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Synthesis and Molecular Geometry of [*trans*-$PtCl_2PBu_3$]$_2$(di-t-Bu-diimine) Containing a σ,σ′-N,N′ Bridging Diimine with a Planar Anti-(*trans*-P–Pt–NCCN–Pt–P-*trans*)-skeleton

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Complexes of the type [$MCl_2XR'_3$]$_2$R-dim (M = Pd or Pt; XR'_3 = arsine or phosphine) are formed in almost quantitative yield in the reactions of [MCl_2-XR'_3]$_2$ with α-diimine (1/1 molar ratio Pt-dimer/R-dim).

An X-ray study of [$PtCl_2PBu_3$]$_2$t-Bu-dim [Z = 2, a = *11.4540(11),* b = *16.1169(7),* c = *12.9202(12) Å and β = 99.82(1); R = 5.9%] reveals a structure consisting of two planar* trans-*$PtCl_2P$-units bridged by a planar NCCN skeleton in anti-configuration [C–C 1.48(2), C=N 1.27(3), N–Pt 2.214(10) Å]. As a consequence of the orthogonal position of the platinum coordination plane and the NCCN plane the β-imine proton resides a short distance from the platinum atom (about 2.6 Å). The structure in solution has been determined by ^1H, ^{13}C, ^{31}P and ^{195}Pt NMR spectroscopy. The observed spectra point to retention of the structural features in solution as evidenced by a large down field shift of the imine protons,* e.g. *9.58 ppm and an AA′MM′ pattern in [$PdCl_2PEt_3$]$_2$t-Bu-dim. The present compounds are the first examples of complexes which contain a σ,σ′-N,N′ planar bridging diimine ligand as a general structural feature.*

Introduction

Considerable interest exists in the study of the coordination properties of the α-diimine molecule RN=CHCH=NR (R-dim) [1–4]. In the bimetallic iron and ruthenium complexes hexacarbonyl(1,4-diazadien)M_2 (M = Fe [5]; M = Ru [6]) the R-dim ligand acts as a σ, μ^2, η^2 binding ligand, whilst the σ,σ coordination mode of the R-dim ligand has been found in mononuclear metal–R-dim complexes [1–4]. However, the flexibility of the R-dim skeleton suggests that these ligands must have a more versatile coordination behaviour. This can be concluded from a study by Kliegmann [7] who showed that in solution the free R-dim molecule exists preferentially in the E(anti) configuration. Later electron diffraction studies on t-Bu-dim [8] showed that in the gas phase the R-dim ligand exists in a gauche form in which the C=N bond systems make an angle of 65° with respect to the syn form. Indeed in our study concerning the interaction of R-dim ligands with Pt^{II}, Pd^{II} and Rh^{I} compounds the first examples of complexes containing σ (monodentate) $PdCl_2$(t-Bu-dim)$_2$ [9, 10], σ↔σ′ (monodentate, fluxional) $PtCl_2PPh_3$t-Bu-dim [10] and σ,σ′ (bridging) Rh(CO_2)-Cl-μ-(t-Bu-dim)-Rh$(CO)_2$Cl [9] R-dim ligands were synthesized. In this paper we report the synthetic details of bimetallic palladium and platinum compounds containing a σ,σ′ bridging R-dim ligand. Moreover, the structures of these compounds were studied both in solution and in the solid state in order to elucidate (*i*) the configuration of the diimine skeleton in the σ,σ′-N,N′ bonded form and (*ii*) the importance of steric interactions between neighbouring substituents in the skeleton on the molecular configuration of the complexes.

The conclusions emerging from this study appeared to be of crucial importance for the interpretation of the bonding and dynamic behaviour of the monodentate bonded R-dim ligands both in the σ-N↔σ′-N and σ-N form. The complex coordination behaviour of the α-diimines in Rh chemistry including a σ,σ′-N,N′ bonding form of the R-dim ligand will be the subject of a future paper [10].

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Experimental

The compounds, di-tert-butyldiimine (t-Bu-dim = t-Bu-NCHCHN-t-Bu) and the starting complexes $[PdCl_2PEt_3]_2$, $[PdCl_2AsEt_3]_2$ and $[PtCl_2PR_3]_2$ (R = n-Bu, Ph) were prepared by standard methods [1, 11].

All preparations of new complexes were carried out in a N_2 atmosphere. Solvents were dried and distilled before use.

