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An Asymmetric Molecular A-Frame: the Crystal Structure of $[Pd_2(Ph_2PCH_2PPh_2)_2(\mu\text{-}I)(CH_3)I][BF_4]\cdot\frac{1}{2}H_2O$

MARILYN M. OLMSTEAD, JAMES P. FARR and ALAN L. BALCH*
Department of Chemistry, University of California, Davis, Cal. 95616, U.S.A.

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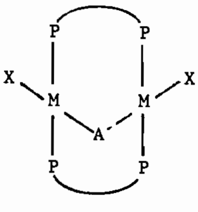
The conversion of a bridging methylene into a terminal methyl group by reaction of fluoroboric acid with $Pd_2(Ph_2PCH_2PPh_2)_2(\mu\text{-}CH_2)I_2$ *has been confirmed by an X-ray crystal structure investigation. The product,* $[Pd_2(Ph_2PCH_2PPh_2)_2(\mu\text{-}I)(CH_3)I]BF_4$, *crystallizes in the monoclinic space group C2/c with 1½ molecules in the asymmetric unit and cell dimensions* a = *37.114(7),* b = *10.275(1),* c = *41.447(6) Å,* β = *101.23(1)°. The measured density at 300 K is 1.68 g* cm^{-3}. *The calculated value of 1.72 g* cm^{-3} *is determined at 140 K (Z = 12). At the present stage of refinement, R = 0.078 (4221 reflections). The Pd–Pd bond lengths of 2.976(6) and 3.01(1) Å are intermediate between those usually found for bonded and non-bonded metal atoms. The overall geometry is that of an unsymmetrical A-frame with one bridging and one terminal iodine, a terminal methyl group, and two bridging phosphine ligands.*

Introduction

In recent years a number of binuclear complexes possessing the molecular A-frame structure *1* have been structurally characterized [1–10]. To date all of these have involved species in which the ligation about the two metal ions is identical. Here we describe the first example of an A-frame which involves dissimilar ligation of the two palladium ions involved. The complex cation, $Pd_2(dpm)_2(\mu\text{-}I)(CH_3)I^+$ (dpm = bis(diphenylphosphino)methane) is formed by protonation of a methylene bridged complex as illustrated in eqn. 1 [11].



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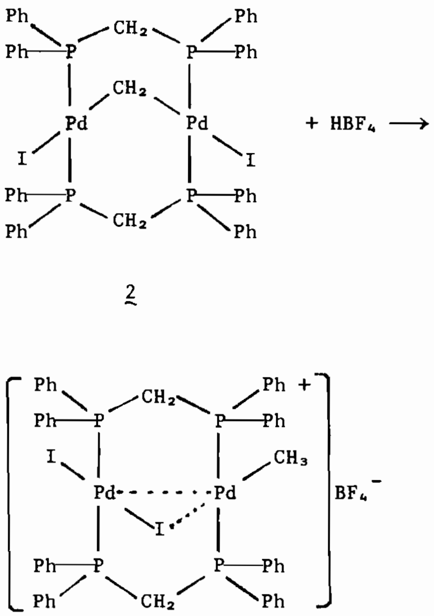

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(*1*)

The present structure determination serves to establish the overall geometry of the cation formed in reaction (*1*) and reveals an interesting effect of the molecular asymmetry on the Pd···Pd separation.

Experimental

[Pd₂(Ph₂PCH₂PPh₂)₂(μ-I)(CH₃)I]BF₄

Full details of the synthesis of the title compound were recently reported [11]. It is isolated from a reaction between fluoroboric acid and $Pd_2(Ph_2\cdot PCH_2PPh_2)_2(\mu\text{-}CH_2)I_2$ in dichloromethane solution. Crystals suitable for diffraction measurements were obtained by diffusion of diethyl ether into a dichloromethane solution in a narrow tube. The crystals grew as fairly flat, deep red-brown needles. The crystal used for data collection was a needle of

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*Author to whom correspondence should be addressed.

dimensions 0.10 × 0.15 mm cut to a length of 0.42 mm.

