Synthesis of arylplatinum(II) complexes with chiral monoanionic aryldiamine ligands.
The X-ray crystal structure of (−)-[(1R,1′R)-2,6-bis{1-(dimethylamino)propyl}-phenyl]chloroplatinum(II) [1]

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Abstract

The new chiral arylplatinum(II) compounds [2,6-bis(1-(dimethylamino)ethyl)phenyl]chloroplatinum(II) (**4**) and (−)-[(1R,1′R)-bis(1-(dimethylamino)propyl)phenyl]chloroplatinum(II) (**5**) have been synthesized. The transmetallation of the corresponding aryllithium compounds does not affect either stereogenic centres of the organic ligand while the rate of the transmetallation is shown to be influenced by the size of the benzylic substituents. The X-ray crystal structure of **5** is reported from which the absolute configuration of both stereogenic centres of the organic ligand was determined to be (R). © 1998 Elsevier Science B.V.

Keywords: (−)-[(1R,1′R)-bis(1-(dimethylamino)propyl)phenyl]chloroplatinum(II); Arylplatinum(II); Chiral monoanionic aryldiamine ligands

1. Introduction

The potentially terdentate, monoanionic aryl ligands $[C_6H_3(CH_2E)_2$-2,6$]^-$ (E = NR$_2$ [1–7], PR$_2$ [8–12] and SR [13–16]) (Fig. 1) have been extensively used during the last two decades to synthesize a wide variety of new and interesting organometallic species. Both main group- and transition-metals have been coordinated to this type of ligand. This includes the isolation and characterization of arylmetal complexes with new physico-chemical properties and novel structural features. In addition,
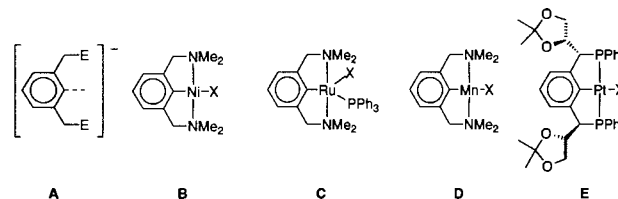

Fig. 1. General structure of terdentate monanionic aryldiamines (E = NR$_2$), aryldiphosphines (E = PR$_2$) and aryldisulphides (E = SR) (**A**) and some organometallic derivatives (**B–E**).
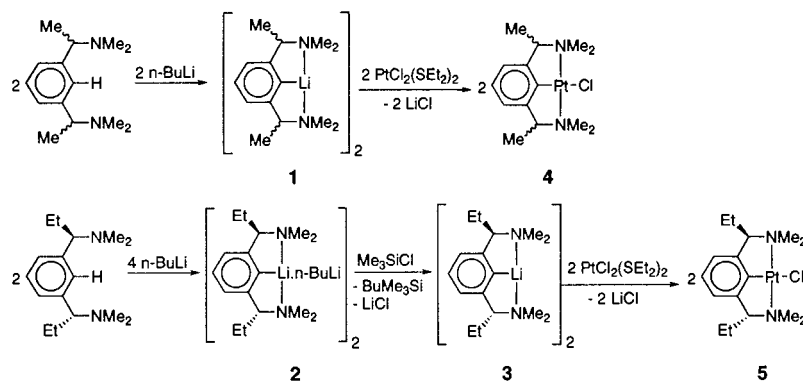
several of these complexes showed remarkable catalytic activity.

For example, the use of the monoanionic aryldiamine ligand 2,6-bis[(dimethylamino)methyl]phenyl (abbreviated as NCN) (Fig. 1**A**, E = NMe$_2$) led to the isolation of NiX(NCN) (Fig. 1**B**) [17], which is an excellent catalyst for the Kharasch addition reaction of polyhalo-

Scheme 1.

genated alkanes to terminal alkenes [18]. We have reported two other examples of catalytically active NCN–metal complexes, i.e., (i) a hydrogen transfer catalyst based on Ru^{II}(NCN) [19] (Fig. 1**C**), and (ii), a Mn^{II}(NCN)X complex (Fig. 1**D**), which is catalytically active in both C–C cross coupling and 1,4-conjugate addition reactions [20]. Recently a platinum compound containing an enantiopure chiral phosphorous derivative, Fig. 1**E**, has been reported. It has been shown that this complex is an excellent catalyst in the enantioselective aldol reaction (e.e. up to 65%) of methyl isocyanate with aldehydes [21].