$[PdCl_2XEt_3]_2$t-Bu-dim (X = As, P)

t-Bu-dim (1.2 mmol) was added to a stirred suspension of $[PdCl_2XR_3]_2$ (1 mmol) in 15 ml of dichloromethane. After stirring for 1 h the solution was filtered through a short layer of aluminium oxide and evaporated to dryness. The residue was washed with hexane (4 X 25 ml) and dried in vacuo at room temperature. Yield 80% of either an orange (palladium) or yellow (platinum) complex. The complexes are slightly soluble in acetone. Purification was achieved by recrystallization from dichloromethane–hexane. *Anal.* calcd. for $[PdCl_2PEt_3]_2$t-Bu-dim: C, 34.80; H, 6.64; N, 3.69; P, 8.16; Cl, 18.67. Found: C, 34.60; H, 6.60; N, 3.54; P, 8.00; Cl, 18.47. $[PdCl_2AsEt_3]_2$t-Bu-dim: C, 31.19; H, 5.92; N, 3.31; Cl, 16.74. Found: C, 31.26; H, 5.91; N, 3.34; Cl, 16.53.

$[PtCl_2PBu_3]_2$t-Bu-dim

t-Bu-dim (1.2 mmol) was added to a stirred suspension of $[PtCl_2PBu_3]_2$ (1 mmol) in 10 ml of methanol. The solution was stirred for 1 h during which time the complex slowly crystallized as bright yellow crystals. For complete crystallizations to occur it was necessary to stand the solution at –30° for several days. The crystals were collected by filtration and washed with hexane (3 X 15 ml). Yield 60%. Purification can be achieved by recrystallization from dichloromethane/hexane mixture. *Anal.* Calcd. for $[PtCl_2PBu_3]_2$t-Bu-dim: C, 36.96; H, 6.75; Cl, 12.83; N, 2.53; P, 5.61; mol. wt. 1104.9 ($CHCl_3$). Found: C, 37.05; H, 6.93; Cl, 12.78; N, 2.48; P, 5.42; mol. wt. 1064.3.

$[PtCl_2XPh_3]_2$t-Bu-dim (X = P or As)

t-Bu-dim (1 mmol) was added to a stirred suspension of $[PtCl_2PPh_3]_2$ (1 mmol) in 15 ml of dichloromethane. After stirring the reaction mixture for 30 min the solvent was removed at low pressure until 5 ml remained. The complex precipitated as a yellow solid which was collected by filtration, washed with hexane (4 X 25 ml) and dried *in vacuo* at room temperature. Yield 60%. *Anal.* calcd. for $[PtCl_2PPh_3]_2$t-Bu-dim: C, 45.11; H, 4.11; N, 2.29; P, 5.06. Found: C, 44.65; H, 4.17; N, 1.73; P, 5.41.

Physical Measurements

Microanalyses were performed by W. J. Buis of the Institute for Organic Chemistry TNO (Utrecht, the Netherlands). Molecular weights were determined using a Hewlett Packard vapour pressure osmometer.

^1H NMR spectra were recorded on a Varian T-60 and a HA-100 spectrometer with tetramethylsilane (TMS) as internal standard; ^1H FT and $^1H\{^{31}P\}$ FT NMR and ^{31}P NMR (H_3PO_4 as external standard) spectra were obtained on a Varian XL-100; ^{13}C NMR spectra were obtained on a Varian CFT-20 with chloroform-d_1 or TMS as internal standard and ^{195}Pt NMR spectra were obtained on a Bruker WH 90 with $\delta^{195}Pt$ of $[PtCl_2PBu_3]_2$ [12] as internal standard ($\delta^{195}Pt$ 1121 ppm).

Infrared spectra of the compounds were measured on a Beckman 4250 as Nujol or Kel-f mulls between CsI plates or as KBr pellets.

Structure Determination and Refinement

Crystals of the title compound which were obtained from CH_2Cl_2/hexane solution, are monoclinic with space group $P2_1/n$ and 2 molecules in a unit cell of dimensions, a = 11.4540(11), b = 16.1169(7), c = 12.9202(12) Å and β = 99.82(1)°. 3504 Reflections with intensities above the 2.5 σ level were collected on a Nonius CAD 4 automatic single crystal diffractometer using graphic monochromatised CuKα radiation. No absorption correction has been applied.

The positions of the Pt, P and Cl atoms were derived from an (E^2-1)-Patterson synthesis. Most of the remaining non-hydrogen atoms were easily found in subsequent difference Fourier syntheses. Two of the n-butyl groups, however, appeared to suffer from disorder, mainly affecting the two terminal atoms of both groups [C(12), C(13) and C(16), C(17)]. C(12) and C(13) were represented by extensive positive regions; C(16) and C(17) by double maxima. No attempt was made to locate the hydrogen atoms.

Refinement was carried out by block-diagonal least-squares calculations. For C(12) and C(13) this led to unacceptable distances and angles. In the final calculations these atoms were kept fixed at geometrically reasonable positions and with an isotropic temperature parameter U of 0.2 Å [2]. C(16) and C(17) were introduced as 4 isotropic half atoms. The remaining atoms were treated anisotropically. Using weights $w = 1/(10.4 + F_0 + 0.0074F_0^2)$ the refinement converged to an R-value of 5.9%. The final coordinates are listed in Table I.

