209. The Coordination Chemistry of 1,2-Bis[(diphenylphosphino)methyl]benzene with Nickel(II), Palladium(II), Platinum(II), and Platinum(0) and the X-Ray Crystals Structure of [Pt{1,2-bis[(diphenylphospino)methyl]benzene}(C_2H_4)]

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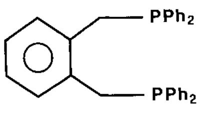
The preparation of complexes [MX_2(**1**)] (M = Ni, Pd, and Pt; X = Cl, Br, and I; **1** = 1,2-bis[(diphenylphosphino)methyl]benzene), [Pt(OSO_2CH_3)Et(**1**)], [Pt(alkene)(**1**)] (alkene = C_2H_4 and CH_2 = CHCN), and [(**1**)Pt(μ-H)$_2$PtH(**1**)][BPh_4] is reported. Their ^{1}H- and ^{31}P-NMR spectra were recorded and used for structural assignments. The X-ray crystal structure of [Pt(C_2H_4)(**1**)] was determined. It is shown that the P–Pt–P bond angle in this complex differs significantly from those found in related compounds with monodentate phosphines, and that this difference is likely to be due to intramolecular contacts.

Introduction. – Transition-metal complexes with bidentate phosphine ligands forming seven-membered chelate rings often show structural and spectroscopic features, as well as reactivity patterns, which differ significantly from those with bidentate phosphines forming smaller chelate rings. Thus, in the series of complexes [$PdCl_2(Ph_2P(CH_2)_nPPh_2)$] ($n$ = 1, 2, or 3) not only there are significant variations of P–Pd–P bond angles (72.68(3), 85.82(7), and 90.58(5)°, resp.) but also changes in Cl–Pd–Cl bond angles (93.63(3), 94.19(7), and 90.78(5)°, resp.) [1]. Furthermore, in the related set of compounds [$Pd(NCS)_2(Ph_2P(CH_2)_nPPh_2)$] when n = 1 or 2, one NCS is *N*- and one is *S*-bonded, while when n = 3, both anions are *N*-bonded [2].

It has also been established that the magnitude of the '^{31}P-NMR coordination chemical shift', *i.e.* the difference between the δ value of a P-atom when free and coordinated [3], which has an approximately constant value for a set of compounds of a given type, is significantly changed by chelation ('ring effect') and that the magnitude of this effect depends on ring size [4]. Finally, while [$RuBr_2(Ph_2P(CH_2)_3PPh_2)_2$] in 1,2-dichloroethane dissociates to [$RuBr(Ph_2P(CH_2)_3PPh_2)_2$]$^+$ and Br$^-$, the corresponding complexes with $Ph_2P(CH_2)_nPPh_2$ (n = 1 or 2) do not [5]. Moreover, the catalytic homogeneous hydrogenation of prochiral (acylamino)alkanoic acid using complexes of the type [Rh(solvent)$_2$(chiral diphosphine)]$^+$ gives high optical yields with a phosphine such as $Ph_2PCH_2CH(CH_3)PPh_2$ (*prophos*), while the corresponding complexes with $Ph_2PCH_2CH_2CH(CH_3)PPh_3$ (*chairphos*) give very low optical yields [6]. However, for other catalytic reactions, *e.g.* hydroformylation, complexes with seven-membered chelate rings give higher optical yields than similar complexes containing six-membered chelate rings [7].

Such effects are still under study but, up to now, there does not appear to be a systematic study of structure-activity relationships in a closely related set of complexes. For this purpose, one needs a chelating diphosphine ligand forming seven-membered rings which could easily be modified with a wide range of substituents and, at the same time, would have only limited conformational flexibility. One set of such compounds could be based on 1,2-bis[(diphenylphosphino)methyl]benzene (**1**).

It is likely that a set of chiral ligands of type **2** can easily be prepared starting from **1**, as it has been shown that *i*) the CH_2 group in $Ph_2P(O)CH_2Ph$ can be readily alkylated [8] and *ii*) chiral phospine oxides can be routinely deoxygenated [9].



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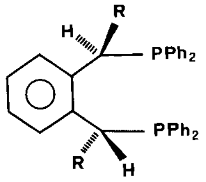

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Prior to studying the coordination behaviour of ligands such as **2**, it was thought useful to gather some basic knowledge on the complexing properties of the unsubstituted ligand **1** as although the preparation of this ligand has been reported for some time [10], its coordination chemistry appears to have been little investigated [11] [12].

We report here the synthesis of complexes $[NiX_2(\mathbf{1})]$ (**3**), $[PdX_2(\mathbf{1})]$ (**4**), and $[PtX_2(\mathbf{1})]$ (**5**), with X = Cl (**a** series), Br (**b** series), and I (**c** series), and of $[Pt(C_2H_4)(\mathbf{1})]$ (**6a**) and some of their reactions, as well as the X-ray crystal structure of **6a**. Finally, we describe the reaction of $[PtX_2(\mathbf{1})]$ (X = Cl, Br; **5a** and **5b**) with $Na[BH_4]$ in reagent-grade MeCN which gives $[Pt(CH_2{=}CHCN)(\mathbf{1})]$ (**6b**), arising from the presence of small amounts of acrylonitrile in commercially available MeCN.

Results and Discussion. – Ligand **1** easily forms complexes of the type $[MX_2(\mathbf{1})]$, *i.e.* **3a–c** (M = Ni^{II}; X = Cl, Br, I), **4a–c** (M = Pd^{II}; Cl, Br, I), and **5a–c** (M = Pt^{II}; X = Cl, Br, I), either by reaction of the ligand and the appropriate metal compound or, for the heavier halide ions, by reacting the chloro complexes with Br_2 or I_2. The complexes prepared are listed in *Table 1*.

While the Pd^{II} and the Pt^{II} complexes are stable both in solution and in the solid state, the Ni^{II} complexes tend to dissociate in solution with liberation of ligand **1** and precipitation of the inorganic salt. The Pd^{II} and Pt^{II} compounds are normal square-planar complexes of the type *cis*-$[MX_2(LL)]$ (LL = chelating ligand) as indicated, in the case of the Pt^{II} complexes, by the values of the $^1J(^{195}Pt,^{31}P)$ coupling constants [3] (see *Table 1*) and, in the case of both sets of complexes, by the form of the signals due to the methylene protons (see *Table 2*, $\delta(H_a)$) which has the typical pseudo-*d* appearance of *cis*-isomeric species (see below).

