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Preliminary communication

σ,σ'-*N,N'* BRIDGING AND σ,σ-*N,N* CHELATING α-DIIMINES. MOLECULAR GEOMETRIES OF $[PtCl_2PBu_3]_2$(t-BuN=CHCH=NBu-t) AND $PtCl_2$(STYRENE)-(t-BuN=CHCH=NBu-t)

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Summary

An X-ray structure analysis of $[PtCl_2PBu_3]_2$(t-BuN=CHCH=NBu-t) has shown the presence of σ,σ'-*N,N'*-bonded diimine, which bridges in the *anti*-configuration two planar *trans*-$PtCl_2PBu_3N$ moieties. The crystal structure of $PtCl_2$(styrene)(t-BuN=CHCH=NBu-t) contains a unidentate-bonded styrene molecule in the equatorial position of a trigonal bipyramidal arrangement with the phenyl ring bent back by 27°.

Recent studies have shown that α-diimines, RN=CHCH=NR, denoted by R-dim, show versatile coordination behaviour towards Rh^I, Pd^{II} and Pt^{II} [1]. In addition to the σ,σ-*N,N* chelating bonding mode, σ-*N* monodentate (e.g. $PdCl_2$(t-Bu-dim)$_2$ [1], σ-*N* $\leftrightarrow$ σ'-*N'* fluxional (e.g. $PtCl_2PPh_3$-t-Bu-dim [2]) and σ,σ'-*N,N'* bridging (e.g. $(Rh(CO)_2Cl)_2$-t-Bu-dim [1]) bonded diimines have also been established. These results contrast with the σ,σ-*N,N* chelating coordination behaviour of bipyridine and phenanthroline which also contain a NCCN skeleton. The difference in behaviour is ascribed to the greater flexibility of the R-dim ligand skeleton, which can attain various conformations by rotation around the central C—C bond [2].

In view of our recent interest [3—5] in the bonding in metal-diimine complexes we determined the crystal structure of $[PtCl_2PBu_3]_2$-t-Bu-dim in order to obtain information about the conformation of a bridging diimine skeleton, and that of $PtCl_2$(styrene)-t-Bu-dim in order to extend our studies of metal olefin rotation in pentacoordinated platinum diimine complexes.

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$(PtCl_2PBu_3)_2$-t-Bu-dim (I) crystallized slowly from methanol containing a 1/1 molar ratio of $PtCl_2PBu_3$-dimer and t-Bu-dim. Elemental analysis and molecular weight data (osmometry in $CHCl_3$ found (calcd.) 1064 (1104)) pointed to a $[PtCl_2PBu_3]_2$-t-Bu-dim stoichiometry. Yellow crystals of I, which were obtained from CH_2Cl_2/hexane solution, are monoclinic, space group $P2_1/n$ and have $Z = 2$ in a unit cell of dimensions a 11.4540(11), b 16.1169(7), c 12.9202(12) Å and β 99.82 (1)°. The structure was refined to $R = 0.059$ for 3504 independent reflection having intensities above the 2.5 σ level*.

The molecular geometry of I as well as some selected bond distances in the molecule are shown in Fig. 1. The inversion center of the space group coincides with the midpoint of the central C—C bond.

The main structural feature is the planarity of the P—Pt—NCCN—Pt—P skeleton. (Deviations of the plane through P(1), Pt(1), N(1), C(1) and C(2): C(2) (+0.005), N (−0.004), C(1) (−0.0010), Pt (+0.0012) and P (−0.074).) The diimine skeleton has the *anti*-conformation (C(1′)—C(1)—N, C(1)—N—C(2), C(1)—N—Pt; 118.2(13), 116.1(13), 123.2(12)°, respectively). The two Pt^{II} coordination planes, which are approximately square planar (regular Pt—Cl, Pt—N and Pt—P distances; *trans*-Cl-atoms with Cl(1′)—Pt—Cl(2) and P—Pt—N angles of 172.4(2)° and 177.0(3)°, respectively) are perpendicular to the

