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meso-(1,1,4,7,10,10-Hexaphenyl-1,4,7,10-tetraphosphadecane-P,P',P'',P''') platinum(II) Bis(tetraphenylborate)

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Abstract. meso-[Pt($C_{42}H_{42}P_4$)][B($C_{24}H_{20}$)]$_2$.3CH$_2$Cl$_2$, $M_r = 1759.05$, monoclinic, $P2_1/c$, $a = 15.761$ (1), $b = 28.731$ (3), $c = 20.832$ (2) Å, $\beta = 114.967$ (6)°, $V = 8551.80$ Å^3, $Z = 4$, $D_m = 1.38$, $D_x = 1.366$ Mg m^{-3}, λ(Cu $K\alpha$) = 1.5418 Å, $\mu = 5.921$ mm^{-1}, $F(000) = 3584$, $T = 283$ K, final $R = 0.080$ for 7308 observed reflections. The X-ray structure analysis shows a slightly distorted square-planar coordination of the Pt atom by the P atoms. All four P atoms are located within a plane (maximum deviation 0.016 Å). The Pt atom is 0.161 Å out of this plane. The Pt—PPh bonds [2.274 (4) Å] are significantly shorter than the Pt—PPh$_2$ bonds [2.327 (4) Å]. The PhP—Pt—PPh$_2$ angles and the PhP—Pt—PPh angle are constrained to about 85° (mean value 84.3, Δ_{max} 0.7°). The Ph$_2$P—Pt—PPh$_2$ angle is wide open [105.8 (2)°]. The thermodynamic destabilization of the square-planar arrangement of the title compound is compared with the destabilization of the corresponding chiral form and differences are discussed. Short intramolecular contact distances lead, in both cases, to the occurrence of related five-coordinate trigonal-bipyramidal and distorted tetrahedral compounds, thus releasing the strain of a planar P$_4$ configuration.

Introduction. The X-ray structure analysis of chiral [Pt(P_4)](BPh$_4$)$_2$ (2), where P_4 is 1,1,4,7,10,10-hexaphenyl-1,4,7,10-tetraphosphadecane, has been performed only recently (Brüggeller & Hübner, 1990). It has been shown that the square-planar arrangement of P_4 is destabilized in (2). This destabilization is a necessary requirement for the addition of a fifth ligand and the formation of non-planar structures in

several Pt^{II} complexes (De Felice, Ganis, Vitagliano & Valle, 1988). Similar phenomena have been observed for (2) and meso-[Pt(P_4)](BPh$_4$)$_2$ (1) (Brüggeller, 1990). The distortions of square-planar P_4 configurations as well as the possibility of the addition of a fifth ligand which may result in a deviation from a planar P_4 arrangement are of interest in homogeneous catalysis. Preparative results indicate that with respect to a square planar to tetrahedral movement of P_4 upon addition of a fifth ligand, (2) is more destabilized than (1). This is in agreement with molecular modelling studies of chiral and meso P_4, which indicate that there is no smooth transition from planar to non-planar structures in the case of chiral P_4 (Brown & Canning, 1984). In order to establish the kind of destabilization in (1) and to make a comparison with (2) possible, an X-ray structure analysis of (1) was performed.

(1)
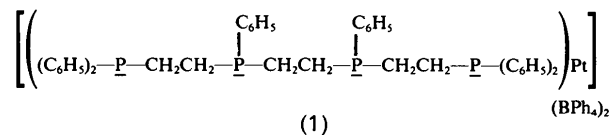
Experimental. Single crystals of (1) have been obtained by the slow production of (1) in a CH$_2$Cl$_2$/EtOH mixture ($v/v = 3/1$) *via* the following stoichiometric reaction:

2 meso-[Pt(CN)(P_4)](BPh$_4$) → meso-[Pt(P_4)](BPh$_4$)$_2$

+ meso-[Pt(P_4)](CN)$_2$.
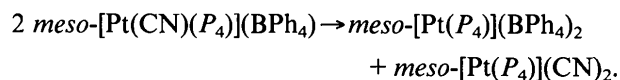
Attempts to prepare suitable crystals from solutions of (1), and from meso-[PtCl(P_4)](BPh$_4$) (Brüggeller, 1989) in the presence of Na(BPh$_4$) by loss of the

