Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Dichloro(norbornadiene)platinum(II): a comparison with dichloro(cyclooctadiene)platinum(II)

Jeffrey L. Butikofer, Eric W. Kalberer, William C. Schuster and Dean M. Roddick*

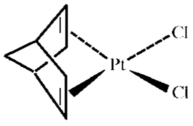
Department 3838, Chemistry, 1000 East University Avenue, University of Wyoming, Laramie, WY 82071, USA
Correspondence e-mail: dmr@uwyo.edu

Received 18 May 2004
Accepted 21 May 2004
Online 30 June 2004

The crystal structure of the title compound, (bicyclo[2.2.1]-hepta-2,5-diene)dichloroplatinum(II), $[PtCl_2(C_7H_8)]$, has been determined from single-crystal X-ray analysis. The coordination sphere about the Pt atom is pseudo-square planar, with shorter Pt—C distances than in the corresponding dichloro(cyclooctadiene)platinum(II) complex.

Comment

In platinum(II) chemistry, norbornadiene (NBD) is generally considered to be a more labile ligand than 1,5-cyclooctadiene (COD; Appleton *et al.*, 1986, 1989). This lability is often attributed to the smaller bite angle of the chelating NBD ligand *versus* COD. However, there are very few corresponding structurally characterized COD (Klein *et al.*, 1999) and NBD (Kickelbick *et al.*, 2002) platinum(II) complexes. We now report the crystal structure of the title compound, $(NBD)PtCl_2$, (I), and compare it with that of $(COD)PtCl_2$, (II) (Syed *et al.*, 1984).



(I)

The two Cl atoms and the centroids of the alkene NBD bonds form an essentially square-planar environment around the Pt atom in (I). The bite angle, as defined by the angle between the two alkene centroid positions and the Pt atom, is 70.3°. This is similar to what has been observed in other $(NBD)Pt^{II}$ complexes, such as (NBD)Pt(Cl)Me (69.1°; Kickelbick *et al.*, 2002) and $(NBD)Pt(2\text{-ethoxynapth-1-yl})_2$ (70.4°; Debaerdemaeker *et al.*, 1987), but is significantly smaller than the bite angle of 87.3° found for (II), as expected. The Cl—Pt—Cl bond angle in (I) [92.02 (8)°] is slightly larger than the corresponding angle in (II) [89.78 (5)°], and this is most likely due to the different bite angles of the NBD and COD supporting ligands.

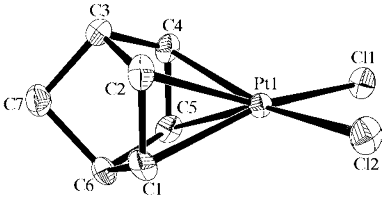


Figure 1
The molecular structure of (I), showing 30% probability displacement ellipsoids. H atoms have been omitted for clarity.

The Pt—C bond lengths in (I) do not reflect the enhanced lability of the NBD chelate. They are, in fact, significantly shorter than those found in (II); the average Pt—C bond length in (I) is 2.145 Å, *versus* 2.170 Å in (II). Therefore, the increased lability often observed for NBD in Pt^{II} systems cannot be attributed to a loosely bound NBD ligand, but probably results from relief of binding strain associated with the small bite angle. The Pt—Cl bond lengths in (I), as well as the C=C alkene bond lengths, are very similar to those found in (II), indicating that NBD and COD have similar donating abilities.

Experimental

We have recently reported an improved synthesis of (I) (Butikofer *et al.*, 2004). Single crystals of (I) were obtained by heating a benzene solution of $(NBD)Pt(CH_2Cl)_2$ at 373 K in a sealed NMR tube. Formation of (I) most likely resulted from thermal decomposition (*via* ethylene loss) of the chloromethyl species at these temperatures.

