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Metalation of a Trialkylphosphine. Structure of Bis(μ-chloro)bis[2-(di-*tert*-butylphosphino)-2-methylpropyl]dipalladium

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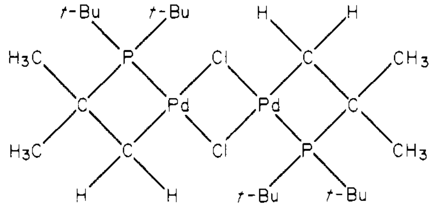
The structure of $[PdCl((t\text{-Bu})_2PCMe_2CH_2)]_2$ has been determined by single-crystal X-ray diffraction techniques. The compound crystallizes in the monoclinic space group $P2_1/c$ with $a = 7.709$ (2) Å, $b = 15.187$ (5) Å, $c = 13.383$ (4) Å, $\beta = 105.77$ (2)°, $V = 1507.9$ Å^3, and $Z = 2$. The structure was refined to $R = 0.037$ (0.043 for R_w) for the 1838 unique reflections with $I \geq 3.0\sigma(I)$. Metalation of a tri-*tert*-butylphosphine ligand has produced a saturated Pd–P–C–C four-atom chelate ring. The coordination about the palladium atom is square planar with the chloride ions cis to each other. Selected metrical details are Pd–P = 2.209 (2) Å, Pd–C(σ) = 2.052 (8) Å, Pd–Cl(trans to P) = 2.429 (2) Å, and Pd–Cl(trans to C) = 2.474 (2) Å. The bond lengths are discussed in terms of trans influences and strain in the chelate ring. Metalation results in severely distorted Pd–P–C and P–C–C angles. The steric bulk of the tertiary phosphine ligand is described with a "ligand profile".

Introduction

Intramolecular metalation of aryl-substituted tertiary phosphine ligands to form metal–carbon bonds has been studied extensively in recent years.[2] The reaction is facilitated by formation of five- and six-membered chelate rings and depends on the steric bulk of the phosphine ligand. In contrast, only a few examples of metalation of purely aliphatic phosphines have been reported.[3-6]

Recently, Goel and Clark[7-10] reported intramolecular metalations of tri-*tert*-butylphosphine complexes to form four-membered M–P–C–C (M = Pt(II), Pd(II)) chelate rings. The dimeric complex (**1**) was isolated from the reaction of $P(t\text{-Bu})_3$ with $PdCl_2(NCPh)_2$ in CH_2Cl_2,[8,9] from the reaction of $P(t\text{-Bu})_3$ with K_2PdCl_4 in *N,N*-dimethylformamide[8] and from internal metalation of $PdHCl(P\text{-}t\text{-Bu})_3)_2$.[10] The crystal structure was initiated to characterize the three-dimensional stereochemistry of the dimer.



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Experimental Section

Pale yellow crystals of the title compound were kindly supplied by Professor H. C. Clark. The data crystal was mounted on a glass fiber and was transferred to an Enraf-Nonius CAD-4 autodiffractometer equipped with a Si(Li) energy-dispersive detector and a graphite incident-beam monochromator.

Table I. Crystal Data and Details of Data Collection for $C_{24}H_{52}Cl_2P_2Pd_2$

fw: 686.3
$a = 7.709$ (2) Å
$b = 15.187$ (5) Å
$c = 13.383$ (4) Å
$\beta = 105.77$ (2)°
$V = 1507.9$ Å^3
$d_{calcd} = 1.51$ g cm^{-3}
$d_{obsd} = 1.47$ g cm^{-3}

monoclinic
systematic absences: $0k0$ for k odd and $h0l$ for l odd
space group: $P2_1/c$
$Z = 2$
$F(000) = 704$ e
$T = 16$ °C

cryst dimens: 0.16 × 0.17 × 0.21 mm
μ(Mo K$\bar{\alpha}$) = 14.71 cm^{-1}
λ(Mo K$\bar{\alpha}$) = 0.710 73 Å
transmission coeff: 0.61–0.67
2914 symmetry-independent reflctns for $3.0° \leqslant 2\theta \leqslant 50.0°$
1838 reflctns above bkgd ($I \geqslant 3.0\sigma(I)$)

Examination of the diffraction symmetry revealed systematic absences consistent with space group $P2_1/c$. The cell parameters listed in Table I were obtained from a least-squares refinement of 25 carefully centered reflections. Intensity data were collected by the θ–2θ scan method with a variable scan rate of 0.65–3.3° min^{-1} determined by a fast (3.3° min^{-1}) prescan. The intensities of two check reflections were monitored every 2 h during data collection and revealed an average deviation from their mean intensities of 2.5%. Stability of the crystal and the electronics of the instrument was thus assured.