The geometry of the Ni^{II} complexes differs depending on the anionic ligand present. When this is thiocyanato (see **3d**), a normal square-planar complex is obtained as

Table 1. *Colour and ^{31}P-NMR Parameters*[a] *of Complexes of the Type [MX_2(**1**)]* (M=Ni^{II}, Pd^{II}, and Pt^{II}; **1** = 1,2-bis[(diphenylphosphino)methyl]benzene) *and of Related Compounds*

Compound	Colour	$\delta(^{31}P)$ [ppm]	$^1J(^{195}Pt,^{31}P)$ [Hz]
$1,2-(Ph_2PCH_2)_2C_6H_4$ (**1**)	colourless	−13.5	
$[NiCl_2(\mathbf{1})]$ (**3a**)	red	[b]	
$[NiBr_2(\mathbf{1})]$ (**3b**)	deep red	[b]	
$[NiI_2(\mathbf{1})]$ (**3c**)	brown	[b]	
$[Ni(NCS)_2(\mathbf{1})]$ (**3d**)	deep yellow	10.9	
$[PdCl_2(\mathbf{1})]$ (**4a**)	pale yellow	16.0	
$[PdBr_2(\mathbf{1})]$ (**4b**)	orange	10.3	
$[PdI_2(\mathbf{1})]$ (**4c**)	red	−0.9	
$[PtCl_2(\mathbf{1})]$ (**5a**)	colourless	−2.4[c]	3575
$[PtBr_2(\mathbf{1})]$ (**5b**)	colourless	−5.3[d]	3525
$[PtI_2(\mathbf{1})]$ (**5c**)	colourless	−13.0[d]	3359
$[Pt(C_2H_4)(\mathbf{1})]$ (**6a**)	colourless	16.5[c]	3581
$[Pt(CH_2{=}CHCN)(\mathbf{1})]$ (**6b**)	colourless	14.2[d][e]	3825
		12.5	3353
$[Pt(C_2H_4)(PPh_3)_2]$ (**7a**)	colourless	33.8[f]	3719
$[Pt(CH_2{=}CHCN)(PPh_3)_2]$ (**7b**)	colourless	28.6[g]	3965
		28.5	3486
$[Pt(OSO_2MeEt(\mathbf{1})]$ (**8**)	colourless	14.8[h]	1703
		9.4	5186
$[(\mathbf{1})Pt(\mu{-}H)_2PtH(\mathbf{1})][BPh_4]$ (**9**)	colourless	11.9[i]	3089

[a] Room-temperature data.
[b] Paramagnetic in solution.
[c] For a discussion of the temperature dependence of this spectrum, see *Discussion*.
[d] The temperature dependence of the spectrum was not studied.
[e] $^2J(P,P) = 24$ Hz.
[f] See [16c].
[g] $^2J(P,P) = 36$ Hz.
[h] $^2J(P,P) = 13.2$ Hz. P-atom in *trans*-position to C.
[i] See also *Discussion*.

indicated by its diamagnetism in solution. The $\tilde{\nu}$(CN) vibration of **3d** occurs at 2090 cm^{-1}. As it is found [13] that the CN-stretching vibration in *N*-bonded thiocyanato complexes occurs near or below 2050 cm^{-1}, while in the *S*-bonded isomers, this vibration is observed near 2100 cm^{-1}, it is probable that this ligand is *S*-bonded in **3d**. In order to confirm this assignment, an attempt was made to identify the CS stretch in complex **3d** as this vibration occurs at 780–860 cm^{-1} in the *N*-bonded and at 690–720 cm^{-1} in the *S*-bonded isomers. However, the IR spectra of the set of compounds $[NiX_2(\mathbf{1})]$ (**3**) shows a very large number of bands in the region 600–900 cm^{-1}, and even comparison of the spectra of **3a** (X = Cl), **3b** (X = Br), and **3d**) (X = NCS) did not allow the unambiguous assignment of the CS vibration. The halide complexes, on the other hand, give paramagnetic species in solution and in the solid state and, therefore, are assigned pseudo-tetrahedral structures analogous to that found in $[NiCl_2(DIOP)]$ (DIOP = (−)-1,4-bis(diphenylphosphino)-1,4-dideoxy-2,3-*O*-isopropyliden-D-threitol) [14]. In this respect, the compounds $[NiX_2(\mathbf{1})]$ (X = Cl, Br, and I) behave like the corresponding complexes $[NiX_2(PPh_2Bz)_2]$ [15].

The ^{31}P-NMR spectra of the thiocyanato-nickel complex **3d**, of the Pd^{II} complexes **4a–c**, and of the Pt^{II} species **5a–c** are characteristic for square-planar complexes of the

Table 2. *Room Temperature ^1H-NMR Data for Complexes of the Type [MX_2(1)]* ($M=Ni^{II}$, Pd^{II}, and Pt^{II}; **1** = 1,2-bis[(diphenylphosphino)methyl]benzene) *and of Related Compounds*

Compound	$\delta(H_a)$[a] [ppm]	J_a[b] [Hz]	$^3J(Pt,H)$ [Hz]	$\delta(H_b)$[c] [ppm]	$^2J(Pt,H_b)$ [Hz]
1	3.31				
3a	[d]				
3b	[d]				
3c	[d]				
3d	3.56				
4a	3.85	10			
4b	3.87	10			
4c	3.91	10			
5a	3.93	10	50		
5b	3.96	10	50		
5c	3.99	10	48		
6a[e]	*ca.* 4.2[f]	[g]	[g]	1.96[h]	60
6b	4.3	[g]	[g]	[i]	
7a				2.04	60
7b				[j]	
8[k]	3.90				
9[l]	4.50	[g]	[g]		

[a] $H_a = CH_2$ protons; *m*.

[b] $J_a = |^2J(P,H) + ^4J(P,H)|$ for CH_2.

[c] H_b = ethene protons.

[d] Paramagnetic in solution.

[e] $\delta(^{13}C$; ethene) = 32.6 ppm; $^1J(Pt,C) = 208$ Hz; $\delta(^{195}Pt) = -5124$ ppm.

[f] Broad signal; at 213 K, one observes two peaks of unequal height centered at *ca.* 4.3 ppm and a complex *m* centered at *ca.* 3.9 ppm.

[g] Non-obtainable because of the complexity of the spectrum.

