | -9 | 453 | 488 |
| 0 | -11 | 135 | 124 |
| 1 | -1 | 679 | 700 |
| 1 | -2 | 196 | -205 |
| 1 | -3 | 692 | 747 |
| 1 | -4 | 0 | 48 |
| 1 | -5 | 554 | 577 |
| 1 | -6 | 304 | 288 |
| 1 | -7* | 136 | 112 |
| 1 | -8 | 304 | 292 |
| 1 | -9 | 251 | -247 |
| 1 | -10* | 103 | 113 |
| 1 | -11 | 319 | -311 |
| 2 | -1 | 247 | 259 |
| 2 | -2 | 438 | 514 |
| 2 | -3 | 274 | -279 |
| 2 | -4 | 548 | 580 |
| 2 | -5 | 452 | -481 |
| 2 | -6 | 307 | 299 |
| 2 | -7 | 372 | -361 |
| 2 | -8 | 0 | -63 |
| 2 | -9 | 267 | -261 |
| 2 | -10 | 257 | -268 |
| 2 | -11* | 97 | -124 |

5KL

| | | | |
|---|---|---|---|
| 2 | -12 | 196 | -208 |
| 3 | -1 | 475 | -505 |
| 3 | -2 | 135 | 114 |
| 3 | -3 | 428 | -418 |
| 3 | -4 | 306 | -299 |
| 3 | -5 | 0 | 0 |
| 3 | -6 | 461 | -473 |
| 3 | -7 | 0 | 58 |
| 3 | -8 | 424 | -438 |
| 3 | -9 | 0 | 11 |
| 3 | -10 | 239 | -238 |
| 4 | -1* | 66 | -68 |
| 4 | -2 | 878 | -888 |
| 4 | -3 | 0 | 29 |
| 4 | -4 | 515 | -533 |
| 4 | -5 | 0 | 5 |
| 4 | -6 | 205 | -186 |
| 4 | -7* | 65 | -64 |
| 4 | -8* | 70 | 61 |
| 4 | -9 | 0 | -40 |
| 4 | -10 | 179 | 177 |
| 4 | -11 | 0 | 4 |
| 4 | -12 | 229 | 225 |
| 4 | -13 | 0 | 29 |
| 4 | -14 | 163 | 162 |
| 5 | -1 | 462 | -452 |
| 5 | -2* | 76 | -65 |
| 5 | -3 | 357 | -344 |
| 5 | -4 | 337 | 318 |
| 5 | -5 | 0 | -52 |
| 5 | -6 | 432 | 424 |
| 5 | -7 | 0 | 50 |
| 5 | -8 | 324 | 302 |
| 5 | -9 | 0 | 63 |
| 5 | -10 | 181 | 175 |
| 6 | -1 | 247 | -191 |
| 6 | -2 | 413 | 422 |
| 6 | -3 | 330 | 311 |
| 6 | -4 | 415 | 421 |
| 6 | -5 | 432 | 438 |
| 6 | -6 | 189 | 175 |
| 6 | -7 | 280 | 266 |
| 6 | -8 | 0 | -50 |
| 6 | -9 | 179 | 179 |
| 6 | -10* | 119 | -128 |
| 6 | -11 | 0 | 83 |
| 6 | -12* | 143 | -121 |
| 7 | -1 | 524 | 548 |
| 7 | -2 | 197 | 185 |
| 7 | -3 | 540 | 551 |
| 7 | -4 | 0 | 48 |
| 7 | -5 | 289 | 267 |
| 7 | -6* | 148 | -131 |
| 7 | -7 | 0 | -8 |
| 7 | -8* | 179 | -168 |
| 7 | -9* | 178 | -168 |
| 7 | -10 | 0 | -83 |
| 7 | -11 | 201 | -188 |
| 8 | -1 | 206 | 197 |
| 8 | -2 | 143 | 129 |
| 8 | -3 | 0 | -22 |
| 8 | -4 | 0 | 0 |
| 8 | -5 | 285 | -288 |
| 8 | -6* | 96 | -93 |
| 8 | -7 | 425 | -416 |
| 8 | -8* | 103 | -83 |
| 8 | -9 | 289 | -258 |
| 9 | -1 | 265 | -246 |
| 9 | -2 | 0 | 11 |
| 9 | -3 | 312 | -304 |
| 9 | -4* | 159 | -138 |
| 9 | -5 | 306 | -310 |
| 9 | -6 | 236 | -209 |
| 9 | -7* | 86 | -89 |
| 9 | -8* | 139 | -119 |
| 9 | -9* | 128 | 122 |
| 9 | -10 | 0 | -26 |
| 9 | -11* | 134 | 164 |
| 10 | -1 | 0 | -90 |
| 10 | -2 | 242 | -224 |
| 10 | -3 | 0 | -2 |
| 10 | -4 | 247 | -246 |
| 10 | -5* | 87 | 100 |
| 10 | -6* | 88 | -103 |
| 10 | -7 | 190 | 162 |
| 11 | -6 | 161 | 188 |
| 11 | -8 | 232 | 210 |
| 12 | -2 | 261 | 245 |

6KL

| | | | |
|---|---|---|---|
| 2 | 0 | 121 | 114 |
| 3 | 0 | 132 | -123 |
| 4 | 0 | 159 | -149 |
| 5 | 0 | 225 | -220 |
| 6 | 0 | 101 | -81 |
| 7 | 0 | 398 | 409 |
| 8 | 0 | 0 | -63 |
| 9 | 0 | 374 | -372 |
| 0 | 2 | 576 | -546 |
| 0 | 4 | 831 | -777 |
| 0 | 6 | 542 | -525 |
| 0 | 8 | 121 | -118 |
| 0 | 10 | 0 | 66 |
| 0 | 12* | 85 | 78 |
| 1 | 1 | 94 | 95 |
| 1 | 2 | 643 | 626 |

