An Amido-bridged Platinum Olefin Dimer. The Synthesis, Characterisation, and *X*-Ray Structure Analysis of Bis{chloro-μ-[1′—2′-η-*o*-isopropenylphenyl(methyl)amido-$C^{1'-2'}$,*N*;μ-*N*]-platinum(II)} †

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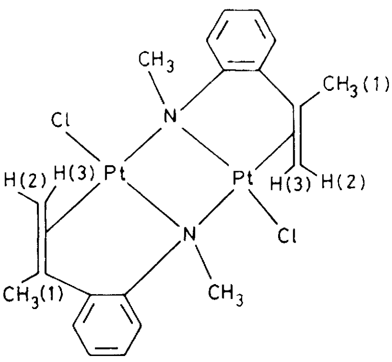
The amido-bridged dimeric molecule $[\{\overline{PtCl(NMeC_6H_4CMe{=}CH_2})\}_2]$ (1) was prepared by deprotonation of the amino-complex $[PtCl_2(NHMeC_6H_4CMe{=}CH_2)]$ using an anion-exchange resin in the hydroxide form in tetrahydrofuran. The molecular structure of compound (1) was established using i.r., ^1H n.m.r., and ^{13}C n.m.r. spectroscopy and *X*-ray analysis. The organic ligand is bidentate, co-ordinated through the olefin group and the amido-nitrogen atom. The dimer has crystallographic C_2 symmetry and is folded about the bridging nitrogen atoms giving a Pt–Pt distance of 2.980(2) Å. Crystals of (1) are orthorhombic, space group *Fdd*2, with unit-cell dimensions, a = 9.892(2), b = 19.488(3), c = 21.679(4) Å, and Z = 8. Full-matrix refinement using 703 diffractometer data with $I/\sigma(I) > 3.0$ has converged at R = 0.046.

Earlier papers report our work on chelating ligands containing both an olefin and a Group 5 donor atom.[1-4] Although this type of ligand with phosphorus or arsenic donor atoms has been investigated for many years [5] the analogous nitrogen compounds have been much less widely studied.[3] These nitrogen-donor ligands are more versatile than those of phosphorus and arsenic, as primary and secondary amine complexes (for which the analogues of P and As are unknown) are capable of reaction with bases. The deprotonation of a secondary amine group has been exploited in this work to prepare an amido-bridged dimeric platinum(II) compound (1). Amido-bridged compounds are relatively rare [6,7] and (1) is the first example of such a bridge involving an olefinic chelating ligand.



(1)

Experimental

Materials.—For preparative work analytical grade solvents were used as supplied, except that diethyl ether was dried over sodium wire. Acid-free deuteriochloroform for n.m.r. spectroscopy was prepared by running it down a short column of activated basic alumina. Trideuterioacetonitrile and heptadeuteriodimethylformamide were used as supplied.

Platinum chemicals were obtained from Matthew Garrett Pty Ltd. Other reagents were obtained from various manufacturers and used without further purification.

Preparations.—*Dichloro*[o-*isopropenyl*(*methylamino*)*benzene*]*platinum*(II), (2). A mixture of platinum(II) chloride (2 mmol), *o*-isopropenyl(methylamino)benzene (2.2 mmol), and chloroform (50 cm^3) was stirred overnight at 40—50 °C. The green-brown suspension of $PtCl_2$ was converted into a pale yellow suspension. The solids were filtered off, washed with diethyl ether, dissolved in acetonitrile, and filtered through microcrystalline cellulose to remove unreacted $PtCl_2$. The purified product was recovered after concentration of the filtrate by evaporation, addition of light petroleum (b.p. 60—80 °C), and refrigeration.

The yellow crystals were filtered off and dried under vacuum (0.05 Torr ≈ 6.7 Pa) at room temperature. Yield *ca.* 80%, m.p. 235 °C (decomp.) (Found: C, 29.15; H, 3.10; Cl, 17.25; N, 3.40; Pt, 47.0. Calc. for $C_{10}H_{13}Cl_2NPt$: C, 29.05; H, 3.15; Cl, 17.15; N, 3.40; Pt, 47.2%). ^1H N.m.r. (in [$^2H_7$]dimethylformamide, $SiMe_4$ reference): H^1, δ 2.15 [J(Pt–H) 39.6]; H^2, 4.85 (69.4); H^3, 4.29 (71.8); and N–Me, 3.11 p.p.m. (36.9 Hz).