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chloride failed. A colourless prism of dimensions 0.15 × 0.15 × 0.15 mm was mounted in a sealed X-ray capillary tube with some mother liquor to diminish crystal deterioration by loss of crystal solvent during data collection. The crystal was examined on an Enraf–Nonius CAD-4 diffractometer using Cu $K\alpha$ radiation from a rotating-anode X-ray generator (Rigaku RU 200). Cell constants were determined on the basis of 25 reflections ($10.5 \le \theta \le 17°$). Data of one quadrant were collected up to $(\sin\theta/\lambda)_{max} = 0.5357$ Å^{-1} ($0 \le h \le 15$, $0 \le k \le 30$, $-22 \le l \le 22$). Periodically monitored intensity check reflections were used to correct for linear and anisotropic crystal decay which amounted to 30% at the end of data collection. Based on a series of ψ scans on a set of eight reflections with $\chi > 80°$ an empirical absorption correction was applied (maximum/minimum transmission factors 0.74/0.94). 10 101 reflections were measured, 9449 were unique and 7308 were considered observed with $I > 2\sigma(I)$. The structure was solved by Patterson and Fourier methods. Structure solution and refinement (least squares on F) were carried out by employing the Enraf–Nonius *Structure Determination Package* (Frenz, 1978). H atoms were omitted from the model, all other atoms except for the three dichloromethane solvent molecules were refined anisotropically. The relative occupancy factors of the CH$_2$Cl$_2$ entities were set to an optimal value in accordance with their apparent peak heights in the difference Fourier syntheses. The occupancies are in the range 0.4–0.8 which is possibly as a result of loss of CH$_2$Cl$_2$ during measurement. For 909 parameters refined, $R = 0.080$, $wR = 0.081$ $\{w = k/[\sigma^2(|F_o|) + 0.0005|F_o|^2]\}$, $S = 1.197$, $(\Delta/\sigma)_{max} = 0.14$, $(\Delta\rho)_{max} = 1.52$, $(\Delta\rho)_{min} = -1.48$ e Å^{-3}. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Discussion. Fractional atomic coordinates and equivalent isotropic thermal parameters are summarized in Table 1, selected bond distances and angles are given in Table 2.* The structure of the cation of (1) is shown in Fig. 1.

The crystal structure consists of discrete [Pt(P_4)]$^{2+}$ cations and (BPh$_4$)$^-$ anions. The *meso*-[Pt(P_4)]$^{2+}$ cation shows an only slightly distorted square-planar coordination geometry. The maximum deviation from the least-squares plane through the four P atoms is 0.016 Å. The Pt atom is displaced 0.161 Å

* Lists of structure factors, positional parameters, anisotropic thermal parameters, bond distances, angles and torsion angles and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54799 (90 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional parameters and equivalent isotropic thermal parameters* (Å^2) *with e.s.d.'s in parentheses*

$$B_{eq} = (4/3)[a^2 B(1,1) + b^2 B(2,2) + c^2 B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)].$$

