

# Chloromethyl( $\eta^4$ -norbornadiene)platinum(II), an unsymmetrical substituted precursor for Pt<sup>II</sup> complexes

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## Key indicators

Single-crystal X-ray study  
 $T = 213\text{ K}$   
 Mean  $\sigma(\text{C}-\text{C}) = 0.009\text{ \AA}$   
 H-atom completeness 73%  
 Disorder in main residue  
 $R$  factor = 0.027  
 $wR$  factor = 0.073  
 Data-to-parameter ratio = 22.4

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound,  $[\text{PtCl}(\text{CH}_3)(\text{C}_7\text{H}_8)]$  or  $[(\text{nbd})\text{PtClMe}]$  (nbd is norbornadiene), was formed in a partial substitution reaction of dichloro( $\eta^4$ -norbornadiene)platinum(II). The Pt atom exhibits tetrahedral coordination, involving the two  $\eta^2-\pi$  bonds to the norbornadiene, one chlorine and one methyl substituent. Probably as a result of the symmetry of the norbornadiene and the approximately equal size of the methyl and chlorine substituents, these two substituents are disordered and have been refined, each with half-occupancy.

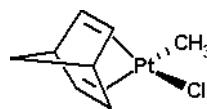
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## Comment

Olefinic coordination compounds of platinum are often used as precursors for other complexes, due to the easy substitution of the olefin by other ligands. One of the most prominent examples of such a precursor is dichloro( $\eta^4$ -cycloocta-1,5-diene)platinum,  $[(\text{COD})\text{PtCl}_2]$ . Another important olefinic ligand is norbornadiene (nbd), whose chemical behavior is quite similar to that of cyclooctadiene.



(I)

The title complex, (I), has Pt—C distances to the olefinic C atoms of 2.191 (6), 2.195 (6), 2.210 (5) and 2.218 (5) Å, indicating a nearly symmetrical bonding situation. Elemental analysis and NMR studies showed that the product of the reaction had both a chlorine and a methyl substituent. However, the methyl and chlorine substituents occupy the same coordination sites and, accordingly, the positions were refined with a half-occupation model. The distances of these substituents were found to be 2.245 (2) (Pt—Cl1/C1A) and 2.294 (2) Å (Pt—Cl2/C2A). These values lie between the Pt—Cl distances in the related  $[(\text{COD})\text{PtCl}_2]$  complex [Pt—Cl 2.315 (1) and 2.309 (1) Å; Syed *et al.*, 1984], and those of dimethyl-substituted COD complexes [2.056 (6) and 2.069 (6) Å; Smith *et al.*, 2000]. The difference between the Pt—Cl and Pt—Me distances can be estimated from the structure of an asymmetrically substituted  $[(\text{COD})\text{PtMeCl}]$  complex. In this compound, the Pt—C distance was found to be 2.164 (8) Å, while the Pt—Cl bond length was 2.330 (2) Å (Klein *et al.*, 1999). Hence, the difference between the distances is approximately 0.166 Å and should be similar in the title complex, if it were not disordered.

The Cl1/C1A—Pt—Cl2/C2A angle is 86.31 (9)° and thus more similar to the Me—Pt—Me angle in  $[(\text{COD})\text{PtMe}_2]$

[85.9 (3)°; Smith *et al.*, 2000] or [(COD)PtMeCl] [85.6 (3)°; Klein *et al.*, 1999] than to the [(COD)PtCl<sub>2</sub>] complex [89.78 (5)°; Syed *et al.*, 1984]. The so-called bite angle of the nbd ligand is much smaller (71.15° is the average C—Pt—C angle) than the angle for the COD ligand (on average around 86°) (Klein *et al.*, 1999).

## Experimental

The title complex was prepared according to a modified reaction procedure for the synthesis of (COD)PtMeCl (Dekker *et al.*, 1992).

### Crystal data

[PtCl(CH <sub>3</sub> )(C <sub>7</sub> H <sub>8</sub> )]	$D_x = 2.662 \text{ Mg m}^{-3}$
$M_r = 337.72$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 4347 reflections
$a = 13.0526 (7) \text{ \AA}$	$\theta = 2.5\text{--}28.3^\circ$
$b = 11.8020 (6) \text{ \AA}$	$\mu = 17.04 \text{ mm}^{-1}$
$c = 12.6014 (6) \text{ \AA}$	$T = 213 (2) \text{ K}$
$\beta = 120.636 (1)^\circ$	Prism, colorless
$V = 1670.25 (15) \text{ \AA}^3$	$0.52 \times 0.16 \times 0.10 \text{ mm}$
$Z = 8$	

### Data collection

Bruker SMART CCD area-detector diffractometer	2062 independent reflections
$\omega$ scans	1910 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$R_{\text{int}} = 0.036$
$T_{\text{min}} = 0.041$ , $T_{\text{max}} = 0.281$	$\theta_{\text{max}} = 28.3^\circ$
5677 measured reflections	$h = -17 \rightarrow 17$
	$k = -15 \rightarrow 13$
	$l = -16 \rightarrow 12$

### Refinement

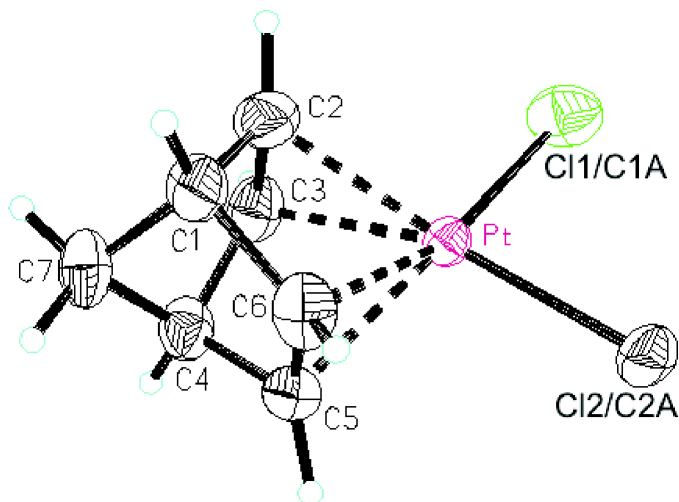
Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0471P)^2 + 3.7959P]$
$R[F^2 > 2\sigma(F^2)] = 0.027$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.073$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.07$	$\Delta\rho_{\text{max}} = 1.72 \text{ e \AA}^{-3}$
2062 reflections	$\Delta\rho_{\text{min}} = -1.65 \text{ e \AA}^{-3}$
92 parameters	Extinction correction: SHELXL97
H-atom parameters constrained	Extinction coefficient: 0.00090 (9)

**Table 1**

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

Pt—C2	2.191 (6)	Pt—C6	2.218 (5)
Pt—C3	2.195 (6)	Pt—Cl1	2.245 (2)
Pt—C5	2.210 (5)	Pt—C2A	2.294 (2)
C2—Pt—C5	77.1 (2)	C3—Pt—C6	77.1 (2)
C3—Pt—C5	64.9 (2)	Cl1—Pt—C2A	86.31 (9)
C2—Pt—C6	65.5 (2)		

H atoms were located in difference Fourier maps and refined with a riding model, with the exception of the methyl H atoms, which were



**Figure 1**

The molecular structure of the title complex, with atom labels and 50% probability ellipsoids for the non-H atoms.

not included in the refinement. The highest and lowest final difference electron density occurred at 0.87 and 0.96  $\text{\AA}$ , respectively, from the Pt atom.

Data collection: SMART (Bruker, 1997); cell refinement: SAINT (Bruker, 1997); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 1998); software used to prepare material for publication: SHELXL97.

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