X-ray Data Collection

The crystal was mounted along the long axis and positioned in the cold stream of a modified LT-1 syntex $P2_1$ diffractometer. The temperature of the crystal was 140 K; the radiation was monochromatic MoKα (λ = 0.71069 Å). The unit cell dimensions were determined using a combination of rotation and axial photographs and the automatic indexing routine of Data General Nova software. This cell was confirmed by oscillation and h0l Weissenberg photographs of a different crystal at room temperature. Based upon a least squares' fit of 22 reflections with $25° < 2\theta < 30°$, the final cell dimensions for a monoclinic C lattice are: a = 37.114(7), b = 10.275(1), c = 41.447(6) Å, β = 101.23(1)°. Systematic absences of hkl, h + k = 2n + 1; h0l, l = 2n + 1 were determined by quick scans of numerous reflections and are consistent with space groups C2/c and Cc. Due to the large number of molecules in the unit cell (Z = 12), the centrosymmetric space group C2/c was assumed to be correct. This in turn required there to be one entire molecule at a general position and another molecule possessing either an inversion center or two-fold rotational symmetry. The calculated value of the density, 1.72 g cm^{-3} at 140 K, is typically a few percent higher than that measured at room temperature by flotation, 1.68(1) g cm^{-3}.

In the interest of time and in consideration of the very high quality of the crystal (a typical peak during an ω scan had a width of 0.24° at half height), intensity data were collected using a 29.3° min^{-1} ω scan over a 0.8° range in ω and 0.8° offset for background counts. Two check reflections were monitored at regular intervals during data collection and showed only random fluctuations. The data were reduced to I_{net} and $\sigma(I_{net})$ as previously described [6]. Of the 10117 unique reflections with $2\theta \leq 45°$, 4221 with $I_{net} > 3\sigma(I_{net})$ were used in the solution and refinement of the structure. Although the number of reflections rejected is fairly large, a ratio of 10 reflections per parameter in the final refinement is still achieved. The large number of rejected reflections stems from the fast method of data collection. Recent studies of this method in our laboratory have yielded reliable results [12]. No correction for absorption was applied. The absorption coefficient is 20.6 cm^{-1} and introduces a range of absorption correction factors of 1.42 to 1.68 in a crystal of these dimensions. The usual corrections for Lorentz and polarization effects were applied to the data.

Solution and Refinement of the Structure

The structure was solved using MULTAN [13] followed by a combination of Fourier and least-squares refinement techniques. The distribution of |E| values clearly indicated the choice of C2/c for space group to be correct, and this was further confirmed by the successful solution of the structure. Atomic scattering factors were those of Cromer and Waber [14a] and the real and imaginary part of anomalous dispersion corrections [14b] were applied to Pd, I, and P. The function being minimized during refinement is $\Sigma w(F_o - k|F_c|)^2$ with the weight, w, given by a Hughes weighting scheme and k is a scale factor. Solution of the structure progressed as follows: the three palladium and three iodine atoms from MULTAN were refined to an R of 0.344 ($R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$). A Fourier map computed at this stage revealed the fourth iodine atom and six phosphorus atoms. Three successive stages of refinement and computations of Fourier or difference Fourier maps eventually revealed the remaining atoms. Due to computer program limitations, the refinement was carried out with two overlapping blocks of 70 and 75 atoms. The final structure factor calculation based on all 100 atoms yielded an R of 0.078. The last shift in any parameter in its final cycle of refinement was <0.1 the esd. Six atoms were not refined but were located on a final difference Fourier map: the BF_4^- group with 0.5 occupancy and an oxygen atom of a water of crystallization. The latter atom is not within bonding distance of any other atoms but is found in a region between the two BF_4^- groups. Thus, it is most likely a water molecule. One cation and one anion are in general positions (Molecule A). A small fraction of these cations appear to have the terminal iodine atom (I(2)) interchanged with the terminal methyl group (C(1)), since the thermal parameter for I(2) is larger than that of the other heavy atoms while that for C(1) is actually negative (Table I). A difference map computed through these atoms showed no sharp peaks but areas of negative electron density near I(2) and positive electron density near C(1) corresponding to *ca.* 1/6 of a carbon atom. However, no effort was made to incorporate this disorder in the refinement. The half cation present in the asymmetric unit (Molecule B) lies on a two-fold axis and is required to have a 50 percent rotational disorder between the terminal iodine and terminal methyl group. Therefore, the methyl group could not be located separately and its existence was assumed. The iodine atom in question had the correct intensity for 50 percent disorder. The half anion is a BF_4^- group that is not found on a special position. In keeping with its intensity, it is only present at one-half of the available sites. Excluding those already mentioned, the largest peaks of a final difference Fourier map were the size of a hydrogen atom.