6KL

| | | | |
|---|---|---|---|
| 1 | 3 | 390 | -360 |
| 1 | 4 | 181 | 151 |
| 1 | 5 | 430 | -399 |
| 1 | 6 | 245 | -229 |
| 1 | 7 | 112 | -87 |
| 1 | 8 | 346 | -335 |
| 1 | 9 | 0 | 9 |
| 1 | 10 | 240 | -230 |
| 1 | 11 | 0 | 9 |
| 1 | 12* | 129 | -126 |
| 2 | 1 | 712 | 736 |
| 2 | 2 | 286 | 246 |
| 2 | 3 | 570 | 527 |
| 2 | 4 | 358 | 324 |
| 2 | 5 | 61 | -52 |
| 2 | 6 | 310 | 311 |
| 2 | 7 | 276 | -260 |
| 2 | 8 | 213 | 199 |
| 2 | 9 | 204 | -188 |
| 2 | 10 | 0 | 15 |
| 2 | 11* | 124 | -122 |
| 2 | 12* | 121 | -107 |
| 3 | 1 | 223 | 211 |
| 3 | 2 | 0 | 11 |
| 3 | 3 | 500 | 490 |
| 3 | 4* | 73 | -56 |
| 3 | 5 | 512 | 518 |
| 3 | 6* | 60 | -44 |
| 3 | 7 | 341 | 367 |
| 3 | 8* | 56 | 58 |
| 3 | 9* | 113 | 122 |
| 3 | 10 | 169 | 160 |
| 4 | 1 | 542 | -563 |
| 4 | 2* | 80 | 7 |
| 4 | 3 | 247 | -254 |
| 4 | 4* | 56 | 69 |
| 4 | 5 | 157 | -140 |
| 4 | 6 | 0 | 54 |
| 4 | 7 | 134 | 122 |
| 4 | 8 | 0 | -7 |
| 4 | 9 | 299 | 310 |
| 4 | 10 | 0 | -11 |
| 4 | 11 | 228 | 235 |
| 5 | 1 | 261 | -262 |
| 5 | 2 | 180 | -158 |
| 5 | 3 | 307 | -323 |
| 5 | 4 | 138 | -132 |
| 5 | 5 | 320 | -334 |
| 5 | 6 | 0 | -39 |
| 5 | 7 | 302 | -330 |
| 5 | 8* | 61 | 77 |
| 5 | 9* | 120 | -136 |
| 5 | 10* | 148 | 135 |
| 6 | 1 | 370 | 382 |
| 6 | 2 | 139 | -119 |
| 6 | 3 | 232 | 230 |
| 6 | 4 | 190 | -196 |
| 6 | 5 | 0 | -13 |
| 6 | 6 | 235 | -241 |
| 6 | 7 | 135 | -138 |
| 6 | 8 | 220 | -207 |
| 6 | 9 | 149 | -135 |
| 7 | 1 | 0 | -15 |
| 7 | 2 | 286 | 305 |
| 7 | 3 | 213 | 209 |
| 7 | 4* | 114 | 123 |
| 7 | 5 | 200 | 202 |
| 7 | 6 | 0 | -65 |
| 7 | 7 | 0 | 10 |
| 7 | 8 | 176 | -170 |
| 7 | 9 | 0 | -34 |
| 7 | 10 | 200 | -194 |
| 8 | 1 | 0 | -2 |
| 8 | 2 | 239 | 263 |
| 8 | 3 | 0 | 3 |
| 8 | 4 | 353 | 383 |
| 8 | 5* | 60 | 86 |
| 8 | 6 | 308 | 277 |
| 8 | 7 | 0 | 53 |
| 8 | 8* | 69 | 97 |
| 9 | 1 | 0 | -29 |
| 9 | 2 | 292 | -306 |
| 9 | 3* | 78 | 119 |
| 9 | 4* | 65 | -52 |
| 9 | 5 | 146 | 160 |
| 9 | 6 | 153 | 143 |
| 9 | 7* | 68 | 101 |
| 9 | 8 | 190 | 186 |
| 10 | 1 | 271 | -308 |
| 10 | 2 | 150 | -154 |
| 10 | 3 | 198 | -230 |
| 10 | 4 | 182 | -188 |
| 10 | 5 | 0 | 1 |
| 10 | 6 | 160 | -140 |
| 11 | 1 | 0 | -48 |
| 11 | 2 | 0 | -8 |
| 11 | 3 | 232 | -215 |
| 11 | 4 | 0 | -18 |
| 11 | 5 | 243 | -240 |
| 0 | -2 | 584 | 581 |
| 0 | -4 | 468 | 508 |
| 0 | -6 | 469 | 479 |
| 0 | -8 | 310 | 301 |
| 0 | -10 | 0 | 31 |
| 0 | -12* | 173 | -168 |
| 0 | -14* | 181 | -195 |
| 1 | -2 | 453 | 461 |

Table 1 (*cont.*)