The data were corrected for Lorentz and polarization effects, as well as absorption as a function of crystal shape.[11] Standard deviations of the structure factors were computed as

$$\sigma(|F_o|) = 0.5(\mathrm{VLP})^{1/2}[(\mathrm{Pk} + \mathrm{Bg} + p^2 I_{rel}^2)/I_{rel}]^{1/2}$$

where VLP is the standard Lorentz–polarization term, Pk is the peak intensity, Bg is the sum of the background counts taken on both sides of the peak, p is the ignorance factor (0.01 in this work), and I_{rel} is Pk − Bg. All data with $I_{rel} > 3.0\sigma(I_{rel})$ were used in the solution and refinement of the structure.

Structure Solution and Refinement. Interpretation of a three-dimensional Patterson map yielded the coordinates of the Pd, Cl, and P atoms. A subsequent difference electron density map revealed the positions of the twelve C atoms of the structure. Full-matrix least-squares refinement of the model employing anisotropic thermal parameters yielded $R_1 = \sum(\Delta F)/\sum|F_o| = 0.052$ and $R_2 = [\sum w(\Delta F)^2/\sum w|F_o|^2]^{1/2} = 0.069$, where $w = \sigma^{-2}(|F_o|)$ and $\Delta F = ||F_o| - |F_c||$.

Refinement was continued after including the 26 H atoms of the structure at their idealized positions (d(C–H) = 0.96 Å) with isotropic

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Table II. Positional Parameters for $C_{24}H_{52}P_2Cl_2Pd_2$

ATOM	X[A]	Y	Z
PD	6113(1)	4865(0)	4009(0)
P	6976(3)	4011(1)	2897(1)
CL	5285(3)	6100(1)	4938(2)
C(1)	8474(9)	4931(5)	2687(5)
C(2)	8663(11)	5126(5)	1594(6)
C(3)	10352(10)	4907(5)	3431(6)
C(4)	7370(11)	5604(5)	3129(6)
C(5)	8225(10)	2951(5)	3324(6)
C(6)	6955(13)	2192(5)	3329(7)
C(7)	9431(12)	2710(5)	2639(8)
C(8)	9357(13)	3066(6)	4438(7)
C(9)	5036(10)	3844(5)	1718(5)
C(10)	3596(11)	3268(6)	1998(7)
C(11)	5525(12)	3417(6)	796(6)
C(12)	4082(11)	4736(6)	1369(6)

[A] NUMBERS IN PARENTHESES IN THIS AND ALL SUBSEQUENT TABLES REFER TO THE ESTIMATED STANDARD DEVIATIONS IN THE UNITS OF THE LEAST SIGNIFICANT DIGITS. POSITIONAL(X10^4) AND THERMAL(X10^4) PARAMETERS ARE PRESENTED.

Table III. Selected Bond Distances (Å)[a]

Pd–Cl	2.429 (2)	P–C(1)	1.882 (7)
Pd–Cl^i	2.474 (2)	P–C(5)	1.884 (8)
Pd–P	2.209 (2)	P–C(9)	1.873 (8)
Pd–C(4)	2.052 (8)	C(1)–C(4)	1.548 (10)

[a] The superscript i refers to the atom at equivalent position $1 - x$, $1 - y$, $1 - z$ in this table and in Table IV.

Table IV. Selected Bond Angles (Deg)

Pd–Cl–Pd^i	92.9 (1)		
P–Pd–Cl	165.3 (1)	Pd–P–C(1)	88.5 (2)
P–Pd–Cl^i	107.1 (1)	Pd–P–C(5)	121.4 (3)
P–Pd–C(4)	70.0 (2)	Pd–P–C(9)	109.2 (3)
Cl–Pd–C(4)	95.9 (2)	P–C(1)–C(2)	120.4 (5)
Cl–Pd–Cl^i	87.1 (1)	P–C(1)–C(3)	113.5 (5)
Cl^i–Pd–C(4)	176.6 (2)	P–C(1)–C(4)	90.6 (4)

thermal parameters of 5.5 Å^2. Parameters of the H atoms were not refined. A correction for extinction, $8.6\ (1) \times 10^{-6}\ e^{-2}$, was also made. In the final least-squares cycle the largest shift/σ of any parameter was 0.6 and the standard deviation of an observation of unit weight was 1.5. The final values of R_1 and R_2 are 0.037 and 0.043, respectively. A final difference electron density map revealed a featureless background below 0.5 e Å^{-3}, except for peaks between −0.8 and 0.9 e Å^{-3} in the vicinity of the Pd, P, or Cl atoms. Atomic scattering factors for all atoms and the anomalous dispersion correction terms for the Pd, P, and Cl atoms were taken from ref 12. Final atomic parameters are given in Table II.