Previously we developed synthetic routes towards enantiopure chiral analogues of the monoanionic aryldiamine ligand systems (see Fig. 2**A**) [22]. Unfortunately, the corresponding organonickel compounds, although active, did not show appreciable stereochemical induction in the Kharasch addition reaction of CCl$_4$ to the C–C double bond of alkenes. It was assumed that this lack of chiral induction results from the fact that the stereochemical information is too far away from the reactive Ni centre. Therefore, we recently explored the synthesis and lithiation of racemic and enantiopure α,α'-substituted aryldiamine ligands (Fig. 2**B**) [23], as well as the transmetallation reaction of the corresponding chiral aryllithium compounds [3].

We report here the transmetallation of both enantiopure and racemic aryldiamine lithium compounds with platinum(II) halide salts to study the effect of the benzylic substituents on the course and the rate of the transmetallation reaction. In addition, an X-ray crystal structure determination of the enantiopure platinum compound provided the absolute stereochemistry of the two chiral centres present in the ligand that was obtained via a recently developed enantioselective route [23].

2. Results and discussion

The heteroatom assisted lithiation of a mixture of the DL and *meso* isomers (1:1 molar ratio) of 1,3-bis[1-(dimethylamino)ethyl]benzene with n-BuLi afforded the corresponding lithiated compound (**1**), see Scheme 1, in quantitative yield. It is obvious that the resulting aryllithium compound is a complex mixture of aggregated diastereoisomers, a topic that will be discussed in a forthcoming paper [23]. It appeared that a similar reaction of enantiopure $(1R,1'R)$-1,3-bis[1-(dimethylamino)propyl]benzene with n-BuLi gives rise to the formation of a mixed organolithium aggregate (**2**) (see Scheme 1), consisting of the parent lithiated compound and n-BuLi in a 1:1 molar ratio [23]. The formation of such mixed aggregates is not unprecedented, e.g., a similar aggregate was obtained by the lithiation of 1,3-bis(dimethylaminomethyl)-2,4,6-trimethylbenzene with n-BuLi [27].

For obvious reasons the 1:1 mixed alkyl–aryllithium aggregate **2** is not suitable as a starting material for other organometallic compounds via a transmetallation reaction. It is expected that the formation of transient metallobutyl intermediates will give rise to extensive decomposition, e.g., via β-elimination reactions. How-
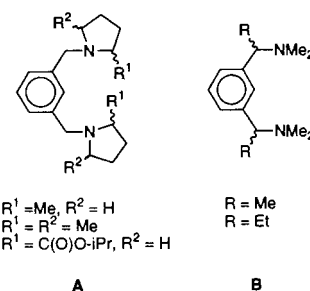
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[3] In this respect it should be noted that aminoarenethiolate ligands derived from enantiopure α-methyl substituted benzylamines are excellent catalyst precursors for, e.g., enantioselective 1,4-conjugate addition reactions (e.e. up to 76%) [24] catalyzed by chiral copper(I) aminoarenethiolates as well as the enantioselective 1,2-addition reactions of dialkylzinc compounds to aldehydes (e.e. up to 98%) [25,26] catalyzed by the corresponding chiral zinc *bis*-(aminoarenethiolates).
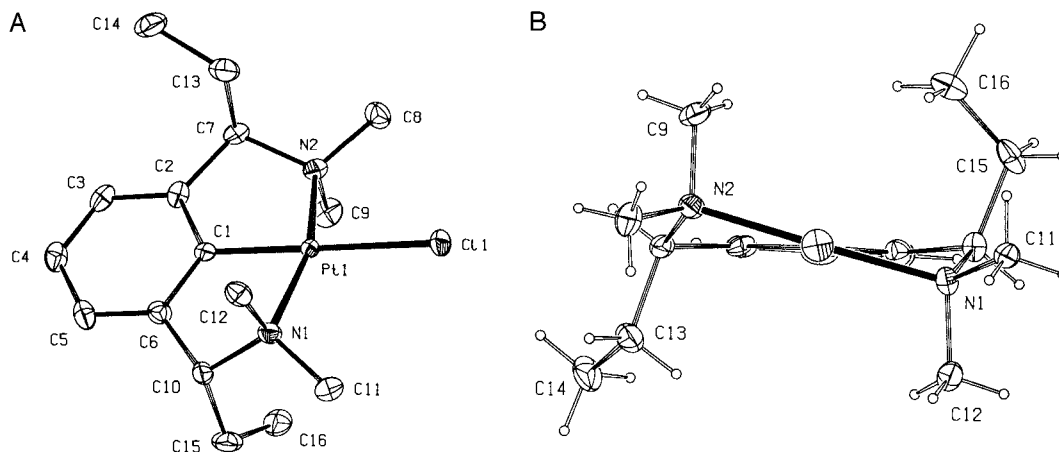
Fig. 2. Chiral terdentate monoanionic aryldiamine ligands.