The final atomic positional and thermal parameters for Molecules A and B are given in Table I. A listing of observed and calculated structure factors is available as supplementary material.

TABLE I. Atomic Potential and Thermal Parameters for $[Pd_2(dmp)_2(\mu\text{-}I)(CH_3)I]BF_4$.

Atom	X	Y	Z	B_{iso}, A^2
Molecule A				
Pd(1)	0.3091(1)	0.3753(3)	0.4492(1)	1.69(8)
Pd(2)	0.3881(1)	0.4225(3)	0.4489(1)	1.28(7)
I(1)	0.3374(1)	0.6027(3)	0.4301(1)	1.57(6)
I(2)	0.4498(1)	0.2997(3)	0.4619(1)	2.56(7)
P(1)	0.2925(4)	0.328(1)	0.3935(3)	1.9(2)
P(2)	0.3217(4)	0.430(1)	0.5051(3)	1.9(2)
P(3)	0.3780(4)	0.324(1)	0.3971(3)	1.6(2)
P(4)	0.4003(4)	0.523(1)	0.4997(3)	1.3(2)
F(1)	0.6187(8)	0.189(3)	0.3714(6)	2.9(6)
F(2)	0.6423(8)	0.232(3)	0.4244(7)	3.7(6)
F(3)	0.650(1)	0.377(4)	0.3849(8)	4.9(8)
F(4)	0.595(1)	0.348(3)	0.3990(8)	5.1(8)
B(1)	0.628(2)	0.276(4)	0.396(1)	2.2(8)
O(1)	0.294	0.175	0.286	3.
C(1)	0.270(1)	0.214(3)	0.4575(7)	−0.6(6)
C(2)	0.331(1)	0.353(4)	0.371(1)	1.7(8)
C(3)	0.359(1)	0.555(4)	0.516(1)	1.7(8)
C(4)	0.256(2)	0.444(5)	0.374(1)	3. (1)
C(5)	0.234(2)	0.497(6)	0.392(2)	4. (1)
C(6)	0.204(2)	0.584(7)	0.376(2)	5. (1)
C(7)	0.201(2)	0.601(5)	0.344(1)	3. (1)
C(8)	0.223(2)	0.549(6)	0.326(1)	4. (1)
C(9)	0.253(1)	0.471(4)	0.342(1)	3. (1)
C(10)	0.271(2)	0.175(5)	0.380(1)	3. (1)
C(11)	0.232(2)	0.165(5)	0.377(1)	3. (1)
C(12)	0.214(1)	0.044(5)	0.367(1)	3. (1)
C(13)	0.236(2)	−0.061(7)	0.360(2)	6. (2)
C(14)	0.273(3)	−0.052(9)	0.360(2)	5. (2)
C(15)	0.291(2)	0.061(8)	0.376(2)	5. (1)
C(16)	0.337(1)	0.303(5)	0.536(1)	2. (1)
C(17)	0.343(1)	0.332(4)	0.570(1)	3. (1)
C(18)	0.355(2)	0.235(6)	0.592(1)	4. (1)
C(19)	0.361(1)	0.107(5)	0.581(1)	4. (1)
C(20)	0.353(1)	0.074(4)	0.548(1)	3. (1)
C(21)	0.341(1)	0.174(4)	0.524(1)	2. (1)
C(22)	0.284(1)	0.518(4)	0.517(1)	2. (1)
C(23)	0.253(3)	0.532(4)	0.489(1)	2. (1)
C(24)	0.220(1)	0.601(5)	0.495(1)	2. (1)
C(25)	0.223(2)	0.657(7)	0.525(1)	5. (2)
C(26)	0.252(2)	0.638(5)	0.551(1)	3. (1)
C(27)	0.284(1)	0.580(5)	0.546(1)	3. (1)
C(28)	0.382(1)	0.142(5)	0.395(1)	2. (1)
C(29)	0.382(1)	0.072(4)	0.422(1)	1. (1)
C(30)	0.382(2)	−0.066(6)	0.419(1)	4. (1)
C(31)	0.380(2)	−0.122(5)	0.386(1)	3. (1)
C(32)	0.379(1)	−0.047(4)	0.361(1)	2. (1)
C(33)	0.382(1)	0.085(4)	0.364(1)	2. (1)
C(34)	0.410(1)	0.394(4)	0.374(1)	1. (1)
C(35)	0.440(1)	0.324(4)	0.366(1)	2. (1)
C(36)	0.465(1)	0.386(4)	0.350(1)	2. (1)