Acetylacetonato[o-*isopropenyl*(*methylamino*)*benzene*]-*platinum*(II) *tetrafluoroborate*, (3). Finely divided dichloroplatinum complex (2) (1 mmol) was added to a mixture of anhydrous silver tetrafluoroborate (2 mmol) in dichloromethane (50 cm^3). Acetylacetone (1.1 mmol) was added and the mixture agitated for 20 min in an ultrasonic bath. Silver salts were removed by filtration on microcrystalline cellulose. The filtrate was evaporated to about 10 cm^3 and the colourless crystalline product obtained after dropwise addition of dry diethyl ether and refrigeration. Yield 87%. ^1H N.m.r. (in [$^2H_3$]acetonitrile, $SiMe_4$ reference): H^1, δ 2.27 [J(Pt–H) 38]; H^2, 4.97 (72); H^3, 4.22 (72); H^4, 5.82 (9); H^5, 2.34 (6); H^6, 2.13 (6); and N–Me, 3.12 p.p.m. (39 Hz); J(H–N–CH_3), 6 Hz.

Bis{*chloro*-μ-[o-*isopropenylphenyl*(*methyl*)*amido*]-*platinum*-(II)}, (1). The title compound (1) was prepared by passage (1 cm^3 min^{-1}) of a solution of the dichloroplatinum complex (2) (0.5 g, 0.66 mmol) in deoxygenated tetrahydrofuran (thf) (125 cm^3) through a column (20 × 1 cm) of Permutit Deacidite FF, 2—3% cross-linked (100—200 mesh), strongly basic anion

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† *Supplementary data available* (No. SUP 23487, 7 pp.): thermal parameters, contact distances, least-squares planes, structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

exchange resin in the hydroxide form. The resin was prepared in aqueous medium then thoroughly washed with deoxygenated thf before use. The eluate containing (1) was concentrated by evaporation to 5 cm^3 and filtered through a short column of Florisil. Light petroleum was added to the filtrate, which was then refrigerated to give (1) as bright yellow crystals. M.p. 186 °C (decomp.) (Found: C, 31.8; H, 3.25; N, 3.50. Calc. for $C_{20}H_{24}Cl_2N_2Pt_2$: C, 31.9; H, 3.20; N, 3.70%). ^{1}H N.m.r. (in $CDCl_3$, $SiMe_4$ reference): H^1, δ 2.27 [J(Pt–H) 40.1]; H^2, 4.79 (63.5); H^3, 3.67 (66.5); and N–Me, 3.40 p.p.m. (44.0 and 31.1 Hz).

^{13}C N.m.r. data are presented in Table 1. Atom numbering is the same as that used in the crystallographic analysis.

Apparatus and Techniques.—The n.m.r. spectra of the compounds were recorded on a JEOL FX60 dual-probe (^{1}H, ^{13}C) Fourier-transform spectrometer, and Varian HA100 (^{1}H) and Perkin-Elmer–Hitachi R24-B (^{1}H) continuous-wave spectrometers. Infrared spectra of the compounds were taken with a Perkin-Elmer PE457 grating spectrophotometer using Nujol mulls between caesium iodide plates (polystyrene calibration). Conductivity in thf was measured at room temperature on a Philips PR9500 conductivity bridge with a dip-type platinum electrode. Melting and decomposition points were measured on a Reichert hot-stage melting-point apparatus with microscope. Microanalyses were performed by the Australian Microanalytical Service, Department of Applied Organic Chemistry, CSIRO, University of Melbourne and by Alfred Bernhardt Mikroanalytisches Laboratorium Elbach, West Germany.

Crystal-structure Determination.—*Crystal data.* (1) $C_{20}H_{24}Cl_2N_2Pt_2$, M = 753.5, Orthorhombic, a = 9.892(2), b = 19.488(3), c = 21.679(4) Å, U = 4 179.2 Å^3, F(000) 2 784, Z = 8, D_c = 2.39 g cm^{-3}, Mo-K_α radiation, λ = 0.710 69 Å, μ(Mo-K_α) = 131.1 cm^{-1}. The space group $Fdd2$ was unambiguously determined from systematic absences in the data: hkl, $h + k, k + l, h + l = 2n + 1$; $0kl$, $k + 1 \neq 4n$; and $h0l$, $h + l \neq 4n$.