	x	y	z	B_{eq}
Pt	−0.00223 (5)	0.36324 (3)	0.23433 (4)	3.22 (1)
P1	−0.0929 (3)	0.4289 (2)	0.2244 (2)	3.6 (1)
P2	0.0420 (3)	0.3359 (2)	0.3492 (2)	3.5 (1)
P3	0.1016 (3)	0.3105 (2)	0.2298 (2)	3.2 (1)
P4	−0.0112 (3)	0.3852 (2)	0.1262 (2)	3.3 (1)
C1	0.124 (1)	0.2855 (7)	0.3628 (9)	4.5 (5)
C2	0.183 (1)	0.2959 (7)	0.3200 (9)	4.3 (5)
C3	0.163 (1)	0.3415 (7)	0.1846 (9)	4.0 (4)
C4	0.093 (1)	0.3636 (8)	0.1156 (9)	4.7 (5)
C5	−0.010 (1)	0.4491 (6)	0.1304 (9)	4.1 (5)
C6	−0.093 (1)	0.4632 (7)	0.1470 (8)	4.3 (4)
C11	−0.214 (1)	0.4192 (7)	0.2041 (9)	4.6 (5)
C12	−0.276 (1)	0.4566 (9)	0.177 (1)	6.9 (7)
C13	−0.369 (2)	0.451 (1)	0.163 (2)	10 (1)
C14	−0.397 (2)	0.407 (1)	0.181 (1)	11 (1)
C15	−0.339 (2)	0.369 (1)	0.206 (1)	8.7 (8)
C16	−0.239 (1)	0.3760 (8)	0.220 (1)	5.9 (6)
C21	−0.055 (1)	0.4717 (6)	0.2974 (9)	4.0 (4)
C22	−0.092 (1)	0.4674 (7)	0.3489 (9)	4.7 (5)
C23	−0.066 (1)	0.5004 (8)	0.402 (1)	5.8 (6)
C24	−0.003 (1)	0.5360 (8)	0.406 (1)	6.3 (6)
C25	0.032 (2)	0.5386 (8)	0.355 (1)	6.0 (6)
C26	0.009 (1)	0.5059 (7)	0.303 (1)	5.4 (6)
C31	−0.054 (1)	0.3113 (6)	0.3640 (9)	4.0 (5)
C32	−0.091 (1)	0.2704 (8)	0.331 (1)	5.4 (6)
C33	−0.167 (1)	0.2497 (9)	0.339 (1)	7.3 (8)
C34	−0.204 (2)	0.273 (1)	0.381 (1)	7.7 (8)
C35	−0.172 (1)	0.3170 (9)	0.410 (1)	7.0 (7)
C36	−0.094 (1)	0.3370 (8)	0.402 (1)	5.2 (5)
C41	0.107 (1)	0.3761 (6)	0.4191 (9)	4.1 (5)
C42	0.125 (1)	0.3644 (9)	0.4895 (9)	5.7 (5)
C43	0.184 (2)	0.3953 (8)	0.544 (1)	6.3 (6)
C44	0.221 (2)	0.4354 (8)	0.528 (1)	6.7 (7)
C45	0.202 (1)	0.4456 (8)	0.458 (1)	6.3 (7)
C46	0.143 (1)	0.4162 (7)	0.401 (1)	5.0 (5)
C51	0.053 (1)	0.2567 (6)	0.1827 (8)	3.6 (4)
C52	−0.043 (1)	0.2554 (7)	0.138 (1)	4.8 (5)
C53	−0.079 (2)	0.2160 (8)	0.097 (1)	6.6 (7)
C54	−0.024 (2)	0.1771 (8)	0.105 (1)	6.7 (7)
C55	0.069 (1)	0.1784 (8)	0.151 (1)	6.1 (6)
C56	0.109 (1)	0.2188 (7)	0.1907 (9)	5.1 (5)
C61	−0.111 (1)	0.3698 (7)	0.048 (1)	4.8 (5)
C62	−0.106 (1)	0.3733 (7)	−0.0184 (9)	4.8 (5)
C63	−0.185 (2)	0.3630 (8)	−0.081 (1)	6.4 (6)
C64	−0.268 (2)	0.3509 (9)	−0.078 (1)	7.2 (8)
C65	−0.271 (2)	0.3465 (9)	−0.011 (1)	7.5 (8)
C66	−0.192 (1)	0.3564 (8)	0.049 (1)	6.0 (6)
B1	0.872 (1)	0.6121 (8)	0.098 (1)	4.2 (5)
B2	0.470 (1)	0.3487 (9)	0.368 (1)	5.2 (7)