6KL

| | | | |
|---|---|---|---|
| 1 | -3 | 287 | 291 |
| 1 | -4 | 116 | 122 |
| 1 | -5 | 149 | 132 |
| 1 | -6 | 166 | -162 |
| 1 | -7 | 122 | 124 |
| 1 | -8 | 313 | -333 |
| 1 | -9* | 91 | 110 |
| 1 | -10 | 326 | -329 |
| 1 | -11 | 0 | -30 |
| 1 | -12 | 199 | -201 |
| 2 | -1 | 442 | 513 |
| 2 | -2 | 240 | -257 |
| 2 | -3 | 166 | 146 |
| 2 | -4 | 527 | -552 |
| 2 | -5 | 116 | -81 |
| 2 | -6 | 397 | -399 |
| 2 | -7 | 166 | -148 |
| 2 | -8* | 141 | -129 |
| 2 | -9 | 266 | -259 |
| 2 | -10 | 0 | 41 |
| 2 | -11 | 235 | -234 |
| 3 | -1 | 231 | -252 |
| 3 | -2 | 399 | -405 |
| 3 | -3 | 599 | -619 |
| 3 | -4 | 188 | -165 |
| 3 | -5 | 614 | -624 |
| 3 | -6 | 158 | 144 |
| 3 | -7 | 362 | -386 |
| 3 | -8 | 201 | 184 |
| 3 | -9 | 125 | -100 |
| 3 | -10* | 113 | 105 |
| 3 | -11 | 0 | 82 |
| 3 | -12 | 0 | 33 |
| 3 | -13* | 156 | 147 |
| 4 | -1 | 736 | -789 |
| 4 | -2 | 165 | -138 |
| 4 | -3 | 517 | -560 |
| 4 | -4 | 0 | -16 |
| 4 | -5 | 0 | -39 |
| 4 | -6 | 0 | 32 |
| 4 | -7 | 398 | 388 |
| 4 | -8 | 0 | 28 |
| 4 | -9 | 373 | 380 |
| 4 | -10 | 0 | -1 |
| 4 | -11 | 232 | 224 |
| 5 | -1* | 50 | 76 |
| 5 | -2 | 269 | -265 |
| 5 | -3 | 422 | 449 |
| 5 | -4 | 0 | -16 |
| 5 | -5 | 610 | 627 |
| 5 | -6 | 229 | 215 |
| 5 | -7 | 393 | 393 |
| 5 | -8 | 210 | 192 |
| 6 | -1 | 351 | 348 |
| 6 | -2 | 216 | 211 |
| 6 | -3 | 238 | 233 |
| 6 | -4 | 466 | 485 |
| 6 | -5 | 0 | 49 |
| 6 | -6 | 358 | 345 |
| 6 | -7* | 154 | -131 |
| 6 | -8 | 0 | 87 |
| 6 | -9 | 230 | -211 |
| 6 | -10* | 97 | -84 |
| 6 | -11* | 180 | -173 |
| 7 | -1 | 144 | -112 |
| 7 | -2 | 384 | 373 |
| 7 | -3* | 90 | -95 |
| 7 | -4 | 159 | 134 |
| 7 | -5 | 0 | -51 |
| 7 | -6* | 131 | -135 |
| 7 | -7* | 136 | 100 |
| 7 | -8 | 308 | -297 |
| 7 | -9* | 136 | -116 |
| 7 | -10 | 258 | -255 |
| 8 | -1 | 0 | 32 |
| 8 | -2 | 276 | -266 |
| 8 | -3 | 0 | 50 |
| 8 | -4 | 315 | -292 |
| 8 | -5 | 0 | -19 |
| 8 | -6 | 313 | -307 |
| 8 | -7 | 121 | -109 |
| 8 | -8 | 195 | -194 |
| 9 | -1* | 146 | -125 |
| 9 | -2 | 210 | -186 |
| 9 | -3* | 148 | -149 |
| 9 | -4 | 0 | -60 |
| 9 | -5 | 163 | -150 |

6KL

| | | | |
|---|---|---|---|
| 10 | -1 | 219 | -208 |
| 10 | -2* | 96 | 110 |
| 10 | -3 | 0 | -62 |
| 10 | -4 | 196 | 165 |
| 11 | -1 | 142 | 137 |
| 11 | -2* | 117 | 128 |
| 11 | -3 | 238 | 243 |
| 11 | -4* | 84 | 72 |
| 11 | -5 | 225 | 203 |
| 12 | -1 | 270 | 254 |

7KL

| | | | |
|---|---|---|---|
| 2 | 0 | 418 | 430 |
| 3 | 0 | 416 | -460 |
| 4 | 0 | 257 | -260 |
| 5 | 0 | 372 | 390 |
| 6 | 0 | 225 | 221 |
| 7 | 0* | 80 | -50 |
| 8 | 0* | 71 | -92 |
| 9 | 0 | 186 | -188 |
| 10 | 0 | 163 | -171 |
| 11 | 0 | 192 | 180 |
| 12 | 0 | 166 | 139 |
| 0 | 1 | 207 | 185 |
| 0 | 3 | 379 | -341 |
| 0 | 5 | 352 | -329 |
| 0 | 7 | 314 | -311 |
| 0 | 9 | 276 | -269 |
| 0 | 11 | 144 | -150 |
| 1 | 1 | 694 | 704 |
| 1 | 2* | 60 | -39 |
| 1 | 3 | 538 | 537 |
| 1 | 4 | 156 | -133 |
| 1 | 5 | 274 | 272 |
| 1 | 6* | 46 | -45 |
| 1 | 7* | 61 | 72 |
| 1 | 8 | 0 | -42 |
| 1 | 9* | 122 | -89 |
| 1 | 10* | 122 | -112 |
| 1 | 11 | 171 | -157 |
| 1 | 12 | 0 | -46 |
| 1 | 13* | 131 | -141 |
| 2 | 1 | 253 | -252 |
| 2 | 2 | 432 | 445 |
| 2 | 3* | 76 | -35 |
| 2 | 4 | 262 | 253 |
| 2 | 5 | 284 | 293 |
| 2 | 6* | 100 | 76 |
| 2 | 7 | 331 | 333 |
| 2 | 8 | 0 | 47 |
| 2 | 9 | 193 | 187 |
| 3 | 1 | 0 | -15 |
| 3 | 2 | 167 | -152 |
| 3 | 3 | 291 | -288 |
| 3 | 4 | 189 | 165 |
| 3 | 5 | 248 | -258 |
| 3 | 6 | 315 | 321 |
| 3 | 7 | 0 | 5 |
| 3 | 8 | 274 | 281 |
| 3 | 9* | 116 | 112 |
| 3 | 10* | 126 | 141 |
| 4 | 1 | 0 | -8 |
| 4 | 2 | 474 | -506 |
| 4 | 3 | 0 | 30 |
| 4 | 4 | 507 | -518 |
| 4 | 5 | 0 | -28 |
| 4 | 6 | 265 | -266 |
| 4 | 7 | 0 | -26 |
| 4 | 8* | 116 | 94 |
| 4 | 9 | 0 | 3 |
| 4 | 10 | 204 | 191 |
| 5 | 1* | 53 | -62 |
| 5 | 2 | 195 | 189 |
| 5 | 3 | 250 | -250 |
| 5 | 4 | 129 | -110 |
| 5 | 5 | 229 | -224 |
| 5 | 6 | 315 | -332 |
| 5 | 7 | 0 | -34 |
| 5 | 8 | 297 | -294 |
| 6 | 1 | 284 | 267 |
| 6 | 2 | 294 | 294 |
| 6 | 3* | 101 | 113 |
| 6 | 4 | 215 | 204 |
| 6 | 5 | 212 | -221 |
| 6 | 6* | 57 | 74 |
| 6 | 7 | 290 | -291 |