Fig. 3. A: molecular structure of **5**, hydrogen atoms have been omitted for clarity. B: projection of **5** along the C_2 axis showing ring puckering of the two chelate rings.

ever, it appeared that Me_3SiCl reacts selectively with the butyl moieties in **2** to give the parent lithiated compound (**3**) and $BuMe_3Si$ (see Scheme 1) in quantitative yield [23]. This provides an excellent route for the synthesis of enantiopure **3**.

The reaction of **1** with one equivalent of $PtCl_2(SEt_2)_2$ in C_6H_6, see Scheme 1, afforded after work-up (see Section 3) a brown solid. The ^{1}H-NMR spectrum of this material showed the presence of two diastereoisomeric arylplatinum compounds **4**, 1,3-bis[1-(dimethylamino)ethyl]benzene ^{4} and $PtCl_2(SEt_2)_2$ in approximately equimolar amounts. Unfortunately we were unable to purify **4** by recrystallization.

The observation of two distinctly different resonance patterns (4.0 and 4.15 ppm ($-CHNMe_2$); 2.79, 3.10 and 2.85, 3.05 ppm ($N(CH_3)_2$) in the ^{1}H-NMR spectrum of **4** (see Section 3) points to the presence of different diastereoisomers, i.e., the DL and *meso* diastereoisomers in a 1:1 molar ratio. In fact, the formation of these diastereoisomers is obvious, since the DL/*meso* ratio in the starting material is also 1:1, vide supra.

That two *N*-methyl resonances are observed for each diastereoisomer indicates that Pt–N coordination is rigid on the NMR time-scale, i.e. pyramidal inversion at nitrogen is blocked, and as a consequence the N-methyl groups are diastereotopic due to the presence of the adjacent chiral centre. Furthermore, the presence of coupling due to NMR active ^{195}Pt nuclei ($^3J(^{195}$Pt-^{1}H)) at the NMe_2 resonances is additional evidence for a strong Pt–N interaction in **4**.

The reaction of enantiopure **3** with one equivalent of $PtCl_2(SEt_2)_2$ in C_6H_6 afforded after work-up (see Sec-

tion 3) the arylplatinum compound (**5**), see Scheme 1, as a white crystalline material in 27% yield. This new, enantiopure compound was characterized by ^{1}H- and ^{13}C{^{1}H}-NMR spectroscopy, elemental analysis and optical rotation (see Section 3). In order to establish the molecular structure of **5**, and in particular, to determine the absolute stereochemistry of the stereogenic centres, an X-ray crystal structure determination of **5** was carried out.

The crystal structure of **5** involves the packing of two crystallographically equivalent discrete mononuclear molecules in the monoclinic unit cell, space group $P2_1$. In Fig. 3A the molecular geometry of **5** is shown with the adopted numbering scheme while relevant bond distances and angles are given in Table 1. The overall structural features found for **5** are closely related to that of earlier reported [PtBr{$C_6H_3(CH_2NMe_2)_2$-2,6}] [28]. The coordination-geometry of the platinum(II) centre in **5** is distorted square-planar with C(1) and Cl(1), and N(1) and N(2) in *trans* positions. The C(1)–Pt–Cl bond angle is 178.82(19)° while the N(1)–Pt–N(2) bond angle is 161.5(2)° showing an angular deviation from perfect *trans* coordination. The deviation of the latter bond angle from 180° is a result of the acute N–Pt–C(1) bite angles in the two five-membered chelate rings of 80.1(2) and 81.59(2)°, respectively. The Pt–C bond distance of 1.921(6) Å found in **5** is short when compared with this distance in other arylplatinum(II) compounds for which this distance lies in the range of 1.98