Crystal data

$[PtCl_2(C_7H_8)]$
$M_r = 358.12$
Monoclinic, $C2/c$
$a = 12.8717$ (17) Å
$b = 11.5173$ (12) Å
$c = 12.6441$ (13) Å
$\beta = 120.507$ (12)°
$V = 1615.0$ (3) Å^3
$Z = 8$

$D_x = 2.946$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 35 reflections
$\theta = 4.8$–12.5°
$\mu = 17.95$ mm^{-1}
$T = 298$ (2) K
Rectangular prism, colorless
0.52 × 0.12 × 0.08 mm

Data collection

Bruker *P*4 diffractometer
ω scans
Absorption correction: ψ scan (*SHELXL*97; Sheldrick, 1997)
$T_{min} = 0.080$, $T_{max} = 0.237$
2291 measured reflections
1843 independent reflections
1559 reflections with $I > 2\sigma(I)$

$R_{int} = 0.055$
$\theta_{max} = 27.5°$
$h = -1 \rightarrow 16$
$k = -1 \rightarrow 14$
$l = -16 \rightarrow 14$
3 standard reflections every 97 reflections
intensity decay: 1%

Table 1
Selected geometric parameters (Å, °).

Pt1—C2	2.140 (8)	Pt1—Cl2	2.3056 (19)
Pt1—C5	2.144 (8)	Pt1—Cl1	2.3058 (19)
Pt1—C1	2.146 (7)	C1—C2	1.391 (12)
Pt1—C4	2.148 (7)	C4—C5	1.386 (12)
C5—Pt1—C1	66.2 (3)	C5—Pt1—Cl1	98.9 (2)
C2—Pt1—C4	65.8 (3)	C4—Pt1—Cl1	97.9 (2)
C2—Pt1—Cl2	98.8 (2)	Cl2—Pt1—Cl1	92.02 (8)
C1—Pt1—Cl2	97.8 (2)		

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.035$	$w = 1/[\sigma^2(F_o^2) + (0.0552P)^2]$
$wR(F^2) = 0.090$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{\max} < 0.001$
1843 reflections	$\Delta\rho_{\max} = 2.00$ e Å^{-3}
91 parameters	$\Delta\rho_{\min} = -2.24$ e Å^{-3}

H atoms were added in calculated positions and treated as riding, with C—H distances in the range 0.97–0.98 Å and with $U_{\rm iso}(\rm H) = 1.2U_{\rm eq}(\rm C)$.

Data collection: *XSCANS* (Bruker, 1997); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Bruker, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

This work was supported by the National Science Foundation (grant No. CHE-0093049).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1667). Services for accessing these data are described at the back of the journal.

References

Appleton, T. G., Berry, R. D., Hall, J. R. & Neale, D. W. (1989). *J. Organomet. Chem.* **364**, 249–273.

Appleton, T. G., Hall, J. R. & Williams, M. A. (1986). *J. Organomet. Chem.* **303**, 139–149.

Bruker (1997). *SHELXTL* (Version 5.10) and *XSCANS* (Version 2.31). Bruker AXS Inc., Madison, Wisconsin, USA.

Butikofer, J. L., Hoerter, J. M., Peters, R. G. & Roddick, D. M. (2004). *Organometallics*, **23**, 400–408.

Debaerdemaeker, T., Weiseman, C. & Brune, H. A. (1987). *Acta Cryst.* C**43**, 432–434.

Kickelbick, G., Stohr, F. & Schubert, U. (2002). *Acta Cryst.* E**58**, m387–m388.

Klein, A., Klinkhammer, K.-W. & Scheiring, T. (1999). *J. Organomet. Chem.* **592**, 128–135.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.

Syed, A., Stevens, E. D. & Cruz, S. G. (1984). *Inorg. Chem.* **23**, 3673–3674.

m354 Jeffrey L. Butikofer *et al.* • $[\rm PtCl_2(C_7H_8)]$ *Acta Cryst.* (2004). C**60**, m353–m354