7KL

| | | | |
|---|---|---|---|
| 6 | 8 | 0 | -28 |
| 6 | 9 | 186 | -173 |
| 7 | 1 | 317 | 339 |
| 7 | 2* | 92 | 101 |
| 7 | 3 | 370 | 400 |
| 7 | 4 | 126 | 124 |
| 7 | 5 | 272 | 271 |
| 8 | 1* | 120 | -135 |
| 8 | 2 | 0 | 29 |
| 8 | 3 | 138 | 134 |
| 8 | 4* | 120 | 107 |
| 8 | 5 | 212 | 201 |
| 8 | 6* | 66 | 101 |
| 8 | 7 | 235 | 213 |
| 8 | 8 | 0 | 10 |
| 8 | 9 | 188 | 174 |
| 9 | 1 | 314 | -365 |
| 9 | 2* | 62 | -93 |
| 9 | 3 | 208 | -239 |
| 10 | 1 | 0 | 32 |
| 10 | 2 | 192 | -212 |
| 10 | 3 | 0 | -76 |
| 10 | 4 | 151 | -152 |
| 0 | -1 | 813 | 822 |
| 0 | -3 | 806 | 813 |
| 0 | -5 | 381 | 401 |
| 0 | -7* | 114 | -21 |
| 0 | -9 | 199 | -180 |
| 0 | -11 | 201 | -203 |
| 0 | -13 | 189 | -183 |
| 1 | -1 | 394 | 385 |
| 1 | -2 | 432 | 444 |
| 1 | -3 | 106 | -114 |
| 1 | -4 | 232 | 226 |
| 1 | -5 | 394 | -431 |
| 1 | -6* | 74 | -59 |
| 1 | -7 | 405 | -433 |
| 1 | -8* | 76 | -82 |
| 1 | -9 | 261 | -260 |
| 1 | -10* | 72 | -71 |
| 1 | -11* | 121 | -100 |
| 2 | -1 | 256 | -314 |
| 2 | -2* | 50 | 35 |
| 2 | -3 | 351 | -383 |
| 2 | -4 | 389 | -416 |
| 2 | -5 | 309 | -310 |
| 2 | -6 | 395 | -409 |
| 2 | -7* | 102 | -103 |
| 2 | -8 | 255 | -246 |
| 2 | -9* | 137 | 109 |
| 2 | -10* | 147 | -119 |
| 2 | -11 | 173 | 182 |
| 3 | -1 | 0 | -22 |
| 3 | -2 | 542 | -605 |
| 3 | -3* | 90 | -87 |
| 3 | -4 | 461 | -492 |
| 3 | -5 | 0 | -2 |
| 3 | -6 | 197 | -201 |
| 3 | -7* | 137 | 140 |
| 3 | -8* | 114 | 109 |
| 3 | -9 | 199 | 180 |
| 3 | -10 | 211 | 245 |
| 3 | -11 | 0 | 57 |
| 3 | -12 | 219 | 210 |
| 4 | -1 | 105 | -85 |
| 4 | -2 | 0 | -22 |
| 4 | -3* | 50 | -64 |
| 4 | -4 | 159 | 157 |
| 4 | -5* | 57 | 13 |
| 4 | -6 | 412 | 439 |
| 4 | -7* | 91 | 93 |
| 4 | -8 | 450 | 461 |
| 4 | -9 | 0 | 56 |
| 4 | -10 | 248 | 225 |
| 5 | -1 | 0 | 1 |
| 5 | -2 | 380 | 369 |
| 5 | -3 | 0 | 26 |
| 5 | -4 | 360 | 359 |
| 5 | -5 | 159 | 137 |
| 5 | -6 | 260 | 239 |
| 5 | -7 | 173 | 180 |
| 5 | -8 | 0 | -28 |
| 5 | -9* | 92 | 122 |
| 5 | -10 | 194 | -194 |
| 6 | -1 | 264 | 230 |
| 6 | -2 | 0 | 24 |
| 6 | -3 | 250 | 250 |

7KL

| | | | |
|---|---|---|---|
| 6 | -4 | 185 | -158 |
| 6 | -5 | 225 | 201 |
| 6 | -6 | 208 | -209 |
| 6 | -7* | 72 | 73 |
| 6 | -8 | 192 | -182 |
| 6 | -9* | 79 | -117 |
| 6 | -10* | 164 | -139 |
| 6 | -11* | 170 | -184 |
| 7 | -1 | 145 | 151 |
| 7 | -2 | 223 | -215 |
| 7 | -3* | 82 | -83 |
| 7 | -4 | 154 | -131 |
| 7 | -5 | 229 | -216 |
| 7 | -6 | 0 | 8 |
| 7 | -7 | 294 | -272 |
| 7 | -8 | 0 | -4 |
| 7 | -9 | 238 | -225 |
| 8 | -1 | 432 | -420 |
| 8 | -2* | 112 | -95 |
| 8 | -3 | 406 | -400 |
| 8 | -4 | 0 | -11 |
| 8 | -5 | 220 | -210 |
| 9 | -1 | 229 | -215 |
| 9 | -2 | 187 | -185 |
| 9 | -3 | 0 | 47 |
| 9 | -4 | 0 | -86 |
| 9 | -5 | 226 | 216 |
| 9 | -6 | 0 | 20 |
| 9 | -7 | 214 | 217 |
| 10 | -1 | 141 | 143 |
| 10 | -2 | 0 | 13 |
| 10 | -3 | 225 | 208 |
| 10 | -4 | 220 | 207 |
| 10 | -5* | 169 | 164 |
| 10 | -6* | 192 | 199 |