Table 1
Selected bond lengths (Å) and angles (°) of **5** with esd. of the last significant digits given in parentheses

Bond lengths		Bond angles	
N(1)–Pt(1)	2.092(6)	N(1)–Pt(1)–N(2)	161.5(2)
N(2)–Pt(1)	2.091(5)	N(1)–Pt(1)–C(1)	81.5(2)
C(1)–Pt(1)	1.921(6)	N(1)–Pt(1)–Cl(1)	98.31(17)
Cl(1)–Pt(1)	2.4179(17)	N(2)–Pt(1)–C(1)	80.1(2)
		N(2)–Pt(1)–Cl(1)	100.09(15)
		C(1)–Pt(1)–Cl(1)	178.82(19)

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^{4} Since this reaction was carried out on a relatively small scale (see Section 3), it may not be excluded that relatively large amounts of 1,3-bis[1-(dimethylamino)ethyl]benzene, i.e. the hydrolysis product of the parent lithiated compound, is formed prior to the transmetallation reaction due to the presence of trace amounts of moisture.
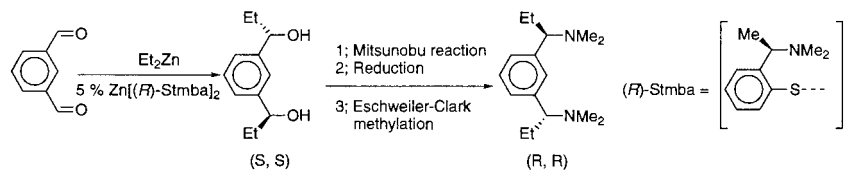
Scheme 2.

to 2.08 Å [29–33], but is comparable to the distance found in previously reported [PtBr{$C_6H_3(CH_2NMe_2)_2$-2,6}] [28]. Furthermore, although not crystallographically, compound **5** exhibits almost perfect C_2 symmetry, as shown in Fig. 3B.

The two five-membered chelate rings are puckered in such a way that the ethyl substituents are oriented in the most favourable position, i.e. perpendicular to the plane of the aryl ring. As a consequence of this puckering, one of the methyl groups of each NMe_2 group is in an equatorial position while the other methyl group is placed pseudo-axial (see Fig. 3B). A similar puckering combined with C_2 symmetry is found in square-planar complexes like [PtBr{$C_6H_3(CH_2NMe_2)_2$-2,6}] [28] and [PdCl{$C_6H_3(CH_2PPh_2)_2$-2,6}] [11] or octahedral complexes, e.g. [PtI$_2${$C_6H_3(CH_2NMe_2)_2$-2,6}(C_6H_4Me-4)] [34].

The absolute configuration of both stereogenic centres is determined to be (R) (based on refinement of the Flack parameter, see Section 3).

A molecular weight determination (by cryoscopy in C_6H_6) showed that **5** in solution exists as a discrete monomeric species. The observed specific rotation of **5** in CHCl$_3$ solutions ([α]$_D^{22}$ = − 101.7°) indicates that one enantiomer is in greater abundance. That the molecular structure as found for **5** in the solid state is most likely retained in solution became evident from the observed ^{1}H- and ^{13}C{^{1}H}-NMR spectra (see Section 3) of **5** in benzene-d$_6$ solution. The observation of one distinct resonance pattern both in the ^{1}H and ^{13}C{^{1}H}-NMR spectrum is unambiguous and again indicates that the complex has not racemized to the meso form. It should be noted that the ^{1}H and ^{13}C{^{1}H}-NMR spectra of recrystallized and crude material are identical, indicating that no diastereoselection has occurred during the purification procedure. That Pt–N coordination is inert in solution is reflected by the observation of two N(CH$_3$)$_2$ resonances in both the ^{1}H (2.65 and 2.67

ppm) and ^{13}C{^{1}H} (48.4 and 54.9 ppm)-NMR spectrum as a result of the diastereotopicity of this group for reasons outlined for **4**, vide supra.