Results and Discussion

Synthetic Aspects

The compounds $[MCl_2XR_3]_2$t-Bu-dim (M = Pd, X = P or As, R = Et; M = Pt, X = P or As; R = Bu, Ph) have been obtained in almost quantitative yield from the reaction of t-Bu-dim with the corresponding metal complexes $[MCl_2XR_3]_2$ in a 1/1 molar ratio (t-Bu-dim/dimer). The stable, yellow, solids are soluble

TABLE 1. Fractional Coordinates and Thermal Parameters $U_{ij} \times 10^3$. Estimated Standard Deviations in Brackets.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt	0.22324(4)	0.09384(3)	0.08259(4)	41.9(3)	42.2(3)	51.4(3)	−0.2(2)	−5.5(2)	−3.6(3)
Cl(1)	0.2455(5)	0.0070(3)	0.2255(3)	147(4)	70(3)	68(3)	−23(3)	−16(3)	17(2)
Cl(2)	0.1746(5)	0.1764(3)	−0.0636(3)	144(4)	68(3)	67(3)	−4(3)	−28(3)	13(2)
P	0.3029(4)	0.2033(3)	0.1735(3)	65(2)	50(2)	69(3)	−1(2)	−11(2)	−13(2)
N	0.1499(8)	−0.0078(6)	−0.0112(8)	43(5)	47(6)	59(6)	1(5)	11(5)	−6(5)
C(1)	0.040(2)	−0.026(1)	−0.026(2)	49(8)	65(9)	74(9)	4(7)	3(7)	−17(7)
C(2)	0.228(1)	−0.063(1)	−0.066(1)	60(8)	65(9)	76(10)	5(7)	18(7)	−22(8)
C(3)	0.178(2)	−0.066(2)	−0.184(2)	137(19)	204(25)	75(13)	15(17)	26(13)	−30(14)
C(4)	0.356(2)	−0.031(2)	−0.044(2)	35(8)	123(16)	199(22)	−8(9)	33(11)	−80(16)
C(5)	0.219(2)	−0.153(2)	−0.020(2)	102(14)	63(11)	191(23)	23(10)	42(15)	5(13)
C(6)	0.379(2)	0.183(1)	0.306(1)	65(9)	74(10)	59(9)	1(8)	−14(7)	−17(8)
C(7)	0.498(2)	0.133(1)	0.307(1)	60(9)	81(10)	56(8)	7(8)	−12(7)	−3(8)
C(8)	0.538(2)	0.101(2)	0.421(1)	85(11)	106(14)	72(10)	9(10)	−20(8)	18(10)
C(9)	0.662(2)	0.057(2)	0.431(2)	85(13)	150(20)	110(14)	13(13)	−29(11)	34(14)
C(10)	0.191(2)	0.282(1)	0.184(1)	106(14)	75(11)	136(18)	28(11)	−26(13)	−44(12)
C(11)	0.094(2)	0.248(1)	0.237(2)	86(12)	130(16)	140(18)	8(12)	39(12)	−52(14)
C(12)[a]	0.015	0.325	0.234						
C(13)[a]	−0.088	0.308	0.275						
C(14)	0.411(2)	0.256(1)	0.105(2)	106(13)	66(10)	82(11)	−36(10)	−8(9)	1(8)
C(15)	0.467(2)	0.336(2)	0.157(2)	144(19)	90(15)	122(16)	−47(13)	−5(14)	−20(12)
C(16)A[b]	0.595(4)	0.357(3)	0.099(4)	106(14)					
C(16)B[b]	0.527(5)	0.388(3)	0.088(4)	119(15)					
C(17)A[b]	0.528(5)	0.382(4)	−0.015(5)	145(19)					
C(17)B[b]	0.610(5)	0.359(4)	0.030(5)	142(20)					

[a] Not refined. [b] Population parameter 0.5.