Intensity measurements. Data were collected on a crystal of dimensions 0.16 × 0.14 × 0.12 mm on a Philips PW1100 four-circle diffractometer using the technique previously described[4] with a scan width of 1.0°. The method of data processing has been described previously,[4] and no absorption corrections were applied. Of a total of 1 034 unique data examined in the range θ 3.0—25.0°, 703 with $I/\sigma(I) > 3.0$ were used in subsequent stages.

Structure solution and refinement. The Pt and Cl atoms were located from a Patterson synthesis; the remaining non-hydrogen atoms were found from a difference synthesis. The Pt and Cl atoms were assigned anisotropic thermal parameters in the final cycles of full-matrix refinement. The hydrogen atoms of the phenylene ring were included at calculated positions (C–H 1.08 Å) with their isotropic thermal parameters set to be equal to an extra variable in the refinement (final value 0.051 Å^2). The final R and R'[4] were both 0.046. The SHELX 76 programs[8] were used and the scattering factors were those of Cromer and Mann[9] with corrections for the real and imaginary parts of the anomalous dispersion. Final atomic co-ordinates are listed in Table 2 and bond lengths and angles in Table 3.

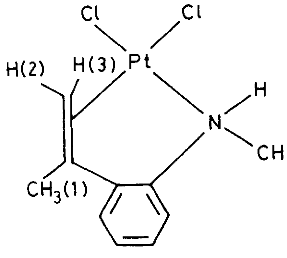
Results and Discussion

Evidence for the existence of compound (1) was first obtained in solution when (2) was treated with bases such as triethylamine, pyridine, 2,6-dimethylpyridine, and hydroxide. A sharp single strong i.r. absorption at 330 cm^{-1}, diagnostic of a terminal chloro-ligand, and the absence of any N–H vibrations in the range 3 000—4 000 cm^{-1}, indicated the presence of a dimeric or oligomeric species, with amido-bridges, formed by loss of HCl from the dichloro-complex (2).

Table 1. ^{13}C N.m.r. data for the dimer (1) in deuteriochloroform

Atom	Chemical shift (p.p.m.)[a]	Single-bond proton coupling constant (Hz)	^{195}Pt Coupling constant (Hz)
C(1)	67.6	*b*	172.4
C(2)	114.6	*c*	183.0 and 5.7
C(3)	23.9	129.8	22.7
C(4)	52.3	138.3	29.1 and 11.4
C(11)	139.7	*c*	17.7 and 10.6
C(12)	155.3	*c*	17.7 and 9.2
C(13)	125.5	162.5	16.8 and 10.0
C(14)	127.5	164.2	9.3
C(15)	127.6	164.2	9.3
C(16)	123.0	*b*	28.6 and 9.0

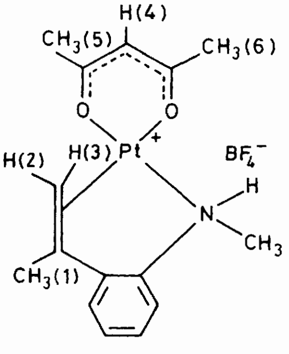
[a] With reference to $SiMe_4$. [b] Obscured. [c] Not applicable.



(2)

Preliminary attempts to isolate compound (1) by AgCl-elimination reactions in the presence of base were unsuccessful because the product was found to decompose in solution in the presence of free base. This problem was overcome by using an anion-exchange resin in the hydroxide form to remove the HCl from compound (2). Since thf was the most suitable solvent for (2), the ion-exchange resin was pre-treated with thf completely to remove water. The stoicheiometric amount of water formed in the HCl elimination from compound (2) was apparently strongly held in the resin matrix as no absorptions due to H_2O were observed in the i.r. spectrum of the resultant solutions.