2.1. Concluding remarks

It is remarkable that whereas the earlier reported [PtCl{$C_6H_3(CH_2NMe_2)_2$-2,6}] is indefinitely stable in the solid state as well in solution, solutions of compound **5** in CHCl$_3$, CH$_2$Cl$_2$ or C_6H_6 slowly decompose into metallic platinum and unidentified organic products. Furthermore, it appeared that the presence and bulk of the benzylic substituent influences the reaction time required for the transmetallation reaction; one day for compound **4** versus three days for compound **5**.

The apparent influence of the substituents at the benzylic positions on the transmetallation of **1** and **3** suggests that primary attack of the platinum(II) salts is at C(1) implying the formation of a transition state in which the aryl group is two-electron fourcentre bonded between platinum and lithium, schematically shown in Fig. 4A. This proposed binding is comparable with that encountered in stable heterodinuclear rhodate and iridate compounds which contain an aryl ligand bridging between lithium and the transition metal.

The X-ray crystal structure determination of **5** has unambiguously shown that the absolute configuration at both substituted benzylic centres is (R). This strongly suggests that the configuration of these chiral centres in the starting 1,3-bis[1-(dimethylamino)propyl]benzene is also (R). We prepared this ligand via a recently developed enantioselective route [23] outlined in Scheme 2. The absolute stereochemistry of the product was hitherto unknown but has now been established by the structural characterization of **5** [5].

We are currently investigating the use of these and related chiral aryldiamine ligands for the synthesis of new enantiopure NCN–metal compounds and their use in homogeneous catalysis.
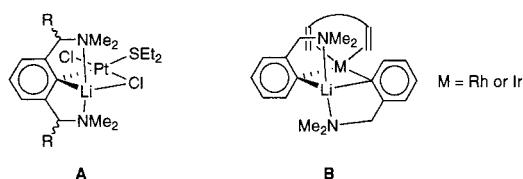
Fig. 4. A: proposed mixed lithium–platinum intermediate formed during the transmetallation of **1** and **3** to **4** and **5**, respectively. B: isolated lithium–rhodate and –iridate compounds [35].

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[5] It should be noted that, when using the (Zn[(R)-Stmba]$_2$) catalyst, the expected configuration of the benzylic chiral centres in the diol (see Scheme 2) based on the predictions made by Noyori is (S,S) (cf. [25,26]). The subsequent Mitsunobu reaction proceeds with inversion of configuration and thus would provide the (R,R) diamine.

3. Experimental

All experiments in which organometallic compounds are involved were performed in a dry, nitrogen atmosphere using standard Schlenk techniques. Solvents were stored over sodium benzophenone ketyl and distilled prior to use. Elemental analysis was provided by Domis u. Kolbe, Mülheim a.d. Ruhr, Germany; ^{1}H- (200 or 300 MHz) and ^{13}C{^{1}H}- (50 or 75 MHz) NMR spectra were recorded on Bruker AC200 or AC300 spectrometers at ambient temperature unless otherwise stated. Melting (decomposition) points were determined by using a Büchi melting point apparatus. Optical rotation was determined at 22°C using a Perkin Elmer 241 polarimeter. The *cis*-PtCl$_2$(SEt$_2$)$_2$ [36], 2,6-bis[1-(dimethylamino)ethyl]phenyllithium [22]b and (1R,1'R)-2,6-bis[1-(dimethylamino)propyl]phenyllithium [22]b were prepared according to published procedures.

3.1. Synthesis of [2,6-bis{1-(dimethylamino)ethyl}-phenyl]chloroplatinum(II) (4)

A 1:1 molar mixture of the DL/*meso* isomers of 2,6-bis[1-(dimethylamino)ethyl]phenyllithium (0.84 mmol) was dissolved in C$_6$H$_6$ (25 ml) after which a solution of PtCl$_2$(SEt$_2$)$_2$ (0.84 mmol) in C$_6$H$_6$ (10 ml) was added. The reaction mixture was stirred for 1 day at room temperature. The reaction mixture was filtered over Celite and the solvent of the filtrate was removed in vacuo. The crude platinum complex was isolated as a brownish solid that contained both PtCl$_2$(SEt$_2$)$_2$ and 1,3-bis[1-(dimethylamino)ethyl]benzene. Attempts to purify this crude product by washing the brown solid with pentanes or by recrystallization from saturated CHCl$_3$ or C$_7$H$_8$ solutions were unsuccessful. ^{1}H-NMR (C$_6$D$_6$): 6.95 (m, 1H, ArH), 6.65 (m, 2H, ArH), 4.15 and 4.05 (q, ^3J = 9.0 Hz, 1H, CH), 3.15, 3.10, 2.85 and 2.79 (s, (^{195}Pt-^{1}H)J = 42 Hz, 6H, N(CH_3)$_2$), 1.3 and 1.4 (d, ^3J = 7.2 Hz, 3H, CH$_3$).