[h] $\delta(^{13}C$; ethene) = 38.4 ppm; $^1J(Pt,C) = 197$ Hz; $\delta(^{195}Pt) = -5068$ ppm; broad signal; at 213 K it resolves into a main pattern of *AB* type with Pt-satellites.

[i] The CH_2=CHCN moiety appears as an *ABC* pattern in the $^1H\{^{31}P\}$-NMR spectrum with the following parameters: $\delta(H) = 2.16$ (H_A), 2.0 (H_B), and 1.79 ppm (H_C); $^3J_{AB} = 10$, $^3J_{BC} = 5$, and $^2J_{AC} = 10$ Hz; $^2J(Pt,H)$ couplings are not observed.

[j] These resonances give an AB_2 system in the $^1H\{^{31}P\}$-NMR spectrum with the following values: $\delta(H) = 2.34$ ($1H_A$) and 2.09 ppm ($2H_B$); $^3J_{AB} = 10$, $J(Pt,H_A) = 66$, $J(Pt,H_B) = 51$, $J(P_1,H_A) = 4$, $J(P_2,H_A) = 9$, $J(P_1,H_B) = 4$, and $J(P_2,H_B) = 7$ Hz.

[k] $\delta = 2.0$ (br. *s*, CH_3SO_3Pt), 1.3 (br. *m*, $Pt-CH_2CH_3$), and 0.3 ppm (br. *m*, $Pt-CH_2CH_3$); no $J(Pt,H)$ couplings were observed.

[l] δ(H; hydrido) = -4.7 ppm (*quint. quint.*); $^2J(Pt,H) = 428.5$ and $^2J(P,H) = 39.3$ Hz.

type *cis*-[MX_2L_2]. This is best seen by comparing the magnitude of the $^1J(Pt,P)$ coupling constant (see *Table 1*) of the Pt^{II} complexes **5a–c** with literature values for related compounds [3].

Examination of molecular models of compounds of type *cis*-[MX_2(**1**)] indicates that the chelate ring can exist in different conformations, some of which contain magnetically inequivalent P-atoms. In order to establish whether more than one conformer was formed in solution, a study of the temperature-dependence of the ^{31}P-NMR spectrum of *cis*-[$PtCl_2$(**1**)], (**5a**), was undertaken: While at room temperature **5a** in $CDCl_3$ shows a *s* at -2.4 ppm (with $^1J(^{195}Pt,^{31}P) = 3575$ Hz), at 213 K in addition to a *s* at -2.12 ppm (with $^1J(^{195}Pt,^{31}P) = 3571$ Hz), one observes 2 *d* at -2.16 (with $^1J(^{195}Pt,^{31}P) = 3571$ Hz), and 1.31

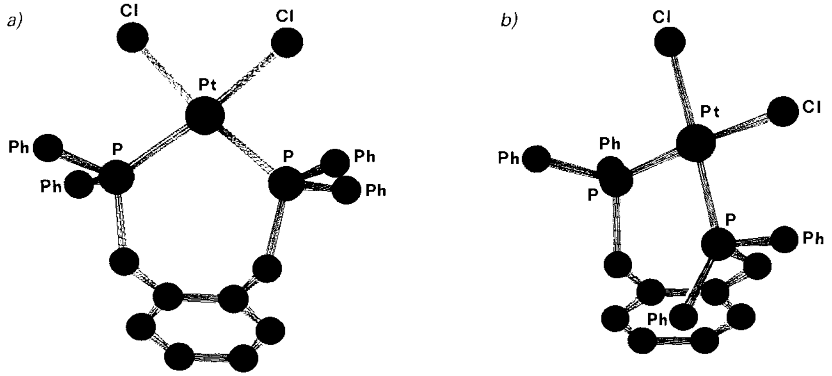


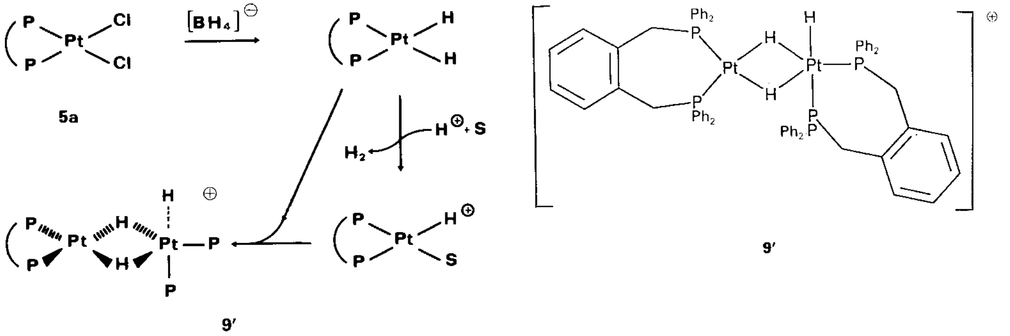
Fig. 1. *Two possible conformers of [PtCl$_2$(***1***)]* (**5a**). *a)* C_2 form (conformer **A**); *b)* C_s form (conformer **B**).

ppm (with $^1J(^{195}Pt,^{31}P) = 3549$ Hz) with a $^2J(^{31}P,^{31}P)$ value of 11 Hz. The approximate intensity ratios of the *s* and the sum of the 2*d* is 1:4. This effect is solvent-dependent as it is found that in CD_2Cl_2 at 193 K, the ratio of the two sets of signals is *ca.* 3:2. These data are interpreted as follows: two forms of complex **5a** are present in solution, one of them, conformer **A**, with magnetically equivalent P-atoms giving rise to the *s*, and the other, conformer **B**, where the 2 P-atoms are different. These two forms are in equilibrium, and at room temperature, only conformer **A** is present in detectable amounts, while at lower temperature, in the more polar solvent, **B** is prefered. Further study of this equilibrium was prevented by the low solubility of **5a**. Examination of molecular models of **5a** show that the more stable conformer is one where the Pt and P-atoms as well as the C-atom of the CH_2 groups are coplanar, while the benzene ring bends away from this plane (see *Fig. 1a*). This form has a mirror plane bisecting the Pt-atom and the bridging benzene ring (C_2 form). This chelate ring conformation is that found in [Pt(C_2H_4)(**1**)] (**6a**; see below). Another easily constructed conformation contains a twisted chelate ring where the CH_2 C-atoms do not lie in the coordination plane (C_s form) (see *Fig. 1b*). If one assumes that molecular models can be reliably used to assign conformation, the C_2 form could be that giving rise to the *s* (conformer **A**), while the other could produce the 2*d* (conformer **B**), in the ^{31}P-NMR spectrum. The ^{195}Pt-NMR spectrum (CD_2Cl_2, 213 K) of [PtCl$_2$(**1**)], (**5a**) is also quite informative (2*t*'s, a sharp one at −4539 ppm with $^1J(^{195}Pt,^{31}P) = 3575$ Hz (probably C_2 form) broad one at −4550 ppm with $^1J(^{195}Pt,^{31}P) \approx 3400$ Hz (probably C_s form)).