from this plane towards the axial site containing four phenyl groups (see Fig. 1). In [FeH(N$_2$)(P_4)]Br (3) (Ghilardi, Midollini, Sacconi & Stoppioni, 1981) and [RuCl$_2$(P_4)] (4) (Rivera, De Gil & Fontal, 1985) all P atoms of *meso*-P_4 are located within the equatorial planes of the octahedral configurations and the central atoms are shifted out of these planes in the same directions as in (1) [Fe atom in (3): 0.343, Ru atom in (4): 0.125 Å]. In (3) the enhanced displacement of the Fe atom from the equatorial plane is a result of the steric differences of the axial N$_2$ and H ligands. The presence of central atom shifts from the planar *meso*-P_4 arrangements in (4), where the axial ligands are identical, and in (1), show that the angular requirements of *meso*-P_4, consisting of a chain of P and C atoms with tetrahedral configuration, also produce shifts. The displacement of the central atoms from planar P_4 arrangements is larger in (1)

Table 2. *Selected bond distances* (Å) *and angles* (°)
with e.s.d.'s in parentheses

Pt—P1	2.324 (5)	P3—C2	1.82 (2)
Pt—P2	2.329 (5)	P3—C3	1.84 (2)
Pt—P3	2.262 (5)	P3—C51	1.82 (2)
Pt—P4	2.285 (5)	P4—C4	1.85 (2)
P1—C6	1.88 (2)	P4—C5	1.84 (2)
P1—C11	1.80 (2)	P4—C61	1.77 (2)
P1—C21	1.85 (2)	C1—C2	1.56 (3)
P2—C1	1.88 (2)	C3—C4	1.54 (2)
P2—C31	1.81 (2)	C5—C6	1.55 (3)
P2—C41	1.80 (2)		
P1—Pt—P2	105.8 (2)	C1—P2—C41	104.6 (8)
P1—Pt—P3	165.8 (1)	C31—P2—C41	110.0 (9)
P1—Pt—P4	84.7 (1)	P2—C41—C42	119.0 (2)
P2—Pt—P3	84.7 (2)	P2—C41—C46	118.0 (1)
P2—Pt—P4	166.7 (1)	P3—C3—C4	110.0 (1)
P3—Pt—P4	83.6 (2)	P3—C2—C1	107.0 (1)
Pt—P1—C6	106.4 (7)	Pt—P3—C2	108.7 (8)
Pt—P1—C11	116.6 (7)	Pt—P3—C3	104.2 (7)
Pt—P1—C21	119.6 (6)	Pt—P3—C51	116.4 (6)
P1—C6—C5	111.0 (1)	C2—P3—C3	110.0 (8)
C6—P1—C11	105.1 (8)	C2—P3—C51	108.3 (9)
C6—P1—C21	103.9 (8)	C3—P3—C51	109.2 (9)
P1—C11—C12	118.0 (2)	P3—C51—C52	118.0 (1)
P1—C11—C16	118.0 (1)	P3—C51—C56	120.0 (1)
P1—C21—C22	118.0 (1)	P4—C4—C3	111.0 (1)
P1—C21—C26	121.0 (2)	C4—P4—C5	110.0 (1)
C11—P1—C21	104.0 (1)	P4—C5—C6	106.0 (1)
Pt—P2—C1	107.6 (7)	C4—P4—C61	106.9 (9)
Pt—P2—C31	113.4 (6)	C5—P4—C61	106.3 (8)
Pt—P2—C41	115.8 (6)	Pt—P4—C5	103.6 (7)
P2—C1—C2	108.0 (1)	Pt—P4—C4	109.6 (6)
C1—P2—C31	104.3 (9)	Pt—P4—C61	119.8 (8)

than in (4) (0.161 *vs* 0.125 Å), though an enhanced shift might be expected for (4) where one axial Cl ligand is surrounded by four phenyl groups. This indicates that the replacement of a 4*d* [in (4)] by a 5*d* metal [in (1)] leads to a larger shift. In contrast to (1), (2) shows strong deviations from a planar P_4 coordination (Brüggeller & Hübner 1990). Every two of the P atoms, *trans* to each other, lie above (PPh 0.254, PPh₂ 0.199 Å) and below (PPh 0.273, PPh₂ 0.220 Å) the best plane through the Pt atom and the P atoms. The Pt atom is displaced 0.039 Å from this plane. Complexes of d^8 metals with large D_q values such as Pt^{II} have a large crystal-field stabilization energy in the square-planar environment and solid-state distortions are expected to be moderately high-energy processes (Rahn, O'Donnell, Palmer & Nelson, 1989). Typically, rearrangements towards the sterically more favourable tetrahedral geometry are involved to reduce ligand–ligand interactions if large groups are present (Rappoli, Churchill, Janik, Rees & Atwood, 1987; Atwood, 1985). This kind of distortion occurs in (2), whereas (1) only shows the above described deviation of the central atom from the otherwise planar P_4 coordination.