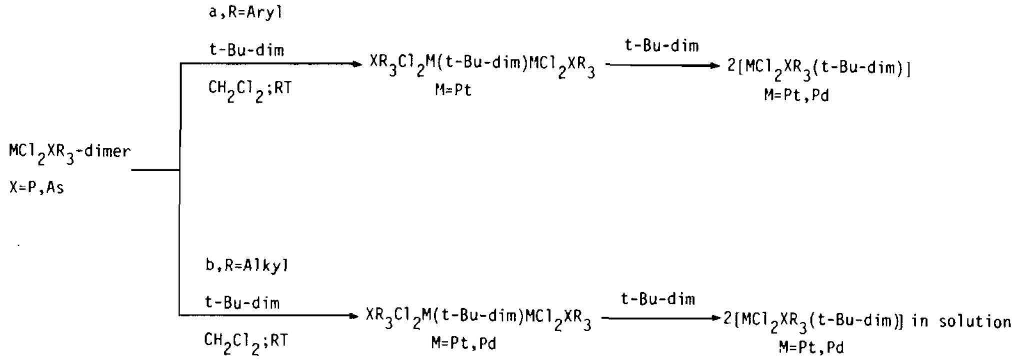
in dichloromethane but are insoluble in acetone, diethyl ether and methanol. The use of excess t-Bu-dim for the aryl-phosphines or -arsine complexes afforded stable $PtCl_2XPh_3$(t-Bu-dim) containing the metal and the t-Bu-dim ligand in a 1/1 molar ratio. Interestingly, for complexes containing alkyl-phosphines only the 2/1 complexes could be isolated although an extensive NMR investigation showed that in solution the 1/1 complexes were formed exclusively [10] (see eqn. 1).

Molecular Geometry of $[PtCl_2PBu_3]_2$*t-Bu-dim*

The asymmetric unit consists of half a $[PtCl_2Bu_3]_2$-t-Bu-dim molecule with the centre of the metal C–C bond lying at an inversion centre of the space group. The shape of the molecule and the atomic numbering scheme are indicated in Fig. 1 in which C(16)B and C(17)B (*cf.* experimental; structure and refinement) have been omitted for clarity. The bond distances and inter-bond angles have been collected in Table II. Each of the imine-nitrogen atoms together with the P, Cl(1) and Cl(2) atoms is coordinated to platinum resulting in an approximately square planar configuration. Only minor deviations of these atoms from the best plane were observed {Pt(0.04), Cl(1) (–0.09), Cl(2) (–0.09), P(0.06) and N(0.07)}.

The Pt–Cl distances of 2.296(4) and 2.300(4) Å are similar to the Pt–Cl distances found in other *trans*-dichloro platinum complexes [*e.g.* 2.304 [8] Å (α-isomer), 2.277(4) Å (β-isomer) in $[Pt_2Cl_2(PPr_3)_2(SCN)_2]$ [13], 2.332(5) Å in $\{Pt[CH_2OC_6H_4PPh_2](C_6H_5N)Cl\}$ [14] and 2.361(6) Å in $[PtCl(PEt_3)_2Phen][BF_4]$ [15]].

The Pt–P distance which is *trans* to the R-dim nitrogen atom is 2.227(5) Å which is in the range of other *trans*-P-Pt(N) complexes (*e.g.* 2.244(4) Å in $[Pt_2Cl_2(PPr_3)_2(SCN)_2]$ [13], 2.290(2) Å in *trans*-$[PtH(PhHNNC_3H_6)(PPh_3)_2][BF_4]\cdot C_6H_6$ [16] and 2.239(7); 2.241(6) Å in $[PtCl(PEt_3)_2Phen][BF_4]$ [15]). The Pt–N distance, 2.214(4) Å, is slightly longer than the Pt–N distance in complexes such as $[Pt_2Cl_2(PPr_3)_2(SCN)_2]$ [2.078(13) Å] [13] and $Pt(PPh_3)_2(PhCONNCOPh)$ [2.047(6) Å] [17] but comparable to the Pt–N distances found in bipy and phen Pt(II) complexes (*e.g.* 2.137(19) Å in $[PtCl(PEt_3)_2Phen][BF_4]$ [15], 2.07, 2.25 and 2.15 Å in [Pt(bipy)Cl(IMN)] $[ClO_4]$ [18] and 2.001(6) Å in $PtCl_2$bipy [19]).



Eqn. 1

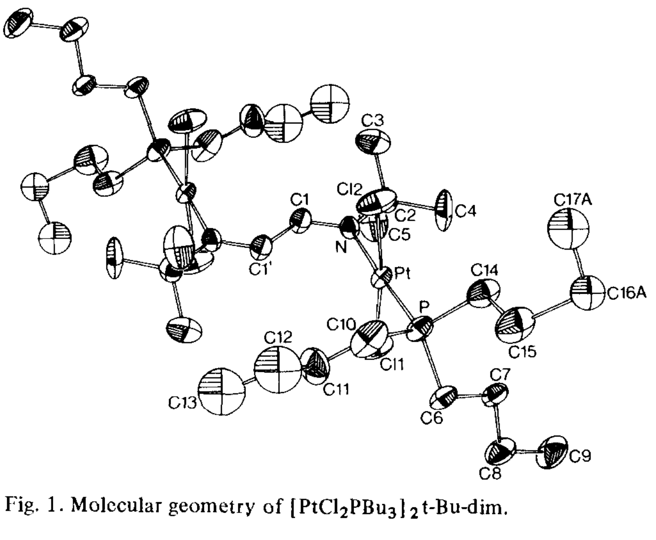


Fig. 1. Molecular geometry of $[PtCl_2PBu_3]_2$t-Bu-dim.