HOL

| H | L | | |
|---|---|---|---|
| 2 | 0 | 563 | -510 |
| 4 | 0 | 1341 | -1369 |
| 6 | 0 | 264 | 225 |
| 8 | 0 | 556 | 541 |
| 10 | 0 | 0 | -30 |
| 12 | 0 | 244 | -229 |
| 14 | 0 | 0 | -30 |
| 8 | 2 | 382 | 391 |
| 8 | 4 | 276 | 277 |
| 8 | 6 | 0 | 49 |
| 8 | 8 | 282 | -259 |
| 8 | 10 | 266 | -264 |
| 9 | 1 | 359 | 367 |
| 9 | 3 | 507 | 518 |
| 9 | 5 | 323 | 336 |
| 10 | 2 | 342 | 336 |
| 10 | 4 | 306 | 310 |
| 10 | 6* | 181 | 172 |
| 12 | 2 | 231 | -260 |
| 13 | 1 | 197 | -211 |
| 13 | 3 | 194 | -203 |
| 8 | -2 | 540 | 542 |
| 8 | -4 | 322 | 308 |
| 8 | -6 | 185 | -170 |
| 8 | -8 | 399 | -414 |
| 8 | -10 | 287 | -311 |
| 8 | -12 | 152 | -151 |
| 9 | -1 | 0 | -4 |
| 9 | -3 | 167 | -150 |
| 9 | -5 | 276 | -260 |
| 9 | -7 | 379 | -369 |
| 9 | -9 | 275 | -289 |
| 10 | -2 | 354 | -358 |
| 10 | -4 | 372 | -377 |
| 10 | -6 | 273 | -241 |
| 11 | -1 | 242 | -263 |
| 11 | -3 | 351 | -361 |
| 11 | -5 | 261 | -252 |
| 11 | -7 | 0 | -4 |
| 11 | -9* | 140 | 128 |
| 11 | -11* | 154 | 136 |
| 12 | -2 | 149 | -149 |
| 12 | -4 | 0 | -98 |
| 12 | -6 | 0 | 44 |
| 12 | -8 | 170 | 170 |
| 12 | -10 | 173 | 171 |

Table 2. *Atom parameters*

| Atom | $x/a$ | $\sigma(x)\times10^4$ | $y/b$ | $\sigma(y)\times10^4$ | $z/c$ | $\sigma(z)\times10^4$ |
|---|---|---|---|---|---|---|
| Pd | 0·6260 | (0·6) | 0·3144 | (0·6) | 0·4499 | (0·5) |
| Cl | 0·3238 | (3) | 0·4201 | (2) | 0·3899 | (2) |
| C(1) | 0·6355 | (12) | 0·0773 | (11) | 0·3130 | (10) |
| C(2) | 0·8817 | (11) | 0·1895 | (11) | 0·4738 | (9) |
| C(3) | 0·7494 | (16) | 0·05959 | (15) | 0·4411 | (13) |

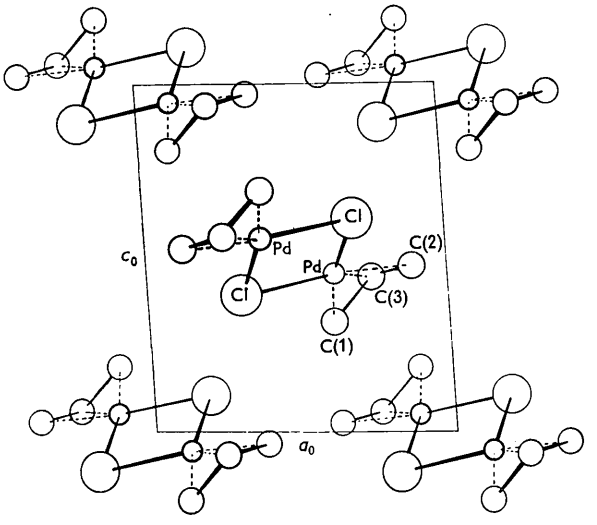



Fig. 1. Unit cell viewed along the *b* axis.

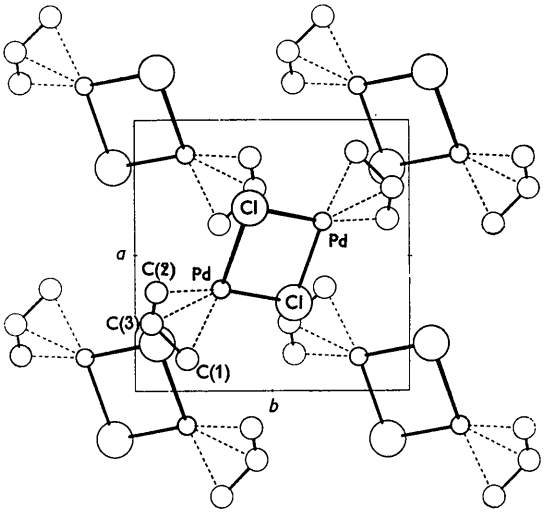



Fig. 2. Unit cell viewed along the *c* axis.

seen in Fig. 3 viewed in and perpendicular to the plane formed by the Pd and Cl atoms. Fig. 4 is a schematic sketch of the dimer. The allylic systems are planar and are related by a center of symmetry. The planes of the allyl groups in the dimer are inclined at 111·5° to the Pd–Cl–Pd plane (Figs. 3 and 4). The central carbon C(3) is 0·52$_8$ Å below the Pd–Cl–Pd plane and the carbon atoms C(1) and C(2) are 0·101 and 0·053 Å above the Pd–Cl–Pd plane respectively. The very slight rotation of the allyl molecule about an axis perpendicular to its plane (Fig. 3), is undoubtedly caused by non-bonded interactions (steric effects) of Cl and H atoms in adjacent molecules.

The bond distances and angles and their standard deviations calculated with the Error Program of Busing & Levy (1959*b*) are listed in Tables 3 and 4. Within the limit of experimental error the C ═ C bonds in the complex are equal with a mean 1·37$_7$ Å,