Proton and ^{13}C n.m.r. spectra of (1) in deuteriochloroform (see above) show a complete set of resonances due to the co-ordinated isopropenyl group confirming that this part of the complex (2) had not reacted with base. That the amine had been deprotonated was confirmed by the absence of ^{1}H n.m.r. resonances exchangeable with deuterium oxide. Complex multiplets were observed in both the ^{1}H and ^{13}C n.m.r. spectra resulting from unequal coupling of the *N*-methyl group to two Pt atoms, consistent with the presence of a bridging amido-group. This interpretation was supported by the intensity ratio of the peaks in the *N*-methyl multiplet. The probability of distribution of platinum isotope ^{195}Pt (spin ½, 33.8% natural abundance) leads to a theoretical spectrum of the *N*-methyl resonance, for unequal coupling to each Pt atom, consisting of nine peaks of intensity ratio 0.26 : 1 : 1 : 0.26 : 3.92 : 0.26 : 1 : 1 : 0.26, whereas for equal platinum coupling constants the number of peaks falls to five with the intensity ratio 0.13 : 1 : 2.21 : 1 : 0.13. The observed ^{1}H n.m.r. spectrum consists of nine peaks and the integrated ratio of the five major peaks was 1 : 1 : 4 : 1 : 1 in agreement with the calculated values. Of the four minor peaks (0.26 in the theoretical intensity ratio) the



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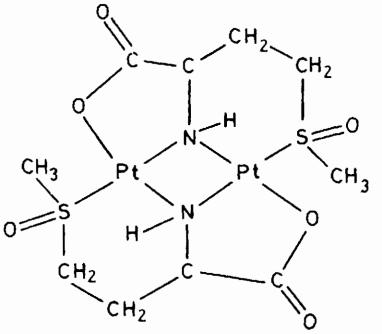

(4)

outer pair were clearly visible above the noise level and the inner pair were seen as shoulders at the foot of the centre peak (3.92 in the theoretical intensity ratio). The ^1H n.m.r. spectrum was recorded at 60 and 100 MHz so that overlap due to the multiplet of H^3 could be distinguished from the *N*-methyl multiplet.

In the ^{13}C n.m.r. the peak-height ratio of the five observed *N*-methyl resonances was the same as that observed for the five major peaks in the ^1H n.m.r. spectrum. The signal-to-noise level in the ^{13}C n.m.r. spectrum was such that the four minor peaks could not be seen.

Other nuclei displaying two platinum coupling constants were some of the aromatic carbon atoms and the benzylic carbon (C^2) of the isopropenyl group.

The product (1) is non-conducting in thf using tetrabutylammonium iodide as reference.

Bridge cleavage and loss of chloride resulted from reaction of compound (1) with acetylacetone and silver tetrafluoroborate at room temperature to give the monomeric cation (3) identified by its ^1H n.m.r. spectrum in deuterioacetonitrile. This cation had been prepared more directly (see above) by the reaction of (2) with anhydrous silver tetrafluoroborate and acetylacetone in dichloromethane.

X-Ray analysis shows that the molecule of (1) has a dimeric structure with the amido-nitrogen bridges predicted from the spectroscopic data. The molecular structure is shown in Figure 1, together with the atomic numbering scheme. There is no sign of further oligomerisation of the molecule as the closest approach to the platinum atom is from a phenyl hydrogen atom of an adjacent molecule, Pt···H(14^{11}) 3.30 Å.