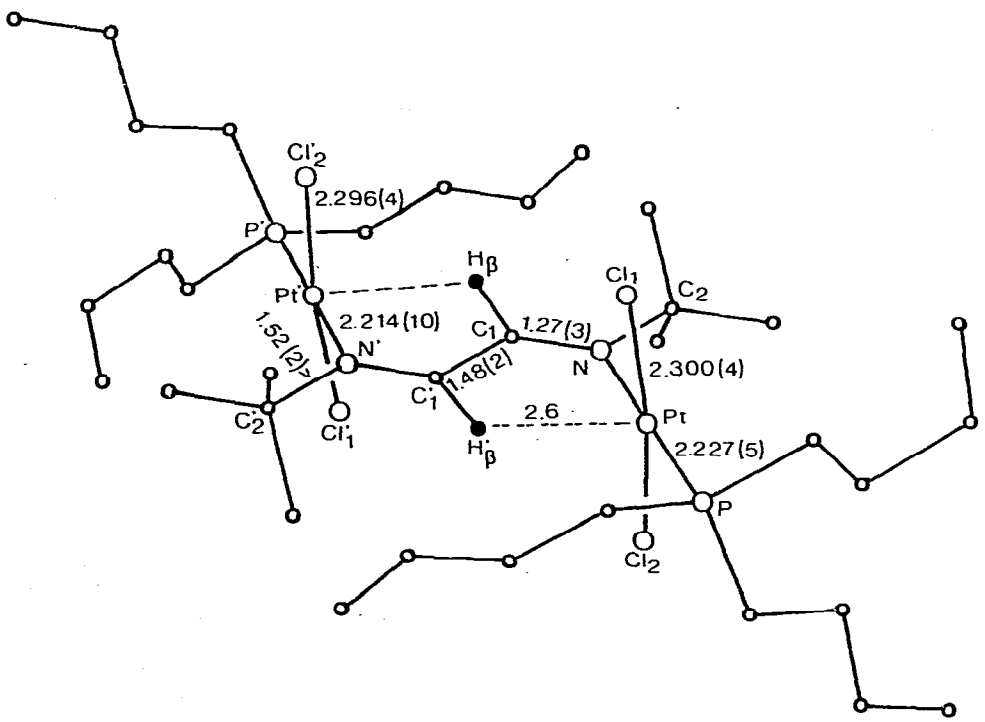

Fig. 1. Molecular geometry and bond lengths of $[PtCl_2PBu_3]_2$-t-Bu-dim (a). The Pt··· H_β distance has been calculated using for C—H_β 1.2 Å.

*Intensities were collected on an ENRAF Nonius CAD-4 diffractometer using graphite monochromatized Cu-K_α radiation. The positions of the Pt, P and Cl atoms were derived from a (E^2-1)-Patterson and refined by block-diagonal least-squares calculations. No absorption corrections have been applied.

P—PtNCCNPt—P plane. These structural features result in a short β-imine-H··· Pt distance (see Fig. 1) which has been calculated to be 2.6 Å (sum of Van der Waals radii is 3.2 Å), and is another example of a non-bonding Pt··· H interaction [2,6,7].

$PtCl_2$(styrene)-t-Bu-dim (II) was prepared by a 1/1 molar reaction of $KPtCl_3$(styrene) with t-Bu-dim in acetone. Osmometric molecular weight determinations ($CHCl_3$ found (calcd.) 499 (538)) revealed that II exists as a monomer in solution. Monoclinic orange coloured crystals of II (obtained from CH_2Cl_2 / hexane solution), space group C_n, have $Z = 4$ in the unit cell with dimension a 12.2146(5), b 15.5558(8), c 12.3919(5) Å and β 119.38(1)°. 1174 reflections with intensities above the 2.5 σ level were collected and refined to $R = 0.048$.

The crystal structure of II consists of discrete monomeric $PtCl_2$(styrene)-t-Bu-dim units having the Cl atoms in the axial positions (Cl—Pt—Cl angle 179.8(3)°) of a trigonal bipyramidal arrangement. The olefinic part of the styrene molecule and the σ,σ-*N,N* chelate bonded diimine reside in one plane (deviations for the best plane through Pt, N(1,2) and C(1,2,11,12): Pt (−0.02), N(1), (+0.04), N(2) (−0.03), C(11) (−0.05), C(12) (+0.06), C(1) (+0.21) and C(2) (+0.21)). The diimine ligand in II also displays a characteristic bite angle of 74.7(10)° (cf. angles of 72.38(34), 78.05(55)° in $Mn(CO)_3$Cl-cyclohexyl-dim [8] and $W(CO)_2$Br-cyclohexyl-dim(π-allyl) [9], respectively) resulting in a considerable distortion of the angles in the equatorial plane from the ideal trigonal bipyramide (see Fig. 2).

These structural features are similar to those in (ethene)butane-2,3-dionebis-(methylhydrazone)dichloroplatinum(III) reported by Maresca et al. [10]. However, the present structure provides important additional information concerning the platinum—olefin interaction.