C(37)	0.459(1)	0.520(4)	0.342(1)	2. (1)
C(38)	0.429(1)	0.576(5)	0.348(1)	3. (1)
C(39)	0.403(1)	0.524(1)	0.364(4)	2. (1)
C(40)	0.434(1)	0.448(4)	0.533(1)	1. (1)
C(41)	0.430(1)	0.316(4)	0.539(1)	2. (1)
C(42)	0.454(1)	0.260(4)	0.565(1)	2. (1)
C(43)	0.482(1)	0.326(5)	0.582(1)	3. (1)
C(44)	0.489(1)	0.462(5)	0.575(1)	3. (1)
C(45)	0.464(1)	0.515(4)	0.550(1)	1. (1)
C(46)	0.421(1)	0.685(4)	0.496(1)	1. (1)
C(47)	0.447(1)	0.701(4)	0.478(1)	1. (1)
C(48)	0.464(1)	0.819(5)	0.477(1)	2. (1)
C(49)	0.451(1)	0.928(5)	0.491(1)	2. (1)
C(50)	0.423(1)	0.912(4)	0.510(1)	2. (1)
C(51)	0.409(1)	0.793(4)	0.512(1)	1. (1)
Molecule B				
Pd(3)	0.4709(1)	0.0105(3)	0.2708(1)	1.35(7)
I(3)	0.5000	0.2282(4)	0.2500	1.65(9)
I(4)	0.4376(2)	−0.1904(6)	0.2862(1)	1.7(1)
P(5)	0.5213(4)	−0.029(1)	0.3136(3)	1.2(2)
P(6)	0.4216(4)	0.052(1)	0.2283(1)	1.5(2)
F(5)	0.176(1)	0.045(4)	0.198(1)	2. (1)
F(6)	0.178(1)	0.173(4)	0.159(1)	2. (1)
F(7)	0.149(1)	0.215(4)	0.196(1)	2. (1)
F(8)	0.208(1)	0.210(4)	0.209(1)	2. (1)
B(2)	0.178(1)	0.140(4)	0.175(1)	3. (1)
C(53)	0.437(1)	0.065(3)	0.189(1)	1. (1)
C(54)	0.512(2)	0.021(3)	0.354(1)	1. (1)
C(55)	0.484(1)	−0.033(3)	0.366(1)	2. (1)
C(56)	0.476(1)	−0.005(3)	0.397(1)	2. (1)
C(57)	0.503(1)	0.076(3)	0.417(1)	2. (1)
C(58)	0.532(1)	0.140(4)	0.405(1)	2. (1)
C(59)	0.536(1)	0.109(3)	0.375(1)	1. (1)
C(60)	0.537(1)	−0.200(4)	0.318(1)	3. (1)
C(61)	0.551(1)	−0.244(4)	0.351(1)	1. (1)
C(62)	0.565(2)	−0.372(4)	0.354(1)	3. (1)
C(63)	0.562(1)	−0.450(4)	0.327(1)	3. (1)
C(64)	0.546(1)	−0.410(4)	0.296(1)	2. (1)
C(65)	0.534(1)	−0.275(4)	0.291(1)	2. (1)
C(66)	0.380(1)	−0.055(4)	0.221(1)	1. (1)
C(67)	0.377(1)	−0.149(5)	0.194(1)	3. (1)
C(68)	0.346(1)	−0.229(5)	0.191(1)	3. (1)
C(69)	0.321(2)	−0.218(6)	0.213(1)	5. (1)
C(70)	0.326(1)	−0.135(4)	0.238(1)	3. (1)
C(71)	0.357(1)	−0.046(4)	0.243(1)	3. (1)
C(72)	0.402(1)	0.214(4)	0.234(1)	2. (1)
C(73)	0.382(1)	0.282(4)	0.207(1)	3. (1)
C(74)	0.369(1)	0.402(4)	0.211(1)	3. (1)
C(75)	0.372(1)	0.459(5)	0.244(1)	4. (1)
C(76)	0.390(2)	0.386(5)	0.271(1)	5. (1)
C(77)	0.405(1)	0.259(4)	0.266(1)	2. (1)

Results and Discussion

The asymmetric unit contains one and one-half complex cations, one and one-half BF_4^- ions and a presumed water molecule. Atomic positional and thermal parameters are given in Table I. Selected interatomic distances and angles are given in Table II.