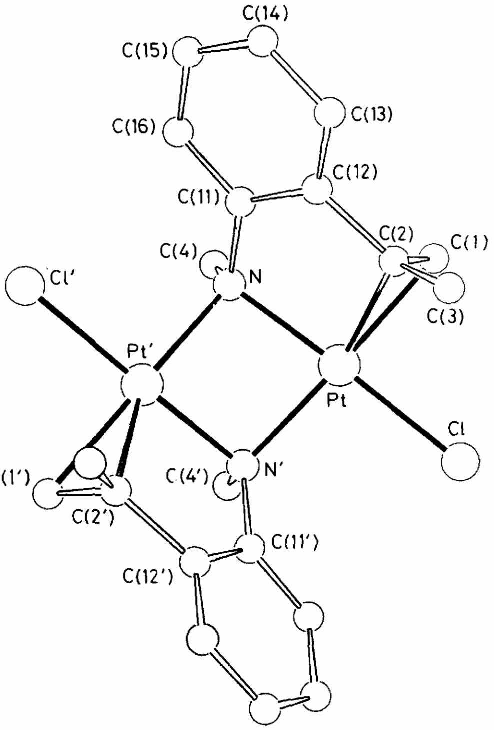

Figure 1. The structure of compound (1) showing the atomic numbering

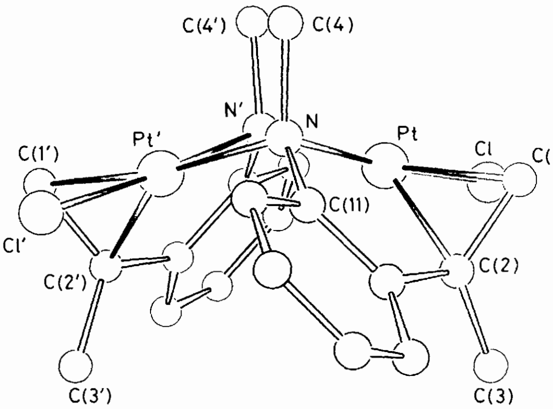

Figure 2. A view of the dimeric molecule (1) showing the bending about the bridging amido-nitrogen atoms

The dimeric molecule has crystallographic C_2 symmetry with the two platinum atoms linked by the two symmetry-related amido-nitrogen atoms of the chelating olefin ligands, with bridging bond lengths Pt–N 2.07(2) and Pt–N' 2.10(2) Å (Table 3). These bridging bonds are longer than the Pt–N bridge distances (2.038—2.046 Å) for the only other amido-bridged platinum(II) compound to have been structurally characterised, (4),[6] but the difference is of low significance. The non-olefinic donor atoms Cl, N, and N' and the platinum atom are planar to within 0.05 Å, and the angle between the two equivalent co-ordination planes is 148.8° so that the dimer may be regarded as folded about the bridging atoms N and N' (Figure 2).

The platinum–olefin bond distance, from the Pt to the mid-point of C(1)–C(2), is 1.99(4) Å and the olefinic bond length is 1.42(5) Å. These lengths are similar to those found in other π-bonded platinum(II) complexes.[10] With chelating olefin ligands of phosphorus and arsenic the midpoint of the olefin is usually *ca.* 0.2 Å out of the plane of the platinum atom and the other donor atoms.[1,2] This is the first reported structure of

Table 2. Fractional atomic co-ordinates for compound (1) with standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pt	0.400 6(1)	0.248 4(1)	0.2500	C(11)	0.263 8(28)	0.118 3(13)	0.234 7(10)
Cl	0.567 4(9)	0.329 8(4)	0.233 1(6)	C(12)	0.360 7(32)	0.115 4(17)	0.188 2(15)
N	0.249 4(28)	0.179 6(10)	0.272 1(8)	C(13)	0.372 5(35)	0.061 0(19)	0.149 5(17)
C(1)	0.554 7(41)	0.171 8(19)	0.242 3(18)	C(14)	0.287 6(37)	0.002 9(21)	0.159 1(16)
C(2)	0.469 6(30)	0.172 6(16)	0.189 3(14)	C(15)	0.191 7(35)	0.003 7(19)	0.206 4(16)
C(3)	0.518 9(40)	0.197 6(20)	0.127 0(17)	C(16)	0.178 8(31)	0.061 5(14)	0.242 7(15)
C(4)	0.255 7(35)	0.160 8(15)	0.340 8(14)				

Table 3. Bond lengths (Å) and interbond angles (°) for compound (1)

Pt–Pt′	2.980(2)	Pt–C(2)	2.09(3)	C(1)–C(2)	1.42(5)	C(12)–C(13)	1.36(5)
Pt–Cl	2.318(9)	Pt–olefin midpoint	1.99(4)	C(2)–C(3)	1.52(5)	C(13)–C(14)	1.43(5)
Pt–N	2.07(2)	N–C(4)	1.54(4)	C(2)–C(12)	1.55(4)	C(14)–C(15)	1.40(5)
Pt–N′	2.10(2)	N–C(11)	1.45(3)	C(11)–C(12)	1.39(4)	C(15)–C(16)	1.38(5)
Pt–C(1)	2.14(4)			C(11)–C(16)	1.40(4)		
Cl–Pt–N	175.2(6)	N′–Pt–C(2)	147.9(10)	Pt–C(2)–C(1)	72(2)	C(12)–C(11)–C(16)	118(3)
Cl–Pt–N′	94.7(6)	Pt–N–Pt′	91.4(6)	Pt–C(2)–C(3)	116(2)	C(2)–C(12)–C(11)	116(3)
Cl–Pt–C(1)	87.6(10)	Pt–N–C(11)	110(2)	Pt–C(2)–C(12)	107(2)	C(2)–C(12)–C(13)	121(3)
Cl–Pt–C(2)	98.7(9)	Pt′–N–C(11)	120(2)	C(1)–C(2)–C(3)	122(3)	C(11)–C(12)–C(13)	122(3)
N–Pt–N′	82.4(10)	Pt–N–C(4)	111(2)	C(1)–C(2)–C(12)	115(3)	C(12)–C(13)–C(14)	119(3)
N–Pt–C(1)	94.7(11)	Pt′–N–C(4)	114(2)	C(3)–C(2)–C(12)	116(3)	C(13)–C(14)–C(15)	120(3)
N–Pt–C(2)	85.6(10)	C(4)–N–C(11)	110(2)	N–C(11)–C(12)	120(3)	C(14)–C(15)–C(16)	119(3)
N′–Pt–C(1)	171.2(11)	Pt–C(1)–C(2)	69(2)	N–C(11)–C(16)	121(2)	C(11)–C(16)–C(15)	121(3)