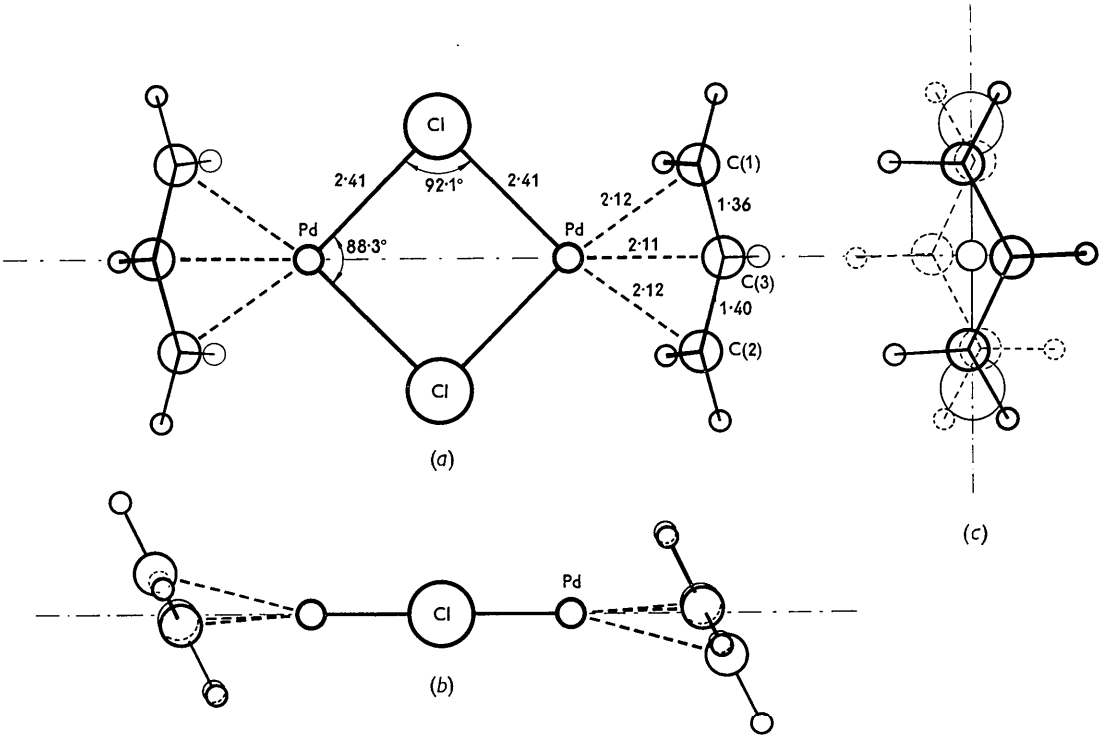



Fig. 3. (*a*) Plan, (*b*) elevation and (*c*) end view of $(C_3H_5PdCl)_2$ dimer with principal bond distances and angles.

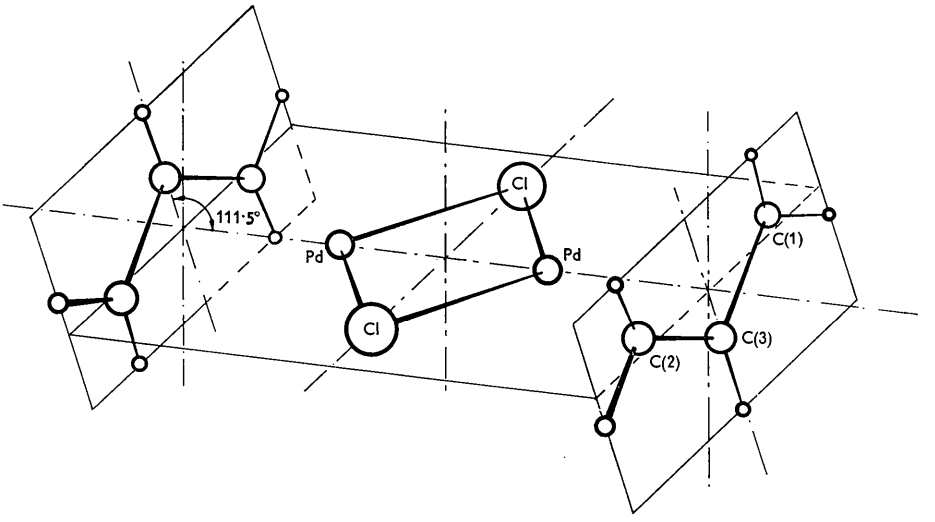



Fig. 4. Schematic drawing of $(C_3H_5PdCl)_2$ dimer.

Table 3. *Bond distances and angles*

| Bond | Distance ($d$) | $\sigma$ ($d$) | Bond angle | | $\sigma$ |
|---|---|---|---|---|---|
| Pd–Cl | 2·413 Å | 0·0020 Å | C(1)–C(3)–C(2) | 119·8° | 0·91° |
| C(1)–Pd | 2·123 | 0·0071 | Cl–Pd–Cl | 88·3 | 0·20 |
| C(2)–Pd | 2·121 | 0·0076 | Pd–Cl–Pd | 92·1 | 0·20 |
| C(3)–Pd | 2·108 | 0·0093 | Cl–Pd–C(1) | 102·3 | 0·24 |
| C(1)–Cl | 3·538 | 0·0078 | Cl–Pd–C(2) | 170·5 | 0·22 |
| C(1)–C(3) | 1·357 | 0·0153 | Pd–C(3)–C(1) | 71·9 | 0·51 |
| C(2)–C(3) | 1·395 | 0·0151 | Pd–C(3)–C(2) | 71·2 | 0·49 |
| Cl(1)–Cl(2) | 3·362 | 0·0035 | Dihedral angle between planes | | |
| Pd(1)–Pd(2) | 3·475 | 0·0020 | Cl–Pd–Cl and C(1)–C(2)–C(3) | 111·5 ± 0·92° | |

Table 4. *Anisotropic thermal parameters*

| Atom | $\beta_{11}$ $\times 10^5$ | $\sigma(\beta_{11})$ $\times 10^5$ | $\beta_{22}$ $\times 10^5$ | $\sigma(\beta_{22})$ $\times 10^5$ | $\beta_{33}$ $\times 10^5$ | $\sigma(\beta_{33})$ $\times 10^5$ | $\beta_{12}$ $\times 10^5$ | $\sigma(\beta_{12})$ $\times 10^5$ | $\beta_{13}$ $\times 10^5$ | $\sigma(\beta_{13})$ $\times 10^5$ | $\beta_{23}$ $\times 10^5$ | $\sigma(\beta_{23})$ $\times 10^5$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Pd | 605 | 8 | 481 | 5 | 568 | 4 | 150 | 8 | 83 | 4 | −12 | 5 |
| Cl | 726 | 32 | 870 | 24 | 959 | 21 | 194 | 23 | −114 | 20 | −340 | 18 |
| C(1) | 997 | 165 | 988 | 118 | 1185 | 108 | 275 | 112 | −170 | 104 | −485 | 90 |
| C(2) | 630 | 121 | 1061 | 107 | 998 | 88 | 474 | 111 | 14 | 83 | −11 | 89 |
| C(3) | 1492 | 223 | 1154 | 144 | 1898 | 173 | 403 | 158 | 471 | 160 | 43 | 133 |

$\sigma = 0{\cdot}015$ Å. They are significantly shorter (0·1% significance level) than the double bond in propylene (~ 1·501 Å) which along with the C–C–C bond angle of 119·8°, $\sigma = 0{\cdot}9°$, confirms the delocalization of the double bond in the complex. The Pd · · · C bonds are also equal within the limit of experimental error, with a mean of $2{\cdot}11_7$, $\sigma = 0{\cdot}008$ Å.