TABLE II. Selected Interatomic Distances (A) and Angles (deg) for $[Pd_2(dpm)_2(\mu\text{-}I)(CH_3)I]BF_4$.[a]

Molecule A		Molecule B	
Pd(1)–Pd(2)	2.976(6)	Pd(3)–Pd(3)′	3.01(1)
Pd(1)–I(1)	2.740(5)	Pd(3)–I(3)	2.697(5)
Pd(2)–I(1)	2.648(5)	Pd(3)′–I(3)	
Pd(2)–I(2)	2.577(6)	Pd(3)–I(4)	2.550(7)
Pd(1)–C(1)	2.28(4)	$[CH_3]$	
Pd–P(av)	2.33(2)	Pd–P(av)	2.33(2)
P–C(av)	1.84(3)	P–C(av)	1.85(1)
P(1)···P(3)	3.15(2)	P(5)···P(6)′	3.11(4)
P(2)···P(4)	3.12(2)	P(6)···P(5)′	
Pd(1)–I(1)–Pd(2)	67.0(1)	Pd(3)–I(3)–Pd(3)′	67.9(2)
Pd(1)–Pd(2)–I(1)	58.0(1)	Pd(3)–Pd(3)′–I(3)	56.1(2)
Pd(2)–Pd(1)–I(1)	55.0(1)	Pd(3)′–Pd(3)–I(3)	
I(2)–Pd(2)–I(1)	162.7(2)	I(4)–Pd(3)–I(3)	174.3(2)
C(1)–Pd(1)–I(1)	163(1)		
I(2)–Pd(2)–Pd(1)	139.2(2)	I(4)–Pd(3)–Pd(3)′	125.4(4)
C(1)–Pd(1)–Pd(2)	141.6(9)		
P(1)–Pd(1)–P(2)	175.8(6)	P(5)–Pd(3)–P(6)	179.0(5)
P(3)–Pd(2)–P(4)	177.6(5)		
B–F(av)	1.38(7)		

[a] Individual bond distances and angles are given with computed esd's. Bond distances listed as (av) are given with average deviations from the mean.

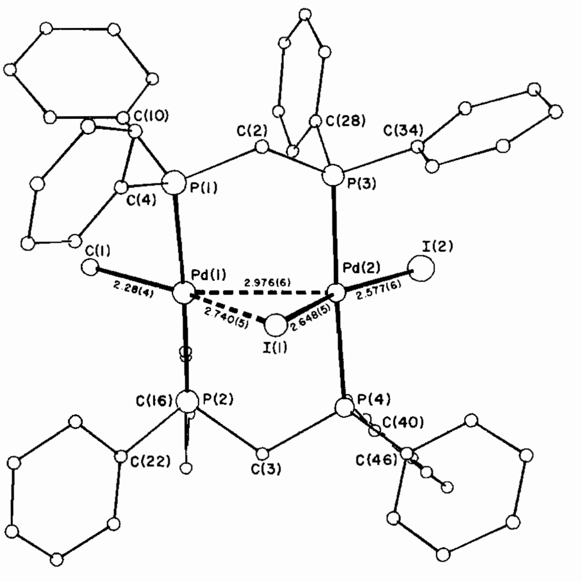


Fig. 1. A perspective drawing of complex cation A.

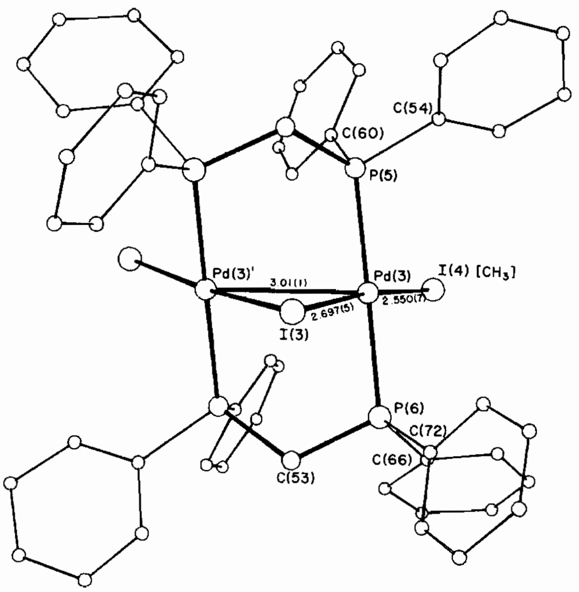


Fig. 2. A perspective drawing of complex cation B.