a complex of this type of ligand with a nitrogen donor and here the olefinic midpoint is further (0.45 Å) out of the co-ordination plane. An interesting consequence of this distortion from the ideal bonding position for the olefin is that C(1) is only 0.22 Å out of the co-ordination plane and the best plane through this atom and Pt, Cl, N, and N′ shows a maximum deviation of only 0.093 Å for the Pt atom. In spite of this, the Pt–C(2) length is 0.05 Å shorter than the Pt–C(1) length (Table 3), although the difference is of very low significance.

The plane of olefin bonding Pt,C(1),C(2) makes an angle of 105.3° with that of the platinum co-ordination (Pt,Cl,N,N′). This distortion from the ideal value of 90°, expected for a symmetrically π-bonded olefin, may be clearly seen in Figure 1. Further evidence of strain within the molecule is obtained from the observation that, although the phenyl ring and the amido-nitrogen atom are coplanar to within 0.03 Å as expected, C(2), which is also bonded to the ring, has been forced out of this plane by 0.33 Å in the direction of C(1).

Some understanding of the steric factors responsible for the distortions within the molecule may be obtained by considering the angles round the four-co-ordinate bridging nitrogen atom. Four angles are in the range 110—114° and may be regarded as approximately tetrahedral. In contrast the other two angles at nitrogen, Pt–N–Pt′ (91.4°) and C(11)–N–Pt′ (120.0°), are far from the ideal value of 109.5°. Clearly a smaller C(11)–N–Pt′ angle would result from a rotation of the chelating ligand about the Pt–N bond so that the C(11)–N bond approached the N–Pt′ bond. Such a rotation would move the midpoint of the olefin even further out of the co-ordination plane. The distortions within the dimeric molecule therefore appear to be due to the conflicting bonding requirements of the co-ordinated olefin and the bridging nitrogen atom. If the bridging system Pt–N–Pt′–N′ were unfolded about the NN′ line to become planar, this would result in a better Pt–N–Pt′ angle of 97.6° but there would be an unfavourable further increase in the C(11)–N–Pt′ angle.

The separation of the platinum atoms is 2.980(2) Å which is similar to that observed for Pt–Pt bonds in polynuclear species.[11] Evidence for metal–metal bonding by oblique overlap of filled nd_{z^2} and empty $(n + 1)p_z$ orbitals on adjacent metal atoms with d^8 configurations and square-planar co-ordination was first deduced from the structure of a sulphur-bridged nickel dimer.[12] Since then several examples of this type of bonding have been reported, and it is thought that the short Pt–Pt distance of 2.8605 Å in compound (4) may also indicate some bonding interaction.[6] It seems probable that in compound (1) also there is some contribution from Pt–Pt bonding to a stabilisation of the dimeric molecule in such a strained conformation.

In square-planar platinum(II) compounds the Pt–Cl bond lengths are very sensitive to the influence of the *trans* ligand. The length of 2.318(9) Å in compound (1) is within the range normally found for Pt–Cl bonds *trans* to phosphine or arsine ligands which are known to exert a strong *trans* influence.[2,10] It may be concluded therefore that in square-planar platinum(II) complexes amido-nitrogens also exert a relatively strong *trans* influence.

Acknowledgements

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