TABLE II. Bond Distances[a] and Interbond Angles[b]. Estimated Standard Deviations in Brackets.

Pt–Cl(1)	2.296(4) Å	Cl(1)–Pt–Cl(2)	172.4(2)°
Pt–Cl(2)	2.300(4)	Cl(1)–Pt–P	94.6(2)
Pt–P	2.227(5)	Cl(1)–Pt–N	88.1(3)
Pt–N	2.214(10)	Cl(2)–Pt–P	89.7(2)
N–C(1)	1.27(3)	Cl(2)–Pt–N	87.8(3)
N–C(2)	1.52(2)	P–Pt–N	177.0(3)
C(1)–C(1)′	1.48(2)	Pt–N–C(1)	123.2(12)
C(2)–C(3)	1.54(3)	Pt–N–C(2)	120.7(7)
C(2)–C(4)	1.53(3)	C(1)–N–C(2)	116.1(13)
C(2)–C(5)	1.58(4)	N–C(1)–C(1)′	118.2(13)
P–C(6)	1.81(2)	N–C(2)–C(3)	109.4(13)
P–C(10)	1.82(3)	N–C(2)–C(4)	109.7(15)
P–C(14)	1.85(3)	N–C(2)–C(5)	106.3(13)
C(6)–C(7)	1.58(3)	C(3)–C(2)–C(4)	112.2(16)
C(7)–C(8)	1.55(2)	C(3)–C(2)–C(5)	107.9(18)
C(8)–C(9)	1.57(4)	C(4)–C(2)–C(5)	111.2(16)
C(10)–C(11)	1.50(4)	Pt–P–C(6)	116.3(6)
C(11)–C(12)	1.53(2)	Pt–P–C(10)	111.1(7)
C(12)–C(13)	1.40	Pt–P–C(14)	111.1(7)
C(14)–C(15)	1.54(4)	C(6)–P–C(10)	106.6(10)
C(15)–C(16)A	1.79(6)	C(6)–P–C(14)	106.4(10)
C(15)–C(16)B	1.48(6)	C(10)–P–C(14)	104.6(10)
C(16)A–C(17)A	1.59(8)	P–C(6)–C(7)	112.0(10)
C(16)B–C(17)B	1.39(9)	C(6)–C(7)–C(8)	106.9(15)
		C(7)–C(8)–C(9)	110.1(17)
		P–C(10)–C(11)	111.3(12)
		C(10)–C(11)–C(12)	99.9(13)
		C(11)–C(12)–C(13)	111.0
		P–C(14)–C(15)	116.0(18)
		C(14)–C(15)–C(16)A	107(3)
		C(15)–C(16)A–C(17)A	98(3)
		C(14)–C(15)–C(16)B	114(3)
		C(15)–C(16)B–C(17)B	125(5)

[a] Distances in Å. [b] Angles in °.

An important aspect of this novel type of R-dim–metal complex is the observation for the first time of a σ,σ′-N,N′ bridging R-dim ligand. The ligand has the anti-configuration and within the limits of accuracy, both platinum atoms reside in the plane through the NCCN skeleton (see Fig. 1) {C(2) (0.005); N(–0.004); C(1) (–0.010); C(1)′ (0.010); N(0.004); C(2)′ (–0.005); Pt(0.012); P(–0.074)}. Comparison of the molecular features of the free R-dim ligand with those of the σ,σ′-N,N′ bridging ligand (in $[PtCl_2PBu_3]_2$t-Bu-dim) and with those of the σ,σ-N,N chelating form (in $PtCl_2$ styrene(t-Bu-dim) [10]) reveals that changes in the C–N=, C_α–C_β and the C=N distances on complexation are negligible. This can be explained on the basis of the perfect planarity of the PtNCCNPt system resulting in a conjugated heterodiene type orbital system. This allows balancing of the σ and π electron density in the metal–ligand system analogous to that which occurs in complexes containing the R-dim ligand in the σ,σ-N,N chelating form. Table III presents evidence for this conclusion.

An intriguing question that remains is whether this planarity of the NCCN skeleton in the R-dim–metal complexes is a general structural feature irrespective of the configuration (syn or anti) of the R-dim ligand. A structural investigation of one of the compounds $[MCl_2PR_3\text{R-dim}]$ or $[PdX_2(\text{R-dim})_2]$ which contains a monodentate bonded R-dim ligand could clarify this point.