In contrast to the symmetric N_2 Pt—ethene bonding in III (Pt—C 2.073(12); Pt—N 2.221(10) Å) II contains unsymmetric Pt—N and Pt—C distances of Pt—N(1)

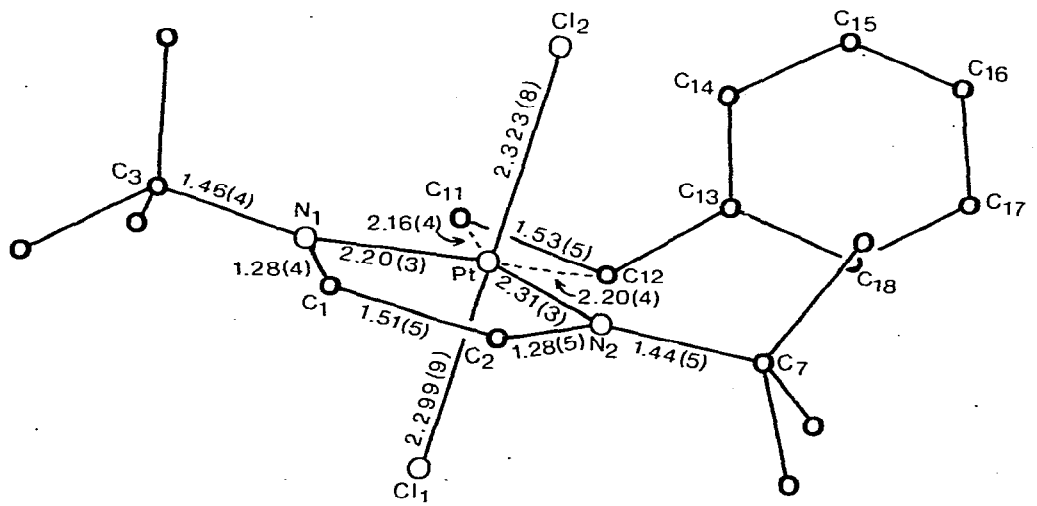

Fig. 2. Molecular geometry and bond lengths of $PtCl_2$(styrene)-t-Bu-dim.

2.20(3); Pt—N(2) 2.31(3); Pt—C(11) 2.16(4); Pt—C(12) 2.20(4) Å. Moreover, the presence of a phenyl substituent in the olefin allows the determination of the degree of back bending in the olefin skeleton which in II amounts to 27°*. This information, which could not be obtained from III, is important in connection with a study of the dynamic ^{1}H, ^{13}C and ^{195}Pt NMR spectra of the very soluble (e.g. in CH_2Cl_2, acetone or toluene) II and the related $PtCl_2$(olefin)-R-dim (e.g. R = $EtMe_2C$ and olefin = styrene, *cis*-butene or methylacrylate). These spectra allow an interpretation of the factors determining the barrier to rotation of the olefin in these pentacoordinate platinum species as well as of the conformation of these complexes in the slow exchange limit**.

Comparison of the structural features of I and II reveals that in both the σ,σ-*N,N*-chelate and the σ,σ'-*N,N'*-bridging bonding mode the diimine skeleton is planar irrespective of whether it has the *syn* or the *anti* conformation. It is also noteworthy that the bond distances in the diimine skeleton are unaffected by complex formation, see Table 1.

TABLE 1

SOME SELECTED DISTANCES[a] IN METAL—(t-BuN=CHCH=NBu-t) (= L) COMPLEXES

Compound	C=N	C—C	C—N
L[b]	1.283(6)	1.537(5)	1.468(16)
$[PtCl_2PBu_3]_2L$	1.27(3)	1.48(2)	1.52(2)
$PtCl_2$(styrene)L	1.28(4)	1.51(5)	1.46(4)
	1.28(5)		1.44(5)

[a]In Å. [b]From electron diffraction measurements see ref. 11.

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*The normal through N(1,2) (C(1,2;11,12) (plane 1 vide supra) and the plane through the styrene-carbon atoms (deviations from the best plane through C(11) to C(18): C(11) (−0.03), C(12) (0.00), C(13) (0.05), C(14) (0.02), C(15) (−0.01), C(16) (−0.01), C(17) (−0.01) and C(18) (0.00) (plane 2)) make an angle of 63°. Accordingly the deviation from the plane through C(11) and C(12) which is perpendicular to plane 1 is 27°.

**For example the ^{13}C NMR data of II at −30°C (rigid rotation). (δ (ppm), $CDCl_3$ internal standard) C=N 158.83, 158.59; C—N 63.92, 63.77 ($^{2}J(^{195}Pt—^{13}C)$ 31 Hz); CH_3 30.03, 29.43; C(11) 51.08 ($^{1}J(^{195}Pt—^{13}C)$ 238 Hz); C(12) 30.47 ($^{1}J(^{195}Pt—^{13}C)$ 253 Hz).