In (1) the Pt—PPh bonds [2.274 (4) Å] are significantly shorter than the Pt—PPh₂ bonds [2.327 (4) Å]. The latter value is identical with the corresponding value in (2). The Pt—PPh bonds are shorter in (2) than in (1) [2.258 (4) *vs* 2.274 (4) Å]. Similar pairwise deviations of the Pt—P bond distances have also been observed for (3) and (4) and have been attributed to the angular requirements of P_4 (Brüggeller

& Hübner, 1990). The PhP—Pt—PPh₂ angles and the PhP—Pt—PPh angle are constrained to about 85° [(1): P1—Pt—P4 84.7 (1). P2—Pt—P3 84.7 (2), P3—Pt—P4 83.6 (2)°], where the mean values of (1) and (2) are identical (84.3°). However, the Ph₂P—Pt—PPh₂ angle is significantly smaller in (1) [105.8 (2)°] than in (2) [109.5 (2)°]. Comparing the corresponding values for (2), (3), (4), and [FeBr(P_4)](BPh₄) (5) (Bacci & Ghilardi, 1974; Bacci, Ghilardi & Orlandini, 1984), it has been argued that replacing a 3*d* by a 4*d* central atom leads to a larger opening of the Ph₂P—M—PPh₂ angles, whereas the replacement by a 5*d* central atom results in no further opening of this angle (Brüggeller & Hübner, 1990). The considerably smaller value in (1) compared with (4), even significantly below the value for the 4*d* complex (4) [105.8 (2) *vs* 109.8 (2)°], reflects the presence of strain and steric interactions in the coordination of *meso*-P_4 in (1). These constraints do not allow ideal overlap of the Pt orbitals with all four P lone pairs and lead to the longer Pt—PPh bonds in (1) compared with (2) (see above). A similar effect has been observed for [PtClMe({6-Mepy-2-CH=N-(S)-CH-(Me)(Ph)}] (6) (Albano, Braga, De Felice, Panunzi & Vitagliano, 1987), [Pt(tri-phos)(PR_3)] species (Chatt, Mason & Meek, 1975), and [Pt(dppp)₂] (7), where dppp is bis(diphenylphos-phino)propane (Harvey, Schaefer & Gray, 1988). In
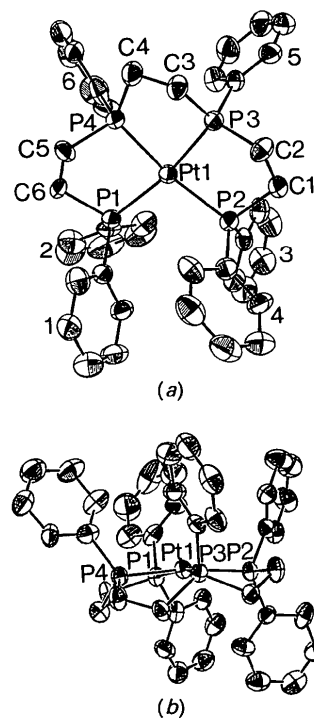

(*a*)

(*b*)

Fig. 1. Structure of the cation of (1). (*a*) The best plane through the P atoms in the projection plane. (*b*) Projection along the best plane through the P atoms.

(2) the tetrahedral distortion of the square-planar configuration leads to a D_q splitting which produces an additional electronic destabilization of (2) not present in the case of (1) where all P atoms occupy one plane.