Since the maxima in the difference Fourier synthesis which were attributed to hydrogen were quite diffuse, H positions which differed slightly from these, based upon a C–H distance of ~ 1·08 Å and an H–C–H bond angle of ~ 118° were used in the calculations. The Pd · · · H distances calculated from the assumed hydrogen coordinates are listed in Table 5. The two H atoms H(1′) and H(2′) (Figs. 3 and 4) are considerably closer to the Pd (~ 2·1 Å) than the others which are ~ 2·96 Å from it. Dehm & Chien (1960), not knowing the actual configuration of the complex, incorrectly assumed that H atoms H(1) and H(2) were closer to the Pd. Reilly & Smutny (Reilly, 1963) have also shown from their nuclear magnetic resonance studies of the $(C_3H_5PdCl)_2$ complex that Dehm & Chien's assignment of protons is incorrect.

Table 5. Pd · · · H *distances*

| | |
|---|---|
| Pd(1) · · · H(1) | $2{\cdot}9_4$ Å |
| Pd(1) · · · H(2) | $2{\cdot}9_8$ |
| Pd(1) · · · H(1′) | $2{\cdot}0_8$ |
| Pd(1) · · · H(2′) | $2{\cdot}1_1$ |
| Pd(1) · · · H(3) | $2{\cdot}9_2$ |

The adjacent molecules of $(C_3H_5PdCl)_2$ are held together only by van der Waals forces. All intermolecular distances of less than ~ 4·0 Å were calculated. There are no abnormally short distances.

The $(C_3H_5PdCl)_2$ complex may possibly be viewed

either as an approximate square planar complex or as a half 'sandwich' complex similar in some respects to the cyclopentadienyliron complex.

Although the nature of the bonding between olefins and metal atoms is not understood in detail, the bonding is generally attributed to interactions of the $\pi$ orbitals of the olefin and the $d$ or hybridized $d$ orbitals of the metal ion. This view was initially proposed by Dewar (1951) and extended by Chatt & Duncanson (1953) and others (Orgel, 1960; Ballhausen, 1962). The bonding then consists of two parts: (1) the formation of a $\sigma$-type bond by overlap of the filled $\pi$ orbitals of the olefin with an empty $d$ or hybridized $d$ orbital of the metal, and (2) the back transfer of an electron from a filled $d$ or hybridized

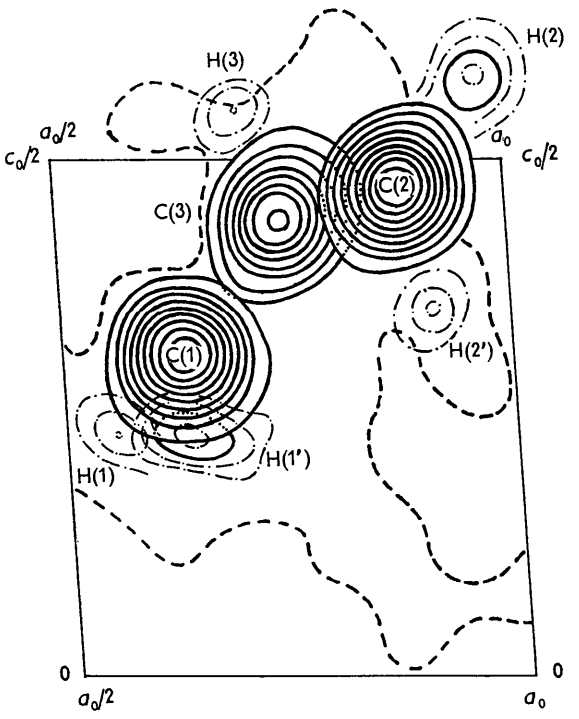



Fig. 5. Composite drawing of three-dimensional electron density map; difference-Fourier contours at arbitrary intervals. H contours —·— at ½ of solid contours.

$d$ orbital to the antibonding $\pi^*$ orbital of the olefin to form a $\pi$-bond. Since the formation of the $\sigma$-type and $\pi$-type bonds involves transfer or partial transfer of charge in opposite directions, both proceed more extensively and form stronger bonds than would be the case if they were operating separately.

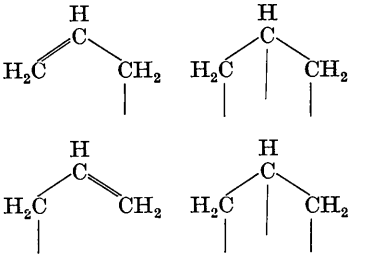
For ligands to form complexes with metal ions it is necessary that the symmetries of the orbitals and those of the metal ion match, and also that the orbitals do not differ too greatly in energy (Orgel, 1960). In the case of square planar complexes only the $d_{x^2-y^2}$ and to a lesser extent the $d_{z^2}$ metal orbitals (or hybrids involving these orbitals) can take part in the $\sigma$-type bonding (Orgel, 1960). (The $z$ axis is taken perpendicular to the plane of the square.) Similarly only the $d_{xz}$ and $d_{yz}$ orbitals can form $\pi$ bonds with the antibonding $\pi$ orbitals of the olefin.

Since the two allyl groups are inclined at 111·5° to the plane of the Pd and Cl atoms, satisfactory arrangements of the orbitals for both $\sigma$ and $\pi$ bonding meeting the symmetry requirements do not appear to be readily constructed. The fact that the carbon atoms are all equidistant from the Pd atoms also suggests it might be better to consider it as a half 'sandwich' type complex.