Discussion

The molecular structure of **1** is shown in Figure 1 and consists of dimeric molecules separated by normal van der Waals contacts. The dimeric molecule crystallizes across the inversion center at ($^1/_2$, $^1/_2$, $^1/_2$); thus only the crystallographically unique atoms in the figure are labeled. The coordination about the Pd atom is distorted square planar with a severe pinch in the angle P–Pd–C(4), 70.0 (2)°. The four-atom chelate ring is puckered as a result of the sp^3 hybridized carbon atoms, C(1) and C(4). The pucker can be described by the endocyclic torsion angles[13] about the bonds Pd–P, P–C(1), C(1)–C(4), and C(4)–Pd. The appropriate values are 15.4, −19.3, 21.6, and −19.5°, respectively. The *tert*-butyl groups are oriented anti to each other. Thus the torsion angles C(4)–C(1)–P–C(5), C(6)–C(5)–P–C(1), and C(12)–C(9)–P–C(5) have the values −143.1, −171.4, and −178.1°, respectively.

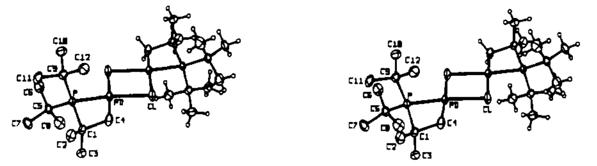

Figure 1. Stereoview of the dimeric molecule. Vibrational ellipsoids of 30% probability are presented, except for the H atoms, which are drawn artificially small.

The bond lengths to the Pd atom define a characteristic trend. For square-planar complexes such as this the bond length distribution about the central atom can be rationalized in terms of the trans influence[14] of the bonded atoms. From this simple model the bond length trans to the atom exerting the stronger trans influence is predicted to be longer than normal. The relative trans influences[14] appropriate to this work are $C(\sigma) > PR_3 > Cl^-$. Thus the Pd–Cl′ bond, 2.474 (2) Å, opposite the Pd–C(4) bond is longer than the Pd–Cl bond, 2.429 (2) Å, as expected. Indeed, the Pd–Cl bond lengths of bridging Cl$^-$ ions trans to Pd–C(σ) bonds in other structures (range 2.45–2.53 Å)[15-18] are very similar to the Pd–Cl′ bond length and also reflect the trans influence.

The Pd–P bond length (2.209 (2) Å) is significantly shorter than the value (2.260 (2) Å) reported in *cis*-$PdCl_2(PMe_2Ph)_2$,[19] which also has a Pd–P bond trans to the Pd–Cl bond. The weak trans influence of the Cl$^-$ ion is one contributor to the shortened bond length. Another contributor to a shortened Pd–P bond has been suggested by Bennett et al.[20] Ring strain within the five-membered chelate ring of this structure was suggested as the cause of a short Pd–P bond (2.258 (1) Å). It is thus not surprising the additional strain induced by the formation of a four-membered chelate ring in **1** would result in an even shorter Pd–P bond length.

Metalation of the tri-*tert*-butylphosphine ligand produces a dramatic alteration of its stereochemistry. Although the P–C and C–C bond lengths are normal, the bond angles involving the atoms P and C(1) are unusual. The observed M–P–C (M = Hg, Pt), C–P–C, and C–C–C angles in other structures[21,22] with tri-*tert*-butylphosphine ligands are approximately tetrahedral. In **1** the angle Pd–P–C(9) is normal but the Pd–P–C(1) angle (88.5 (2)°) is quite small and the Pd–P–C(5) angle (121.4 (3)°) is somewhat large. The combined effect of this distortion moves C(1) nearer to Pd while maintaining a reasonable contact with the *tert*-butyl substituents on C(5). A virtually identical distortion of the P–C–C angles of C(1) moves C(4) within bonding distance of the Pd atom (90.6 (4)°)