Complex [PtCl$_2$(**1**)] (**5a**) reacts with Na[BH$_4$] in the presence of C_2H_4 with formation of the Pt^0 complex [Pt(C_2H_4)(**1**)] (**6a**), which is analogous to [Pt(C_2H_4)(PPh_3)$_2$], (**7a**) [16]. The alkene complex **6a** reacts with Me_3SO_3H giving the Et complex [Pt(OSO_2Me)Et(**1**)] (**8**). The ^{31}P-NMR spectrum of **6a** (see *Table 1*) is typical for complexes of this type [16c]. As found for the Pt^{II} complex **5a**, the Pt^0 complex **6a** gives temperature-dependent ^{31}P-NMR and ^{1}H-NMR spectra, a behaviour attributed again to different conformers present in solution, *i.e.* to those corresponding to **A** and **B** (*Fig. 1*).

At room temperature, the ^{31}P-NMR spectrum (CD_2Cl_2) of **6a** shows the usual pseudo-*t* with $\delta(^{31}P) = 16.4$ ppm and $^1J(Pt,Pt) = 3582$ Hz. However, at 213 K, one observes the pseudo-*t* at 15.8 ppm ($^1J(Pt,Pt) = 3559$ Hz) together with an *AB* system with $\delta(^{31}P)$ values of 11.0 and 6.0 ppm and a $^2J(P,P)$ of 14 Hz. The $^1J(Pt,P)$ values could not be reliably obtained because of signal-to-noise problems.

Scheme



Attempts to prepare the dihydrido complex *cis*-$[PtH_2(\mathbf{1})]$, (**5d**), by reacting chloro compound **5a** with excess Me_4N $[BH_4]$ in wet CH_2Cl_2 in a H_2 atmosphere gave a mixture which contained *ca.* 25% of an unidentified compound with $\delta(^{31}P) = 10.3$ ppm and $^1J(^{195}Pt,^{31}P) = 2041$ Hz, and *ca.* 75% of another species which is assigned the static structure **9'** (*Scheme*). This assignment is based on the ^1H and ^{31}P-NMR data showing the same pattern of resonances and coupling constants as found for the cations $[\{Ph_2P(CH_2)_nPPh_2\}Pt(\mu{-}H)_2PtH\{Ph_2P(CH_2)_nPPh_2\}]^+$ ($n = 2$, 3, and 4) for which a structure corresponding to that postulated for **9'** has been established by X-ray diffraction [17a]. The cations $[\{R(t\text{Bu})P(CH_2)_nPR(t\text{-Bu})\}_2Pt_2H_3]^+$ ($R = t$-Bu, $n = 2$ and 3; R = Ph, $n = 2$) described by *Tulip et al.* [17b] also show the same type of NMR spectra, and the X-ray crystal structure of one of them is closely related to that found by *Knobler et al.* [17a]. A possible reaction pathway leading to the formation of cation **9'** is shown in the *Scheme*.

It is possible that the unidentified compound mentioned above is the dihydride *cis*-$[PtH_2(\mathbf{1})]$ (**5d**) as the related compound *cis*-$[PtH_2\{1,2\text{-}[(t\text{-Bu})_2PCH_2]_2C_6H_4\}]$ shows a $^1J(^{195}P,^{31}P)$ of 2112 Hz [18a], a typically low value characteristic of the presence of a ligand of high *trans*-influence opposite to the P-atom [3]. Other *cis*-dihydridodi(phosphine) complexes of Pt^{II} have been described by *Yoshida et al.* [18b]. On addition of $Na[BPh_4]$ to the solution containing the mixture of **5d** and cation **9'**, one obtains only the $[BPh_4]$ salt of **9'**. Is it noteworthy that if $[PtBr_2(\mathbf{1})]$ (**5b**) is reacted with $Na[BH_4]$ in the absence of H_2, the solutions gradually become red-brown. This could be due to the formation of a compound analogous to red $[Pt_2\{(t\text{-Bu})_2P(CH_2)_3P(t\text{-Bu})_2\}_2]$ described by *Yoshida et al.* [18b]. Cation **9'** can also be obtained by adding an excess of Me_3SO_3H to a CH_2Cl_2 solution of $[Pt(C_2H_4)(\mathbf{1})]$ (**6a**) under H_2. Also in this case, a ^{31}P-NMR spectrum of the solution shows the presence of the presumed dihydride **5d** which, however, on addition of $Na[BPh_4]$, decomposes with formation of **9'** which precipitates as the $[BPh_4]$ salt.

Attempts to prepare dihydride **5d** by reacting $[PtBr_2(\mathbf{1})]$ with $Na[BH_4]$ in MeCN led to the isolation of an air-stable product which was later identified as $[Pt(CH_2{=}CHCN)(\mathbf{1})]$ (**6b**). The acrylonitrile present in this complex originates from the MeCN used as solvent. Apparently, *acrylonitrile is a regular contaminant of reagent-grade MeCN!* Compound **6b** obtained this way was identical with that prepared directly from **5b** and acrylonitrile. The previously reported [19] complex $[Pt(CH_2{=}CHCN)(PPh_3)_2]$ (**7b**) can also be obtained by treating *cis*-$[PtCl_2(PPh_3)_2]$ with $Na[BH_4]$ using reagent grade MeCN as a solvent.

X-Ray Crystal Structure of [Pt(C_2H_4)(1)] (6a). – The crystals of **6a** are built up from well-separated discrete molecules with no crystallographically imposed symmetry. There are no intermolecular contacts significantly shorter than the sums of the *van der Waals* radii of the neighbouring atoms. A computer generated drawing of the molecule is shown in *Fig. 2*, and a list of selected distances and angles is given in *Table 3*.