Both (1) and (2) show short intermolecular contact distances below 3.0 Å [C$_{11}$⋯C$_{21}$, C$_{31}$⋯C$_{41}$ and C$_{x1}$⋯C$_{bridge}$ values, where $x = 1$–6, are 2.9–3.0 Å; shortest contact C$_{11}$⋯C$_{21}$ is 2.87 Å in (1)]. Since it has already been seen in (7) that C⋯C approaches beyond 3.0 Å lead to crowding, responsible for distortions (Harvey, Schaefer & Gray, 1988), the above steric constraints produce the observed deviations in (1) and (2) from a planar PtP_4 arrangement which is the otherwise electronically favoured stable form (Cucciolito, De Felice, Panunzi & Vitagliano, 1989). In (6) a close contact (Cl⋯C16 2.9 Å) leads to the destabilization of the square-planar arrangement. Since the balance between four- and five-coordination for Pt^{II} is subtle (Knobler, Kaesz, Minghetti, Bandini, Banditelli & Bonati, 1983; Bracher, Grove, Pregosin & Venanzi, 1979; Bachechi, Bracher, Grove, Kellenberger, Pregosin, Venanzi & Zambonelli, 1983) it has been found that in the case of [PtClR(N–N')(η^2-olefin)] species the destabilization of the square-planar precursors is a necessary requirement for the formation of these five-coordinate compounds (Cucciolito, De Felice, Panunzi & Vitagliano, 1989; De Felice, Ganis, Vitagliano & Valle, 1988; Albano, Braga, De Felice, Panunzi & Vitagliano, 1987). A similar dependence of the stability of five-coordinate compounds on a destabilization of corresponding four-coordinate complexes has been found for [L_3PtX_2] and [PtClHL_2(C$_2$H$_4$)] species (Holt & Nelson, 1986; Alibrandi, Cusumano, Minniti, Scolaro & Romeo, 1989). The presence of five-membered chelate rings as in (1) and (2) favours penta-coordination (Albano, Demartin, De Renzi, Morelli & Saporito, 1985). It has been pointed out that in the case of more flexible, sp^3-hybridized ligands like P_4, no single steric repulsion as *e.g.* in (6) is responsible for the destabilization of the square-planar arrangement, but more complicated conformational problems have to be faced (Cucciolito, De Felice, Panunzi & Vitagliano, 1989). The intramolecular C⋯C approaches are similar in (1) and (2).

The significantly smaller Ph$_2$P—Pt—PPh$_2$ angle in (1) compared with (2) could be responsible for the shortest C⋯C contact in (1). It has been shown that the lack of destabilization of the square-planar arrangement in [PtClMe(^{i}Pr—N=CHCH=N—^{i}Pr)] (8) leads to exclusively square-planar coordination, whereas replacement of the ^{i}Pr groups by ^{t}Bu groups in (8) completely destabilizes the square-planar complex and upon addition of C$_2$H$_4$ the corresponding five-coordinate species is exclusively formed (De

Felice, Ganis, Vitagliano & Valle, 1988). However, the only moderate destabilization of (6) gives rise to both a square-planar as well as a trigonal-bipyramidal species. The same is true for (1) and (2). Upon addition of a fifth ligand square-pyramidal, trigonal-bipyramidal and distorted tetrahedral complexes are formed (Brüggeller, 1990). Preparative results indicate that in contrast to chiral P_4 five-coordinate species containing *meso*-P_4 show a smooth transition from a square-pyramidal coordination to a distorted tetrahedral P_4 arrangement, which facilitates the onset of the 'Berry' mechanism (Berry, 1960). This is in agreement with molecular modelling studies and experimental results showing that non-planar configurations of chiral P_4 are more destabilized than corresponding *meso*-P_4 arrangements (Brown & Canning, 1984). Furthermore, the *meso* ligand more comfortably adopts a planar coordination (Bosnich, Jackson & Wild, 1973). The kind of destabilization of the square-planar PtP_4 arrangement is completely different in (1) and (2). In (1) one axial site containing four phenyl groups is more crowded than the other containing only two.