3.2. Synthesis of (−)-[(1R,1'R)-2,6-bis(1-(dimethyl-amino)propyl)phenyl]chloroplatinum(II) (5)

To a solution of (1R,1'R)-2,6-bis[1-(dimethyl-amino)propyl]phenyllithium(0.84 mmol) in C$_6$H$_6$ (30 ml) was added at once a solution of PtCl$_2$(SEt$_2$)$_2$ (0.84 mmol) in C$_6$H$_6$ (10 ml) and the mixture was stirred for 3 days at room temperature. The reaction mixture was filtered over Celite and the solvent of the filtrate was removed in vacuo. Slow diffusion of hexane in a saturated solution of **5** in toluene for four days at room temperature gave 108 mg (27%) of **5** as colorless crystals suitable for X-ray analysis. Mp 137–139°C. $[\alpha]_D^{22}$ = − 101.7° (c = 0.015, CHCl$_3$). ^{1}H-NMR (C$_7$D$_8$): 6.95 (t, ^3J = 7.6 Hz, 1H, ArH), 6.65 (d, ^3J = 7.5 Hz, 2H, ArH), 3.05 (dd, ^3J = 9.0 Hz, ^3J = 4.1 Hz,

(^{195}Pt-^{1}H)J = 36 Hz, 2H, CH), 2.65 and 2.67 (s, 12H, N(CH_3)$_2$), 1.3–1.7 (m, 4H, CH_2), 0.78 (t, ^3J = 7.2 Hz, 6H, CH_3). ^{13}C{^{1}H}-NMR (C$_7$D$_8$): 146.5 ({Ar}C), 121.6 ({Ar}CH), 121.1 ({Ar}CH, (^{195}Pt-^{1}H)J = 17 Hz), 85.7 (CH, (^{195}Pt-^{13}C)J = 25 Hz), 54.9 and 48.4 (N(CH_3)$_2$), 26.1 (CH_2), 10.4 (CH_3). Anal. calc. for C$_{16}$H$_{27}$ClN$_2$Pt: C, 40.21; H, 5.69; N, 5.86; found C, 40.29, H, 5.76, N, 5.79.

3.3. Crystal structure determination of (−)-[(1R,1'R)-2,6-bis{1-(dimethylamino)propyl}-phenyl]chloroplatinum(II) (5)

A transparent yellowish, block shaped crystal was mounted on top of a glass-fiber (using the inert-oil technique) and transferred to the cold nitrogen stream of an Enraf–Nonius CAD4T diffractometer for data collection at 150 K (rotating anode, 60 kV, 100 mA, graphite-monochromated MoKα radiation, ω-scan mode). Unit cell parameters were determined from a least squares treatment of the SET4 setting angles of 18 reflections. The unit cell parameters were checked for the presence of higher lattice symmetry [37]. A total of 3147 reflections were collected in ω scan mode; data were corrected for Lp, for the observed linear decay of 1.3% of the three reference reflections and for absorption (DIFABS; [38]; correction-range: 0.613–2.202) and merged into a dataset of 2905 unique reflections. The structure was solved with standard Patterson methods (DIRDIF96; [39]) and subsequent difference Fourier analyses. Refinement on F^2 with all unique reflections was carried out by full matrix least squares techniques. Hydrogen atoms were introduced on calculated positions and included in the refinement riding on their carrier atoms. All non-H atoms were refined with anisotropic thermal parameters; H-atoms with isotropic thermal parameters related to the U_{eq} of the carrier atoms.

Weights were introduced in the final refinement cycles, convergence was reached at $R1$ = 0.0281 (for 2862 reflections with $F_o > 4\sigma(F_o)$), w$R2$ = 0.0559 (for all unique reflections). The absolute structure was checked by refinement of the Flack parameter converging at − 0.007(11). A final difference Fourier map shows some features near Pt within the range − 1.40: + 1.27 e/Å^3.