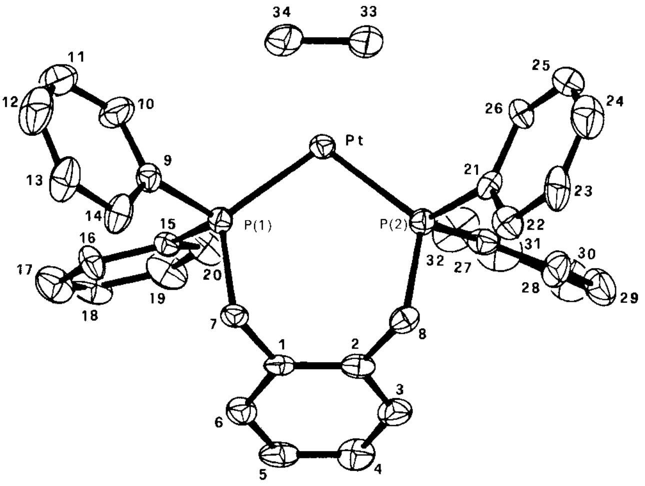


Fig. 2. *An ORTEP view of [Pd(C_2H_4)(*1*)]* (**6a**)

Table 3. *Comparison of Bond Distances and Angles in [Pt(C_2H_4)(*1*)]* (**6**) *and [Pt(C_2H_4)(PPh_3)$_2$]* (**7a**)

Distances [Å]				Angles [°]			
6a[a])		**7a**[b])		**6a**[a])		**7a**[b])	
Pt–P(1)	2.260(3)	Pt–P(1)	2.265(4)	P(1)–Pt–P(2)	105.0(1)	P(1)–Pt–P(2)	111.60(7)
Pt–P(2)	2.257(3)	Pt–P(2)	2.270(4)	C(33)–Pt–C(34)	40.2(6)	C(1)–Pt–C(2)	39.70(35)
Pt–C(33)	2.108(18)	Pt–C(1)	2.116(8)	P(1)–Pt–C(34)	107.8(4)	P(1)–Pt–C(1)	103.88
Pt–C(34)	2.122(17)	Pt–C(2)	2.106(9)	P(2)–Pt–C(33)	106.9(4)	P(2)–Pt–C(2)	104.83
C(33)–C(34)	1.45(2)	C(1)–C(2)	1.434(13)				
Dihedral angle							
PPtP–CPtC	2.3		1.6				

[a]) See *Fig. 2* for atomic numbering.
[b]) See *Fig. 3* for atomic numbering.

The coordination around the Pt-atom, consisting of the two-atoms of ethene and two P-atoms, is approximately planar. If one considers ethene as a monodentate ligand, the Pt-atom is three-coordinate. The chelate ring is folded, the atoms C(7), P(1), Pt, P(2), and C(8) defining one approximate plane, while the other, defined by C(7), C(1), C(2), and C(8), forms a dihedral angle of *ca.* 110°. The geometry of the coordination polyhedron appears normal when compared with similar [Pt(alkene)(PPh_3)$_2$] complexes. Typical parameters for complexes of this type are [16b] [20–23]: P–Pt–P, 101–111°; Pt–P, 2.26–2.34 Å; Pt–C, 2.00–2.12 Å, C–C, 1.42–1.62 Å; dihedral angle P(1)PtP(2)–PtC (alkene)C(alkene), 1.6–12°.

The structural parameters of **6a** are best compared with those of [Pt(C_2H_4)(PPh_3)$_2$] (**7a**; see *Table 3* and *Fig. 3*): Most of the bonding parameters of the two complexes are very similar, with the exception of the P–Pt–P angle which is 105.0(1)° in **6a** and 111.60(7)° in **7a**. It appears unlikely that this change could be induced by differences in electronic effects of the phosphine donors. Thus, the value of *Tolman*'s electronic parameter ν for PPh_3 is 2068.9 cm^{-1}, while for $PPh_2(CH_2Ph)$, one can calculate a value of 2068.1 cm^{-1} [24]. The effect is also unlikely to be mainly of steric origin as *Tolman*'s cone angle Θ for PPh_3 is 145°, while the calculated value for $PPh_2(CH_2Ph)$ is 152° [24]. On this basis, one would then expect that the P–Pt–P angle should be larger in complex **6a** with the ligand **1**, than in the PPh_3 complex **7a**. However, it could be argued that formation of a chelate ring by ligand **1** would disfavour the formation of a large P–Pt–P angle. This cannot be excluded as we find [25] that in the complex [$Ag_2(\mu$–Cl$)_2$(**1**)], the P–Ag–P bond angle is

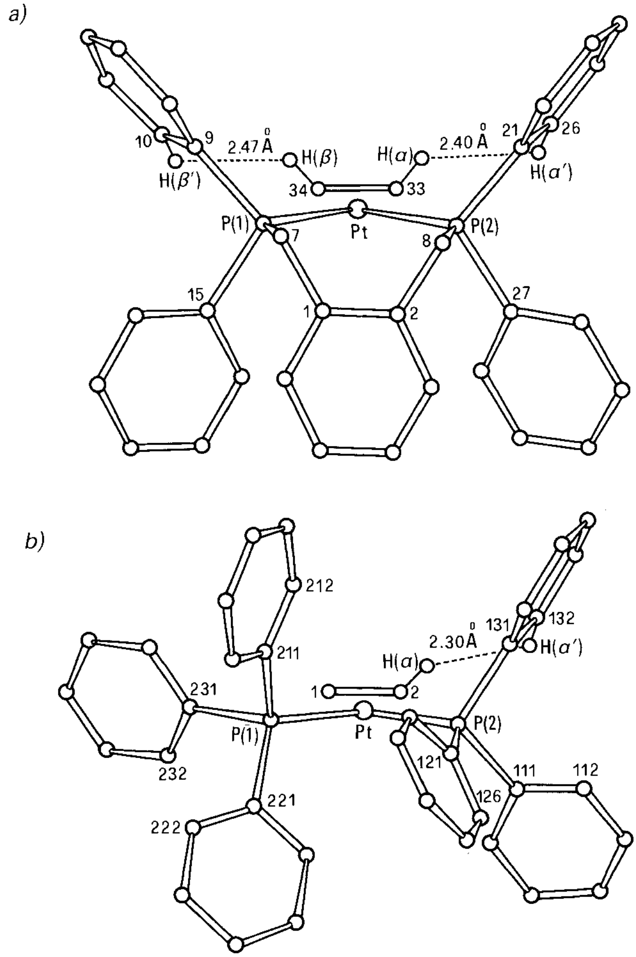


Fig. 3. *Computer-generated drawing* a) *of [Pt(C_2H_4)(***1***)]* (**6a**) *and* b) *of [Pt(C_2H_4)(PPh_3)$_2$]* (**7a**)