This results in cumulative intramolecular C⋯C approaches (see above) on the crowded site and in order to release the strain in the PtP_4 plane, P_4 bends to the sterically less demanding site in accordance with the angular requirements of *meso*-P_4. This leads to the above described displacement of the Pt atom from the P_4 plane (see Fig. 1). In (2) the intramolecular strain (see above) is released by a tetrahedral distortion. Both *meso*- and chiral P_4 also show trigonal-bipyramidal arrangements. In (5) containing *meso*-P_4 the ligand arrangement seems to prevent the coordination of a sixth ligand even as small as hydride (Ghilardi, Midollini, Sacconi & Stoppioni, 1981). This is confirmed by the fact that (5) already shows significant intramolecular strain manifested in the short Br—H contact distances of 2.80 and 2.72 Å (Bacci & Ghilardi, 1974). In chiral [PtH(P_4)](BPh$_4$) (9) (Brüggeller, 1992) the following intramolecular contact distances are observed: C$_{bridge}$⋯C$_{x1}$ ($x = 1$–6) 2.83–2.93, C$_{bridge}$⋯C$_{bridge}$ 2.92–2.96, C$_{x1}$⋯C$_{x1}$ ($x = 1$–6) 2.84–2.89 Å. These C⋯C approaches are comparable to those in (2) indicating that chiral P_4 exerts a similar destabilization effect in the thermodynamic sense in the square-planar and trigonal-bipyramidal case. (5) and (9), respectively, are only one form of the two possible trigonal bipyramids in each case; however, it is assumed that the sterically less-demanding configuration is produced in both cases. It has earlier been recognized that a repulsive interaction between the ligands of the five-coordinate complex in addition to those in the corresponding four-coordinate case complicates the balance of steric effects in the interconversion from the trigonal-bipyramidal geometry to

the square-planar one (Albano, Braga, De Felice, Panunzi & Vitagliano, 1987; Cucciolito, De Felice, Panunzi & Vitagliano, 1989). In the above case the comparable destabilization of complexes containing meso- and chiral P_4 in a square-planar as well as a trigonal-bipyramidal coordination environment leads to the simultaneous occurrence of both configuration types. Furthermore, since tetrahedral coordinations are favoured if steric restrictions are present (Atwood, 1985), distorted tetrahedral P_4 arrangements occur in $[PtX(P_4)]Y$ species ($X =$ various types of fifth ligands, $Y =$ non-coordinating anion) depending on the nature of X (Brüggeller, 1989; Brüggeller, 1990).

The discussed subtle balance of (1) and (2) and corresponding five-coordinate species leads to diastereotopic interactions (Bosnich & Fryzuk, 1981; De Renzi, Di Blasio, Saporito, Scalone & Vitagliano, 1980; Brüggeller, 1989) and differences in the coordination types of five-coordinate species between those containing meso-P_4 and chiral P_4, respectively (Brüggeller, 1990). The main effect is that only in the case of meso-P_4 is a smooth transition from a planar to a distorted tetrahedral coordination observed, which facilitates the occurrence of the 'Berry' mechanism. This might be because the tetrahedral distortion in (2) reflects an already balanced configuration between electronic forces to form a PtP_4 plane and the steric requirements of chiral P_4, whereas the displacement of the central atom from the P_4 plane in (1) could lead to a more flexible variation of the P_4 coordination.

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Structure of Guanidinium Hydrogen Acetylenedicarboxylate, $CH_6N_3^+.C_4HO_4^-$

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Abstract. Guanidinium hydrogen 2-butynedioate, $M_r = 173.13$, monoclinic, $P2_1/c$, $a = 8.837$ (1), $b = 18.961$ (2), $c = 9.067$ (2) Å, $\beta = 92.09$ (1)°, $V = 1518.2$ (4) Å³, $Z = 8$, $D_x = 1.515$ g cm⁻³, λ(Mo $K\alpha$) $= 0.71069$ Å, $\mu = 1.24$ cm⁻¹, $F(000) = 720$, $T = 293$ (2) K, final $R = 0.044$ and $wR = 0.044$ for 1622 observed reflections. The crystal structure consists of infinite chains of hydrogen acetylenedicarboxylate