Apart from the planar N=C–C=N skeleton the configuration around the N(=C) atoms is of interest. Figure 1 shows that the Pt coordination plane is almost perpendicular to the plane through the Pt–N=C–C=N–Pt skeleton (*cf.* angles between the Pt–Cl bonds and the diimine plane of 85 and 87°). Furthermore, the t-Bu group is *cis* to the [C(1)]-H atom. This probably is more favourable than the alternative configuration in which the t-Bu group is *cis* to the [C(1′)]-H atom. As a consequence the platinum coordination plane and the [C(1)′]-H atoms are in *cis*-positions. In this perpendicular arrangement steric contact between the [C(1)′]-H atom and the square-planar Pt substituent is minimized by rotation of the

TABLE III. Comparison of M–N, C=N, C–N, C–C Bonds and N–M–N Angles in α-Diimine Metal Complexes.

Compounds	M–N[a]	ΔNMN[b]	C=N[a]	C–N[a]	C–C[a]	Ref.
tBu-N=CH–CH=N-tBu			1.283(6)	1.468(16)	1.537(5)	8
$[PtCl_2PBu_3]_2$R-dim	2.214(10)		1.27(3)	1.52(2)	1.48(2)	
R = t-Bu						
BrNi R-dim[c]	1.820(13)		1.294(24)	1.483(22)	1.454(24)	20
R = $(i\text{-}Pr)_2$CH-	1.995(14)	82.0	1.294(23)	1.504(20)		
$W(CO)_2$BrR-dim(π-allyl)	2.219(10)	72.38(34)	1.303(16)	1.506(14)	1.466(17)	21
R = c-Hexyl						
$Mn(CO)_3$Cl R-dim	2.057(14)	78.05(55)	1.294(27)	1.453(17)	1.490(22)	22
R = c-Hexyl	2.050(15)		1.274(30)	1.473(22)		
$Re(CO)_3$Cl R-dim	2.258(18)	72.72(73)	1.345(36)	1.508(37)	1.378(45)	23
R = i-Pr	2.232(19)		1.264(49)	1.462(32)		
$Mo(CO)_4$ R-dim	2.263	not available	1.277	not available	1.443	24
R = i-Pr	2.276		1.283			
$Mo(CO)_4$ R-dim	2.238	not available	1.288	not available	1.467	24
R = 2,6-di-i-Pr-anil	2.222		1.275			
$PtCl_2$styrene R-dim	2.20(3)	74.7(10)	1.28(4)	1.46(4)	1.51(5)	10
R = t-Bu	2.31(3)		1.28(5)	1.44(5)		

[a] Distances in A. [b] Angles in degrees. [c] One R group of the R-dim is metallated to the nickel.

coordination plane around the Pt–N bond by 90° with respect to the NCCN plane. The Pt--- [C(1)′] -H distance, calculated assuming sp^2 hybridization at the C(1′) atom and assuming a C–H distance of 1.10 Å, amounts to 2.6 Å, which is within the sum of the van der Waals radii. The corresponding [C(1′)] H--Pt–N angle is 67°. No other significant non-bonding intermolecular contacts (excluding hydrogen) were found.

Structure in Solution

The complexes are monomeric in chloroform having $[MCl_2XR_3]_2$[t-Bu-dim] stoichiometry (see experimental), which is in accord with retention of the solid state structure containing a bridging R-dim ligand. Information concerning the skeletal conformation of the R-dim ligand could not be obtained from the IR spectra.

Only minor changes in the ν(C=N) with respect to the free ligand (1632 cm^{-1} vs) were observed (nujol 1601 cm^{-1} ms). However, the observation of a strong ν_{as}(M–Cl) at 339 cm^{-1} established the presence of *trans*-Cl_2ML units in the $[MCl_2XR_3]_2$t-Bu-dim compounds [*cf.* 342 cm^{-1} in *trans*-$PdCl_2$(t-Bu-dim)$_2$ which could definitely be assigned to the ν_{as}(M–Cl) by comparing the IR spectra of the chloro derivative and the corresponding Br and I complexes [10].

The IR data have been presented in Table IV. The combined ^{1}H, ^{13}C, ^{31}P and ^{195}Pt NMR spectroscopic data of the $[MCl_2XR_3]_2$t-Bu-dim complexes (X = P or As; M = Pt, R = Bu or Ph; M = Pd, R = Et) have been compiled in Tables V and VI.

TABLE IV. Infrared Data[a] for $[MCl_2XR'_3]_2$ R-dim Complexes.