112°, while in $[Ag_2(\mu{-}Cl)_2(PPh_3)_4]$, this angle is 122.9(1) Å [26]. On the other hand, the difference in P—Pt—P bond angles in **6a** and **7a** may be due to non-bonded interactions between the H-atoms of the olefin and of the phosphine ligands. Thus, in **6a**, the shortest intramolecular H···H contacts, *i.e.* those between H(α) and H(α') on one hand and those between H(β) and H(β') on the other, are 2.40 and 2.47 Å, respectively (see *Fig. 3*). It could then be presumed that the reduced flexibility of the chelate ring prevents the P—Pt—P angle from opening up to its 'ideal value' which could be similar to that found in **7a**, *i.e.* 111.6° (actually, a calculation of H···H contacts in **7a** shows that there is only one of them which is short, *i.e.* H(α)···H(α'), which is 2.30 Å (see *Fig. 3b*) but that the position of the other phosphine does not suffer from such constraints). Support for this hypothesis is provided by the values of the P—Pt—P bond angles in the complexes $[Pt(alkene)(PPh_3)_2]$ (alkene = $Cl_2C{=}C(CN)_2$ [20], $Cl_2C{=}CCl_2$ [22], and $(NC)_2C{=}C(CN)_2$ [23]) which fall in the range 100–102°. The larger substituents on the olefin bring about a closing up of the P—Pt—P angle to reduce intramolecular nonbonded repulsions similar to those discussed for the ethene complex. This effect may also account for the observation that a *Newman*-like projection of **6a** viewed along the P(1)—P(2) direction, shows an eclipsed conformation of Ph substituents, while the corresponding view in **7a** shows a staggered conformation of the Ph substituents.

In conclusion, it is likely that chiral ligands of type **2** can be used for a systematic study of organometallic reactions, *e.g.* alkene insertion, as observed for the Pt^{II} complexes of the unsubstituted ligand **1**. Work on this topic is in progress and will be reported at a later date.

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Experimental Part

General. All operations were performed under an O_2-free Ar or N_2 atmosphere. Unless otherwise stated, solvents were dried and deoxygenated prior to use. Elemental analyses were performed by the Microanalytical Laboratory of the Swiss Federal Institute of Technology (ETH). IR spectra: *Beckman-4250* spectrometer; CsI discs. ^{31}P-NMR spectra: at 36.43 MHz on a *Bruker-HX-90* or at 101.21 MHz on a *Bruker-WM-250* spectrometer. ^{1}H-, ^{13}C-, and ^{195}Pt-NMR spectra: *Bruker-WM-250* instrument operating at 250, 62.9, and 53.6 MHz, resp. A positive sign on the chemical shift denotes a resonance to low field of the reference (external H_3PO_4, TMS, and external $Na_2[PtCl_6]$, resp.). Further details have been given elsewhere [27].

1,2-Bis[(diphenylphosphino)methyl]benzene (**1**). NH_3 (600 ml) was condensed in a 2-l flask, and Na (12.36 g, 0.537 mol) was added. PPh_3 (68.09 g, 0.259 mol) was added to the stirred deep blue soln. within 1 h. NH_4Cl (14.4 g, 0.269 mol) was slowly added to the resulting mixture (red soln. and white precipitate). Stirring was continued for an additional 30 min, then 1,2-bis(dichloromethyl)benzene (23.564 g, 0.135 mol) was added within 10 min and stirring continued for an additional 2 h. The NH_3 was then allowed to evaporate slowly, and the residual orange-yellow solid was extracted with CH_2Cl_2 (450 ml). The soln. was filtered under Ar and evaporated. The crude pale yellow product was recrystallized from hot EtOH (600 ml) under Ar. The white needles were dried under high vacuum: 29.4 g (46%). M.p. 127–129° (under Ar). The pure dry solid is fairly stable towards air oxidation although it is easily oxidized in soln.

{1,2-Bis[(diphenylphosphino)methyl]benzene}dichloronickel(II) ($[NiCl_2(\mathbf{1})]$; **3a**). Ligand **1** (200 mg, 0.42 mmol) was added to a soln. of $NiCl_2 \cdot 6H_2O$ (150 mg, 0.63 mmol) in EtOH (2 ml). The mixture was stirred for 1 h at r.t. and the precipitate filtered off. The crude product was recrystallized from CH_2Cl_2/EtOH. Yield 82%. M.p. 220° (dec.). Anal. calc. for $C_{32}H_{28}Cl_2NiP_2$: C63.62, H 4.67; found: C 63.66, H 5.03.

{1,2-Bis[(diphenylphosphino)methyl]benzene}dibromonickel(II) ($[NiBr_2(\mathbf{1})]$; **3b**) was prepared as described for **3a** from $NiBr_2 \cdot 3H_2O$ (150 mg, 0.55 mmol) and **1a** (200 mg, 0.42 mmol). The crude product was recrystallized

from $EtOH/Et_2O$. Yield 66%. M.p. 205° (dec.) Anal. calc. for $C_{32}H_{28}Br_2NiP_2$: C 55.46, H 4.07; found: C 54.95, H 4.10.

{1,2-Bis[(diphenylphosphino)methyl]benzene}diiodonickel(II) ([NiI_2(**1**)]; **3c**). Ligand **1** (200 mg, 0.42 mmol) was added to a soln. containing [Bu_4N]I (200 mg, 0.54 mmol) and $Ni(NO_3)_2 \cdot 6\ H_2O$ (150 mg, 0.52 mmol) in EtOH (2 ml), and the mixture was stirred for 30 min. The brown precipitate was filtered off and washed with EtOH and Et_2O and dried under high vacuum. Complex **3c** is very unstable in soln. Yield 55%. M.p. 200° (dec.). Anal. calc. for $C_{32}H_{28}I_2NiP_2$: C 48.84, H 3.95; found: C 48.29, H 3.64.