The overall geometry of the two independent complex cations is similar. Figure 1 shows a perspective view of complex cation A. This ion has no crystallographically imposed symmetry. Figure 2 shows a similar view of complex cation B. A stereoscopic view of cation B from a different perspective is shown in Fig. 3. This ion is crystallographically required to possess a two fold rotation axis. As a consequence the terminal methyl and iodide ligands in cation B are disordered and less information is given by this molecule. The disorder in the structure arises because of the similarity in sizes, particularly in van der Waals radii, of the terminal iodide and methyl ligands [15] and because of the high degree of exterior symmetry

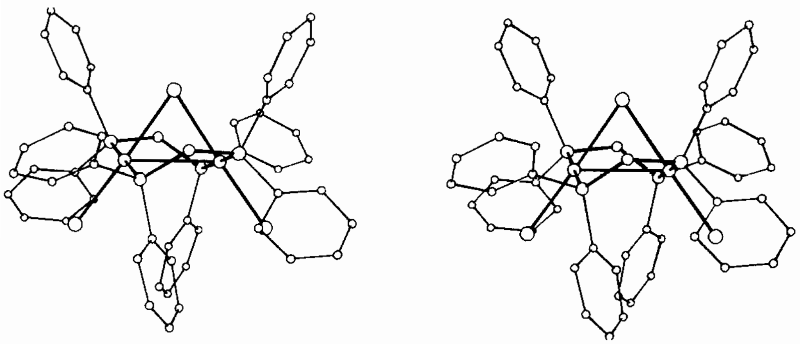


Fig. 3. A stereoscopic drawing of complex cation B.

TABLE III. Selected Least-Squares Planes for $[Pd_2(dpm)_2(\mu\text{-}I)(CH_3)I]BF_4$.

Molecule A		Molecule B	
Atom	dev from plane, A	Atom	dev from plane, A
Plane 1: $-2.3311x + 3.1706y + 39.0921z = 17.9694$		Plane 1: $18.7652x - 0.0y + 30.9931z = 17.1309$	
Pd(1)	0.061	Pd(3)	0.099
Pd(2)	0.013	Pd(3)′	−0.099
C(1)	−0.034	I(3)	0.000
I(1)	−0.030	I(4)′	0.049
I(2)	−0.011	I(4)	−0.049
Plane 2: $31.0584x - 5.5559y - 3.2753z = 5.8743$		Plane 2: $20.7780x - 5.6627y - 29.673z = 1.6855$	
Pd(1)	0.170	Pd(3)	0.004
C(1)	−0.187	I(4)	−0.007
I(1)	−0.154	I(3)	−0.007
P(1)	−0.154	P(5)	0.005
P(2)	0.075	P(6)	0.006
Plane 3: $5.4797x - 9.5858y + 12.1592z = 3.5273$		Plane 3: $0.1418x + 10.2749y + 0.0254z = 5.3304$	
Pd(1)	0.031	Pd(3)	−0.012
Pd(2)	0.008	Pd(3)′	0.004
P(1)	−0.288	P(5)	−0.419
P(2)	0.256	P(6)	0.410
P(3)	0.265	P(6)′	0.433
P(4)	−0.271	P(5)′	−0.418
Plane 4: $24.2358x + 6.9859y - 18.8347z = 4.0749$			
Pd(2)	−0.171		
I(2)	0.220		
I(1)	0.210		
P(3)	−0.129		
P(4)	−0.131		

between the two ends of the molecule. Due to this disorder, most of the discussion will concern complex cation A. It should be realized, however, that this ion appears also to be somewhat disordered due to the interchange of terminal methyl and iodide ligands. Therefore, because of some degree of averaging, the true molecular asymmetry in complex ion A may be larger than that revealed in the data. Whenever possible, we look to complex ion B to confirm our observations made on complex ion A.