Compounds	νC=N	ν_{as}Pt/Pd–Cl
$[PdCl_2PEt_3]_2$(i-Pr-dim)	1610 cm^{-1}	346 cm^{-1}
$[PdCl_2AsEt_3]_2$(t-Bu-dim)	1612	345
$[PdCl_2PEt_3]_2$(t-Bu-dim)	1614	350
$[PtCl_2AsPh_3]_2$(t-Bu-dim)	1606	347
$[PtCl_2PBu_3]_2$(t-Bu-dim)	1607	343
$[PtCl_2$PBu3]$_2$(t-Bu-dim)	1601	339

[a] All spectra run as Nujol mull between CSI pellets.

TABLE V. ^{1}H NMR Spectra[a] of $[MCl_2XR'_3]_2$R-dim Complexes.

Compounds	CH_3	C–H	H–C=N
Ligands			
i-Pr-dim	1.24 d	3.45 m	7.93 s
t-Bu-dim	1.30 s		7.93 s
Complexes			
$[PdCl_2PEt_3]_2$(i-Pr-dim)	1.62 d	4.43 m	9.10 b
$[PdCl_2AsEt_3]_2$(t-Bu-dim)	1.73 b		9.75 b
	1.76 s		9.74 m –55°
$[PdCl_2PEt_3]_2$(t-Bu-dim)	1.7 b		9.6 b
	1.73 s		9.58 m –55°
$[PtCl_2AsPh_3]_2$(t-Bu-dim)	1.83 s		9.37 s
$[PtCl_2PPh_3]_2$(t-Bu-dim)	1.58 s		9.1 m
$[PtCl_2PBu_3]_2$(t-Bu-dim)	1.72 s		10.21 m

[a] Recorded at ambient temperature unless indicated otherwise; $CDCl_3$ as solvent with TMS as internal standard.

TABLE VI. ^{13}C and ^{31}P NMR Spectra[a] of [$MCl_2XR'_3$]$_2$R-dim Complexes.

Compounds	$^{13}CH_3$ [b]	$^{13}C{-}N$ [b]	$^{13}C{=}N$ [b]	^{31}P [c]	$J^{31}P^{195}Pt$ [d]
Ligands					
i-Pr-dim	23.47	60.87	156.46		
t-Bu-dim	28.42	56.94	156.59		
Complexes					
[$PdCl_2PEt_3$]$_2$(i-Pr-dim)	23.01	61.34	161.87	35.05	
[$PdCl_2AsEt_3$]$_2$(t-Bu-dim)	31.09	65.21	163.28		
[$PdCl_2PEt_3$]$_2$(t-Bu-dim)	31.05	64.53	162.86	34.68	
[$PtCl_2AsPh_3$]$_2$(t-Bu-dim)	31.70	68.42	163.75		
[$PtCl_2PPh_3$]$_2$(t-Bu-dim)	31.77	67.17	165.44	1.92	3679
[$PtCl_2PBu_3$]$_2$(t-Bu-dim)	31.41	66.73	162.96	−8.43	3448

[a] Recorded at ambient temperature in $CDCl_3$ δ ppm. [b] $CDCl_3$ as internal standard. [c] H_3PO_4 as external standard. [d] $J^{31}P^{195}Pt$ in Hz.

It is important to note for the following discussion that no evidence could be obtained for the occurrence of intermolecular exchange, on the NMR time scale, between the [MCl_2XR_3]$_2$t-Bu-dim and either the [MCl_2XR_3]t-Bu-dim species at small M/t-Bu-dim molar ratios or the MCl_2XR_3 starting dimers at high M/t-Bu-dim molar ratios (*cf.* ref. 10). Since the NMR data of the respective compounds appeared to be similar with respect to the dynamic features, the discussion will be limited to the [$PtCl_2PBu_3$]$_2$t-Bu-dim, for which the molecular structure in the solid state is known unambiguously (*vide supra*).

^{1}H and ^{13}C NMR spectra show (see Figs. 2 and 3) that in the temperature range studied (−55° to +34 °C) the structural features of [$PtCl_2PBu_3$]$_2$t-Bu-dim observed in the solid are retained in solution. The ^{31}P NMR spectrum showed only one singlet (δ − 8.43 ppm) with satellites due to $^1J^{195}Pt^{31}P$ of 3448 Hz. The ^{13}C NMR spectrum revealed a single set of resonances pointing to equivalent (*trans*-$PtCl_2PBu_3$)t-Bu-N=C halves. The ^{1}H NMR data are in full agreement with these conclusions and, moreover, indicate a surprising rigidity of the molecular configuration of the compound on the NMR time scale.