It is perhaps of interest to consider the $(C_3H_5PdCl)_2$ complex as analogous to the ferrocene or cyclopentadienylmanganese tricarbonyl complex from the resonating-bond viewpoint of Pauling (1960). The C ═ C distance of $1{\cdot}37_7$ Å corresponds to a bond number (Pauling, 1960, p. 255) of $\sim 1{\cdot}60$ and the Pd · · · C distance $2{\cdot}11_7$ corresponds to a bond number of $\sim 0{\cdot}78$. The latter value is calculated from Pauling's (1960, p. 256) formula:

$$D(n) = D(1) - 0{\cdot}60 \log n \,,$$

where $D(n)$ is the bond length for bond number $n < 1$, and $D(1)$ is the bond length for a single bond of similar type. Taking the Pd single bond radius as $\sim 1{\cdot}283$ from Pauling's (1960, p. 256) table and the single bond radius of carbon as $\sim 0{\cdot}77$ Å, the above value 0·78 is obtained for the Pd · · · C bond number in the complex. If the following resonance forms are assumed to exist in the complex




there are eight out of twelve carbon bonds to the Pd giving a bond number of 0·75 for the Pd · · · C bond. Two out of eight C–C bonds are double giving a total bond number of $\sim 1{\cdot}25$ for the C ═ C bonds in the complex. Although the latter value is in poor agreement with that calculated from the C═C bond lengths, the uncertainties in these distances are approximately twice those of the Pd═C bond distances. The relatively high bond number for the Pd · · · C bonds suggests that the Pd–Cl bond in the complex should be longer than normal. Although very few Pd–Cl distances involving bridged Cl atoms have been reported, that of 2·31 Å found in $PdCl_2$ (Wells, 1938) is appreciably shorter than that (2·41 Å) in the $(C_3H_5PdCl)_2$ complex.

*Note added in proof.*—I am indebted to Professor L. F. Dahl and W. E. Oberhansli for forwarding a pre-

print of their paper on a three-dimensional structural determination of $(C_3H_5PdCl)_2$ at room temperature (Dahl & Oberhansli, 1965). Both structure determinations are in agreement within the limit of experimental error. The standard deviations in bond lengths and angles for the low temperature work are, as expected, somewhat lower, *i.e.* only about one-third those of the room temperature determination. In addition it was possible to locate the H atoms approximately in the low temperature determination.

The author is indebted to W. R. Busing and H. Levy for making their least-squares and error programs available and to A. Zalkin for his Fourier synthesis program. He is also indebted to W. F. Birka for the design and construction of the constant level device and for aid with some of the calculations. He also wishes to thank J. L. Van Winkle for the preparation of the complex and for valuable discussions.

### References

Ballhausen, C. J. (1962). *Introduction to Ligand Field Theory*. New York: McGraw-Hill.
Busing, W. R. & Levy, H. A. (1959*a*). Oak Ridge National Laboratory Report 59–4–37.
Busing, W. R. & Levy, H. A. (1959*b*). Oak Ridge National Laboratory Report 59–12–3.
Chatt, J. & Duncanson, L. A. (1953). *J. Chem. Soc.* p. 2939.
Cruickshank, D. W. J. (1960). *Acta Cryst.* **13**, 774.
Dahl, L. F. & Oberhansli, W. E. (1965). *J. Organometallics*. In the press.
Dauben, C. H. & Templeton, D. H. (1955). *Acta Cryst.* **8**, 841.
Dawson, B. (1960). *Acta Cryst.* **13**, 403.
Dehm, H. C. & Chien, J. C. W. (1960). *J. Amer. Chem. Soc.* **82**, 4429.
Dewar, M. J. S. (1951). *Bull. Soc. Chim. Fr.* **18**, C79.
Hughes, E. W. (1941). *J. Amer. Chem. Soc.* **63**, 1737.
*International Tables for X-Ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.
Levdik, V. F. & Porai-Koshits, M. A. (1962). *J. Struct. Chem.* (p. 455, Trans-Consultants Bureau 1963).
McWeeny, R. (1951). *Acta Cryst.* **4**, 513.
Moiseev, I. I. *et al.* (1959). *J. Inorg. Chem.* (*USSR*), **4**, 2641.
Orgel, L. E. (1960). *An Introduction to Transition Metal Chemistry*. London: Methuen.
Pauling, L. (1960). *The Nature of the Chemical Bond*. 3rd Ed. Ithaca: Cornell Univ. Press.
Reilly, C. A. (1963). Private communication.
Rowe, J. M. (1962). *J. Chem. Soc.* p. 66.
Smidt, J. & Hafner, W. (1959). *Angew. Chem.* **71**, 284.
Wells, A. F. (1938). *Z. Kristallogr.* **100** (A), 189.

*Acta Cryst.* (1965). **18**, 340

# The Crystal Structure of Uranium Chloride $\pi$-Tricyclopentadienyl

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The crystal structure of uranium chloride $\pi$-tricyclopentadienyl has been determined by analysis of X-ray diffraction data. The crystals are monoclinic, space group $P2_1/n$, with $a = 8{\cdot}26$ Å, $b = 12{\cdot}50$ Å, $c = 13{\cdot}81$ Å, and $\beta = 90{\cdot}6°$. There are four molecules per unit cell. The coordinates for the uranium atom were determined from two Patterson projections. The structure was then deduced from a three-dimensional Fourier synthesis and, later, a difference synthesis. The positional and vibrational parameters for the uranium and chlorine atoms were refined by least-squares calculations, and the positional parameters for the carbon atoms were refined by another difference synthesis. The bond lengths are: U–Cl = 2·559 ± 0·016 Å, U–C = 2·74 Å. A regular planar pentagonal structure for the cyclopentadienyl rings with C–C $\simeq$ 1·4 Å is compatible with the difference maps. These results indicate that the U–Cl bond is essentially ionic, and that there are approximately three pairs of electrons responsible for the bonding between the uranium atom and the three cyclopentadienyl groups. The cyclopentadienyl rings and the chlorine atom form a distorted tetrahedron about the uranium atoms.

## Introduction

A number of structural studies of sandwich compounds and their derivatives have been reported during recent years, but no investigation of the structure of a metal tricyclopentadienyl has yet been reported. We have chosen uranium chloride $\pi$-tricyclopentadienyl for it is the only metal tricyclopentadienyl compound that has been reported to have sandwich-type bonding* (Reynolds & Wilkinson, 1956). Because of the intrinsic difficulties involved in obtaining good intensity data (see Experimental), and because of the great difference

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