{1,2-Bis[(diphenylphosphino)methyl]benzene}di(thiocyanato)nickel(II) ([$Ni(NCS)_2$(**1**)]; **3d**) was prepared as described for **3c** from $Ni(NO_3)_2 \cdot 6H_2O$ (300 mg, 1.03 mmol) and KNCS (100 mg, 1.03 mmol) in EtOH (30 ml). The crude product was recrystallized from CH_2Cl_2/EtOH. Yield 86%. M.p. 245° (dec.). Anal. calc. for $C_{34}H_{28}N_2NiP_2S_2$: C 62.89, H 4.35, N 4.31; found: C 62.74, H 4.68, N 4.54.

{1,2-Bis[(diphenylphosphino)methyl]benzene}dichloropalladium(II) ([$PdCl_2$(**1**)]; **4a**). A soln. of **1** (1.55 g, 3.27 mmol) in CH_2Cl_2 (50 ml) was added to a stirred soln. of [$PdCl_2(MeCN)_2$] [28] (80 mg, 3.08 mmol) in CH_2Cl_2 (50 mol). After 3 h, the soln. was evaporated to *ca.* 50 ml, and EtOH (*ca.* 50 ml) was added, resulting in the formation of a pale yellow precipitate which was filtered off and dried: 1.57 g (78%). M.p. 265° (dec.). Anal. calc. for $C_{32}H_{28}Cl_2P_2Pd$: C 51.90, H 3.81, Cl 9.85; found: C 51.40, H 3.87, Cl 10.10.

{1,2-Bis[(diphenylphosphino)methyl]benzene}dibromopalladium(II) ([$PdBr_2$(**1**)]; **4b**). Bu_4NBr (250 mg, 0.78 mmol) was added to a soln. of **4a** (212 mg, 0.33 mmol) in CH_2Cl_2 (25 ml). The soln. was stirred for 4 h and then EtOH added dropwise until it became cloudy and then left at r.t. This gave 234 mg of crude **4b** which was recrystallized from CH_2Cl_2/acetone: 215 mg (89%). M.p. 315° (dec.). Anal. calc. for $C_{32}H_{28}Br_2P_2Pd$: C 51.89, H 3.81, Br 21.58; found: C 51.61, H 3.92, Br 21.07.

{1,2-Bis[(diphenylphosphino)methyl]benzene}diiodopalladium(II) ([PdI_2(**1**)]; **4c**) was prepared in 95% yield analogously to **4b**, from **4a** and Bu_4NI. M.p. 320° (dec.). Anal. calc. for $C_{32}H_{28}I_2P_2Pd$: C 46.05, H 3.38, I 30.41; found: C 44.95, H 3.30, I 29.11

{1,2-Bis[(diphenylphosphino)methyl]benzene}dichloroplatinum(II) ([$PtCl_2$(**1**)]; **5a**). *Method 1:* Ligand **1** (1.10 g, 2.32 mmol) was added to a mixture of *cis*- and *trans*-[$PtCl_2(PPh_3)_2$] [29] (1.06 g, 2.15 mmol) in CH_2Cl_2 (150 ml) and the soln. stirred for 18 h at r.t. Acetone was added dropwise to the resulting suspension to complete the precipitation of **5a**. The crude product thus obtained was recrystallized from CH_2Cl_2/EtOH: 1.31 g (82%). M.p. *ca.* 300° (dec.). Anal. calc. for $C_{32}H_{28}Cl_2P_2Pt$: C 51.90, H 3.81, Cl 9.58; found: C 51.40, H 3.87, Cl 10.10.

Method 2: A suspension of *cis*-[$PtCl_2(MeCN)_2$] [28] (1.23 g, 4.01 mmol) in MeCN (90 ml) was refluxed until a clear yellow soln. was obtained. Ligand **1** (1.91 g, 4.03 mmol) was then added and the suspension refluxed for another 20 min. It was then cooled and the solvent volume reduced to *ca.* 10 ml. The white powder was filtered off and dried: 2.75 g (92%). This product was sufficiently pure to be used for the preparation of the other complexes.

{1,2-Bis[(diphenylphosphino)methyl]benzene}dibromoplatinum(II) ([$PtBr_2$(**1**)]; **5b**) was prepared in 89% yield, analogously to **4b**. M.p. *ca.* 310° (dec.). Anal. calc. for $C_{32}H_{28}Br_2P_2Pt$: C 46.34, H 3.40, Br 19.27; found: C 46.05, H 3.38, Br 18.80.

{1,2-Bis[(diphenylphosphino)methyl]benzene}diiodoplatinum(II) ([PtI_2(**1**)]; **5c**) was prepared in 94% yield, analogously to **4c**. M.p. *ca.* 315° (dec.). Anal. calc. for $C_{32}H_{28}I_2P_2Pt$: C 41.62, H 3.05; found: C 41.40, H 3.08.

{1,2-Bis[(diphenylphosphino)methyl]benzene}(ethene)platinum(0) ([$Pt(C_2H_4)$(**1**)]; **6a**). Ethene was bubbled through a stirred suspension of **5b** (966 mg, 1.17 mmol) in CH_2Cl_2 (30 ml) and EtOH (30 ml) for *ca.* 30 min. Na[BH_4] (232 mg, 6.75 mmol) was then added within *ca.* 15 min. Stirring was continued for *ca.* 30 min, and then additional Na[BH_4] (150 mg) was added. EtOH (120 ml) was added to the resulting pale yellow suspension. The resulting floculent precipitate was allowed to coagulate for *ca.* 10 min, and then it was filtered off under an ethene atmosphere. The resulting yellowish solid was washed successively with H_2O, EtOH, and pentane and recrystallized, in an ethene atmosphere, from CH_2Cl_2/pentane: 740 mg (91%). M.p. 165° (dec.). Anal. calc. for $C_{34}H_{32}P_2Pt$: C 58.58, H 4.62; found: C 58.29, H 4.67.