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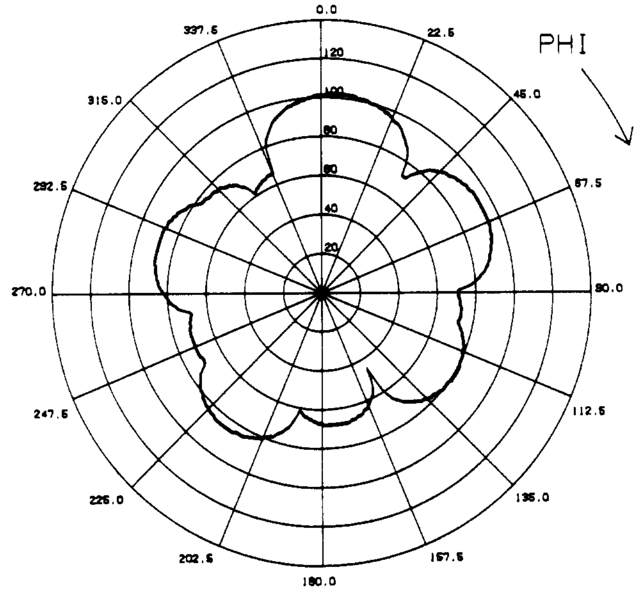

Figure 2. Ligand profile ($\theta/2$ vs. ϕ) about the Pd–P bond.

and maintains a reasonable contact between C(4) and C(2) (120.4 (5)°).

The steric bulk of tertiary phosphine ligands has been described by Tolman[23] in terms of cone angles. Various authors[24-26] have expanded this concept using crystallographic structural data to calculate half-cone angles ($\theta/2$) as a function of rotation (ϕ) about the metal to phosphorus bond, thereby generating a "ligand profile". The ligand profile defined by the tri-*tert*-butylphosphine of **1** is shown in Figure 2. The metalated carbon atom C(4) was omitted from the calculation so the resultant $\theta/2$ values would not be dominated by its contribution. This profile is surprisingly similar to that of the tri-*tert*-buytylphosphine ligand in $(CH_3CO_2)_2HgP(t\text{-}Bu)_3$.[21]

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Note Added in Proof. After this article was accepted for publication, we learned other researchers had solved the structure of this complex and that of the isomorphous Pt(II) analogue and had published a communication describing that crystallographic study.[27] The results of the two independent investigations are virtually identical in every detail.

Registry No. **1**, 69393-58-4.

Supplementary Material Available: Listings of anisotropic thermal parameters, H atom parameters, nonessential bond lengths and bond angles, and structure factor amplitudes (14 pages). Ordering information is given on any current masthead page.

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Heteropolyatomic Anions of the Post Transition Metals. Synthesis and Structure of the Ditindibismuthide(2–) Anion, $Sn_2Bi_2^{2-}$

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Reaction of the binary alloys KSn_2 and K_3Bi_2 or of the ternary alloy composition KSnBi with 2,2,2-crypt in ethylenediamine (en) produces a dark red-brown solution from which black crystals of $(2,2,2\text{-crypt-}K^+)_2Sn_2Bi_2^{2-}\cdot$en may be precipitated. The anion was originally thought[2] to be Sn_4^{2-} before atomic absorption and microprobe analysis established its composition to be $Sn_2Bi_2^{2-}$. The compound crystallizes in the monoclinic space group $P2_1$ with a = 12.640 (3) Å, b = 20.943 (5) Å, c = 12.353 (3) Å, β = 118.97 (2)°, V = 2861 (1) Å^3, and Z = 2. X-ray diffraction data were collected over two octants on an automated diffractometer at room temperature using monochromatized Mo Kα radiation, and the structure was solved by conventional Patterson and Fourier methods. Positional and thermal parameters of the 62 non-hydrogen atoms, with anisotropic thermal parameters for bismuth, tin, and potassium, were refined by full-matrix, least-squares techniques to R = 0.088 and R_w = 0.107 for 2944 independent reflections ($I > 3\sigma_I$). The structure contains $Sn_2Bi_2^{2-}$ anions with the metal atoms disordered equally over the four sites; the geometry is effectively tetrahedral, the bond distances ranging from 2.934 (3) to 2.971 (6) Å. $Sn_2Bi_2^{2-}$ is the first heteroatomic member of the P_4 family of 20-electron tetrahedral clusters, in contrast to the butterfly shape of the isoelectronic $Tl_2Te_2^{2-}$.

Introduction

Recent application of 2,2,2-crypt as an alkali metal complexing agent has made possible the isolation of stable salts of many polyatomic "Zintl" anions[3,4] from alloys of the post transition elements. The complexing serves both to increase the solubility of the salt and to prevent the reversion to the otherwise more stable intermetallic phases. Homopolyatomic anions such as Sn_9^{4-},[5] Ge_9^{4-} and Ge_9^{2-},[6] Pb_5^{2-} and Sn_5^{2-},[7] Bi_4^{2-},[8] Sb_4^{2-},[9] and Sb_7^{3-} [10] and, more recently, the heteropolyatomic

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