Crystal data and numerical details of the structure determination are given in Table 2. Final atomic coordinates and equivalent isotropic thermal parameters are listed in Table 3.

Neutral atom scattering factors and anomalous dispersion factors were taken from [40]. All calculations were performed with SHELXL96 [41] and the PLATON [42] package (geometrical calculations and illustrations) on a DEC-5000 cluster.

Table 2
Crystal data and details of the structure determination for **5**

Crystal data	
Formula	$C_{16}H_{27}N_2PtCl$
M_r	477.94
Crystal system	monoclinic
Space group	$P2_1$ (Nr. 4)
a, b, c (Å)	6.6490(6), 10.236(6), 12.451(1)
β (°)	99.63(1)
V (Å^3)	835.5(1)
Z	2
D_{calc} (g cm^{-3})	1.900
$F(000)$	464
μ (cm^{-1})	85.5
Crystal size (mm)	$0.63 \times 0.62 \times 0.20$
Data collection and refinement	
Temperature (K)	150
$\theta_{min}, \theta_{max}$	1.66, 25.00
Radiation	MoKα (graphite-monochr.), 0.71073 Å
$\Delta\omega$ (°)	$0.80 + 0.35 \tan\theta$
Hor. and vert. aperture (mm)	3.05, 4.00
Reference reflections	$-1\ 1\ 7$, $2\ -3\ -3\ -2$, $-3\ -5\ 1$
Data set	$h\ -7{:}0$; $k\ -12{:}12$; $l\ -14{:}14$
Total data	3147
Total unique data	2905
No. refined params.	200
Weighting scheme	$w = 1.0/[\sigma^2(F_o^2) + (0.0331 * P)^2 + 3.61 * P]$
Final R1$[\Sigma(\|\|F_o\|-\|F_c\|\|)/\Sigma\|F_o\|]$	0.0211
wR2 $[\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{0.5}$	0.0559
S $[\Sigma[w(F_o^2-F_c^2)^2]/(n-p)]^{0.5}$	1.087
$(\Delta/\sigma)_{av}$ and max. in final cycle	0.000, 0.001

Table 3
Final coordinates and equivalent isotropic thermal parameters of the non-hydrogen atoms for **5**

Atom	x	y	z	U_{eq} (Å^2)
Pt1	0.16915(3)	0.49214(4)	0.34837(1)	0.0116(1)
Cl1	0.3937(3)	0.53310(15)	0.51875(13)	0.0211(5)
N1	0.0096(9)	0.3332(5)	0.3981(5)	0.0168(17)
N2	0.2712(8)	0.6357(5)	0.2508(4)	0.0165(17)
C1	−0.0137(9)	0.4615(5)	0.2141(5)	0.0126(19)
C2	−0.0322(10)	0.5562(7)	0.1332(5)	0.0143(17)
C3	−0.1626(11)	0.5320(6)	0.0357(6)	0.0188(19)
C4	−0.2756(12)	0.4178(8)	0.0235(6)	0.022(2)
C5	−0.2565(11)	0.3238(7)	0.1073(6)	0.022(2)
C6	−0.1248(10)	0.3450(6)	0.2031(5)	0.0173(17)
C7	0.0925(10)	0.6788(6)	0.1657(5)	0.0163(17)
C8	0.3825(12)	0.7478(7)	0.3088(7)	0.024(2)
C9	0.4175(11)	0.5695(7)	0.1890(6)	0.024(2)
C10	−0.0691(10)	0.2519(6)	0.2970(6)	0.0168(17)
C11	0.1246(10)	0.2529(7)	0.4869(6)	0.0195(19)
C12	−0.1704(11)	0.3862(7)	0.4396(6)	0.0204(19)
C13	−0.0381(11)	0.7828(7)	0.2098(7)	0.027(3)
C14	−0.1967(12)	0.8417(8)	0.1208(8)	0.033(3)
C15	0.0808(12)	0.1469(7)	0.2707(6)	0.026(2)
C16	0.2830(11)	0.1959(7)	0.2410(6)	0.025(2)

$U_{eq} = 1/3$ of the trace of the orthogonalized U tensor.

Complete tables of atomic coordinates, bond lengths and angles have been deposited with the Cambridge Crystallographic Data Centre. Lists of observed and calculated structure factors and of thermal displacement parameters are available from the authors.

Acknowledgements

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