(Acrylonitrile){1,2-Bis[(diphenylphosphino)methyl]benzene}platinum(0) ([$Pt(CH_2{=}CHCN)$(**1**)]; **6b**). *From Reagent-Grade MeCN* (it was discovered later that this solvent contained $CH_2{=}CHCN$; ^{1}H-NMR integration of its signal against an internal 1,4-dimethoxybenzene standard gave a $CH_2{=}CHCN$ concentration of *ca.* $5 \cdot 10^{-3}$ M). Complex **5b** (300 mg, 0.36 mmol) was suspended in reagent-grade MeCN (120 ml; containing *ca.* 0.6 mmol of $CH_2{=}CHCN$), H_2 was bubbled through the suspension, and Na[BH_4] (700 mg, 18.5 mmol) was added. H_2O (400 ml) was then added dropwise and the precipate formed was filtered off and dried. Yield 81%. This product can be recrystallized either from CH_2Cl_2/MeCN or CH_2Cl_2/MeOH. M.p. *ca.* 240° (dec.). Anal. calc. for $C_{35}H_{31}NP_2Pt$: C 58.17, H 4.32, N 1.94; found: C 57.93, H 4.28, N 2.01.

By Alkene Exchange from **6a**. $CH_2=CHCN$ (150 µl) was added to the ethene complex **6a** (304 mg, 0.43 mmol) in CH_2Cl_2 (10 ml), and the soln. was stirred for 2 h at 35°. The volume was then reduced to *ca.* 5 ml and Et_2O added until precipitation occurred. The product was filtered off, washed with small amounts of Et_2O, and dried under high vacuum. Yield 87%.

(Ethene)di(phosphine)platinum(0) ($[Pt(C_2H_4)(PPh_3)_2]$; **7a**). The complex *cis*-$[PtCl_2(PPh_3)_2]$ [29] (3.26 g, 4.12 mmol) was suspended in CH_2Cl_2 (35 ml) and EtOH (35 ml). Ethene was bubbled through the soln. for *ca.* 10 min. Then, the soln. was cooled to 0°, $Na[BH_4]$ (0.77 g, 20 mmol) added over *ca.* 10 min, and the bubbling of ethene continued for another 40 min. EtOH (150 ml) was then added while ethene was bubbled through the soln. The solid thus formed was filtered off in a stream of ethene, washed successively with H_2O, EtOH, Et_2O, and hexane and then dried under high vacuum. Yield 94%. M.p. 125° (dec.) [30].

(Acrylonitrile)di(phosphine)platinum(0) ($[Pt(CH_2=CHCN)(PPh_3)_2]$; **7b**) was prepared and purified as described for **6b**. Yield 87%. Anal. calc. for $C_{39}H_{33}NP_2Pt$: C 60.62, H 4.30, N 1.81; found: C 59.64, H 4.39, N 1.60. **7b** could also be prepared directly by adding $CH_2=CNCN$ to a CH_2Cl_2 soln. of **7a** [19].

{1,2-Bis[(diphenylphosphino)methyl]benzene}(ethyl)(methanesulfonato)platinum(II) Dichloromethane (1/1) ($[Pt(OSO_2Me)Et(\mathbf{1})]\cdot CH_2Cl_2$; **8**). Methanesulfonic acid (26.5 µl, 4 mmol) was added to a stirred soln. of **6a** (300 mg, 0.43 mmol) in CH_2Cl_2 (10 ml). The pale yellow soln. slowly darkened. Stirring was continued for 1 h, the soln. filtered, and the solvent evaporated to *ca.* 3 ml. Upon addition of Et_2O, the product precipitated. It was filtered off and dried. Yield 78%. Anal. calc. for $C_{36}H_{38}Cl_2O_3P_2PtS$: C 49.21, H 4.36; found: C 50.02, H 4.43.

Bis{1,2-bis[(diphenylphosphino)methyl]benzene}di-µ-hydrido-hydridodiplatinum(II) Tetraphenylborate ($[(\mathbf{1})Pt(\mu-H)_2PtH(\mathbf{1})][BPh_4]$; **9**). To a soln. of **5b** (249 mg, 0.30 mmol) in CH_2Cl_2 (40 ml), a threefold excess of $Me_4N[BH_4]$ was added while H_2 bubbled through the soln. H_2O (30 ml) was added dropwise, and after 3 h, a clear two-phase soln. had formed. After separation, the org. phase was concentrated to *ca.* 5 ml under reduced pressure, and then $Na[BPh_4]$ (20% excess) in MeOH was added. The precipitate was filtered off and dissolved in hot acetone and the soln. stored at −22°. The crystalline precipitate formed after 2 days was filtered off and dried. Yield 81%. M.p. *ca.* 200° (dec.). Anal. calc. for $C_{88}H_{79}BP_4Pt$: C 63.62, H 4.79; found: C 64.25, H 4.75.

Collection and Reduction of X-Ray Intensity Data. Colourless single crystals of **6a** were grown from CH_2Cl_2/EtOH solns. A summary of crystal data together with various details concerning intensity measurements is given in *Table 4*. Intensities of four standard reflections remained constant throughout the data collection. The data were corrected for absorption [31] and *Lorentz* and polarization effects. Atomic scattering factors and anomalous dispersion terms were taken from [32].

Table 4. *Crystal Data for {1,2-Bis[(diphenylphosphino)methyl]benzene}(ethene)platinum(0)* (**6a**)

Formula	$C_{34}H_{32}P_2Pt$	Crystal dimension [mm]	0.33 × 0.18 × 0.10
F_w	697.67	Radiation	Mo$K\alpha$ (graphite monochrom.)
a [Å]	15.407(3)	Diffractometer	*Nicolet R3*
b [Å]	21.251(3)	Scan mode	2Θ–Θ
c [Å]	8.909(2)	Scan range [°]	0.95
α [°]	90	Background counts	1/4 of scan time at ±0.5° from the center of scan range
β [°]	90		
γ [°]	90	2Θ limits [°]	3–60
V (Å^3)	2916.9(9)	Reflect. collected no.	4963
Z	4	No. unique data	3238
Space group	$P2_12_12_1$	Final no. of variables	334
		Final R, R_w	0.036, 0.059

Solution and Refinement of the Structure. The structure was solved by the usual combination of *Patterson* and *Fourier* techniques. A full-matrix least-squares refinement of atomic positions and anisotropic displacement parameters of the non-H-atoms was applied subsequently. The H-atoms were included at fixed positions, d(C–H) = 0.96 Å and C–C–H angle = 120°. The quantity minimized was $\Sigma w(|F_o|-|F_c|)$ with $w = (a + F_o + bF_o^2)$ where a and b are of the order of $2F_o(\min)$ and $2/F_o(\max)$ [33]. The calculations were performed using the CAOS program [34] on *Eclipse MV/8000 II Data General* computer. Final positional and displacement parameters and tables of observed and calculated structure factors are deposited as supplementary material and are available upon request.

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