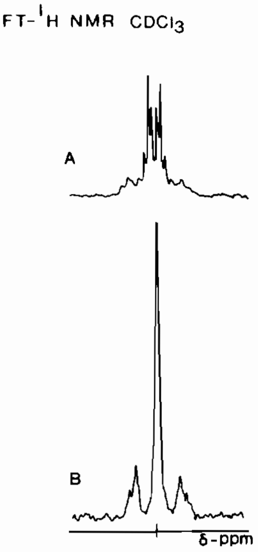


Fig. 2. The imine proton region of the ^{1}H NMR (FT, 100 MHz) spectra of [$PtCl_2PBu_3$]$_2$t-Bu-dim. a) ^{31}P and ^{195}Pt coupled spectrum; b) ^{31}P decoupled and ^{195}Pt coupled spectrum.

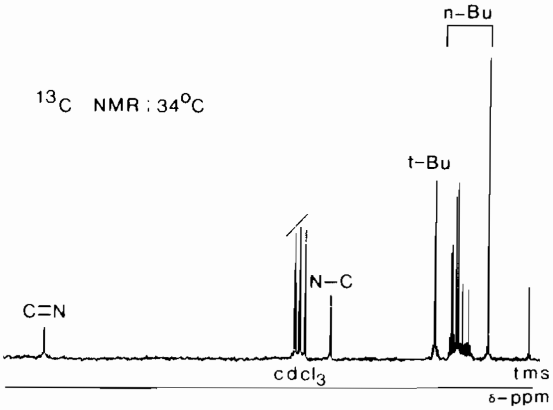


Fig. 3. ^{13}C NMR spectrum (20 MHz) of [$PtCl_2PBu_3$]$_2$t-Bu-dim.

^{31}P decoupled spectra show one sharp resonance at δ 10.2 ppm for the imine proton with accompanying satellites due to Pt–H coupling in [$PtCl_2PBu_3$]$_2$t-Bu-dim molecules having the various $^{195}Pt_{2-n}\,^{197}Pt_n$ (n = 0 or 1) combinations. The ^{1}H NMR spectra without ^{31}P decoupling show a complex multiplet resonance for the imine protons, which is caused by the spin coupling non-equivalence of these isochronous protons arising from the two phosphorus and the two platinum nuclei in the molecule. Attempts to derive the values of the two Pt–H couplings from the ^{195}Pt NMR spectra failed. Only a broad Pt resonance (1051.36 ppm) was observed which probably results from quadrupole relaxation of the coordinated ^{14}N ligand [25]. In contrast the $^{31}P-^{1}H$ coupling data could be obtained by analyses of the spectrum of the corresponding palladium compound $[PdCl_2PEt_3]_2$t-Bu-dim in which the imine proton couples exclusively with phosphorus nuclei. Computer simulation of the AA'MM' spectrum for the imine proton resulted in a good fit of the measured and calculated multiplet (see Fig. 4 for the spectrum and $^4J^{31}P^1H$, $^5J^{31}P'$, ^1H, $^3J^1H^1H'$, and $^7J^{31}P^{31}P'$ data used).

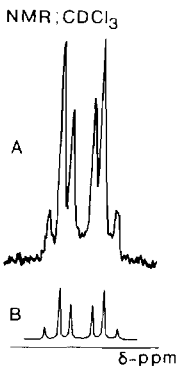


Fig. 4. a) ^{1}H NMR spectrum of the imine proton in $[PdCl_2PEt_3]_2$t-Bu-dim. b) Computer simulation of spectrum a: $^4J(^{31}P-^{1}H)$ 13.4, $^5J(^{31}P'-^{1}H)$ 0.6, $^3J(^{1}H-^{1}H')$ 8.2 and $^7J(^{31}P-^{31}P')$ 0 Hz; linewidth 0.5 Hz.

Furthermore, in the platinum compound $[PtCl_2PBu_3]_2$t-Bu-dim, a sharp multiplet pattern (see Fig. 2) for the imine proton is found at approximately 2.5 ppm downfield from the chemical shift position of this proton in the free ligand. It is well established that protons residing at a short distance from and above the square planar coordination plane of a metal d^8 center undergo a large downfield shift. This deshielding effect arises from the anisotropy in the magnetic susceptibility of the metal center [10, 26–30]. Its effect on the chemical shift is very dependent on the magnitude of the angle θ between the Pt....H vector and the vector passing through the metal center and perpendicular to the coordination plane. The deshielding effect is a maximum when θ = 0 but drops dramatically with increasing values of θ [26], which makes the chemical shift of the imine proton a useful probe for the detection of the stereochemistry of the R-dim ligand in the $[MCl_2PR_3]_2$R-dim complexes. The invariance of this chemical shift value of the imine proton over the temperature range studied can only be explained by proposing that rotation around both the Pt–N and the C(1)–C(1)' axis is blocked, thus resulting in a fixed position (fixed value for θ) of the imine protons above the metal centers. These results suggest that the *trans*-PPtNCCNPtP-*trans* skeleton is not only planar in the solid but also that this is the predominant configuration (on the NMR time scale) for this part of the molecule in solution.

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