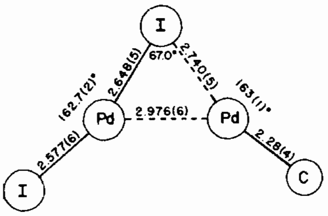
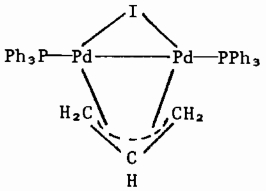


Fig. 4. A planar projection of the $Pd_2(\mu\text{-}I)(CH_3)I$ portion of complex cation A.

Both cations may be described as molecular A-frames. The coordination about each palladium ion is nearly planar. The equations of some least squares planes in the cations are given in Table III. For Pd(1) of cation A the coordination involves the pair of *trans* phosphorus atoms, one from each of the two bridging bis(diphenylphosphino)methane ligands, the bridging iodide ligand and the methyl group. For Pd(2) of cation A the coordination involves a similar pair of *trans* phosphorus atoms, the bridging iodide ion and the terminal iodide ligand. The two metal ions are pulled slightly toward one another. This can be seen in the projection of the planar Pd_2I_2C portion of complex ion A shown in Fig. 4. The C(1)–Pd(1)–μ-I(1) angle is 163(1)°, the μ-I(1)–Pd(2)–I(2) angle is 162.7(2)°, and the Pd–Pd distance is 2.976(6) Å. The basic features of the metal coordination are maintained in the ions in site B; however due to disorder, the asymmetry is lost. Nevertheless it is significant to note the Pd–Pd separation in complex ion B; 3.01(1) Å. Within the error limits, the Pd···Pd separation in the two cations are the same. This palladium–palladium distance is longer than the distances found in directly bonded, dpm bridged species ($Pd_2(dpm)_2Br_2$, 2.699(5) Å [16] and $Pd_2(dpm)_2(SnCl_3)Cl$, 2.644(2) Å [17]) and shorter than that found for molecular A-frames in which no direct metal–metal bond is present: $(Pd_2(dpm)_2(\mu\text{-}CNCH_3)(CNCH_3)_2^+$; 3.215(2) [1]; $Pd_2(dpm)_2(\mu\text{-}S)Cl_2$, 3.258(2) [6]; $Pd_2(dpm)_2(\mu\text{-}SO_2)Cl_2$, 3.383(4) and 3.220(4) [6]; $Pd_2(dpm)_2(\mu\text{-}C_2\{CF_3\}_2)Cl_2$, 3.492(1) [5]).

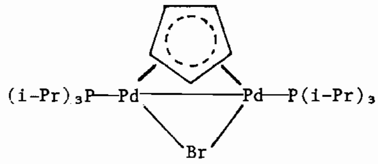
The terminal Pd(2)–I(2) distance of 2.577(6) Å in cation A is somewhat shorter than other terminal Pd–I distances. Comparative distances are 2.601(2) (*trans* to N) and 2.624(2) Å (*trans* to S) in diiodo-(5-methyl-1-thia-5-azacyclooctane)palladium(II) [18], 2.638(3) and 2.619(3) Å in the red isomer of $(Me_2PhP)_2Pd_2I_2$ and 2.592(3) Å in the yellow isomer [19]. In cation A the bridging iodide ligand is asymmetrically placed between the two palladium ions. The Pd(1)–I(1) distance, 2.740(5) Å, which involves the bond *trans* to the terminal methyl group, is longer than the Pd(2)–I(1) distance, 2.648(5), which involves the bond *trans* to the terminal iodide ligand. In cation B the bridging iodide is required to be symmetrically disposed between the two metal ions and the Pd–I distance is the average of the two values observed in cation A.

The geometry of the Pd_2I triangle in $Pd_2(dpm)_2(\mu\text{-}I)(CH_3)I^+$ can be compared to a similar triangle in $Pd_2(\mu\text{-}C_3H_5)(\mu\text{-}I)(PPh_3)_2 \cdot C_6H_6$, *4*.



4

This complex exhibits a Pd–Pd distance of 2.686(7) Å, which is characteristic of a Pd–Pd single bond, a Pd–I distance of 2.650(4) Å, and a Pd–I–Pd angle of 60.9(1)°. For complex cation A the Pd–I distances are comparable to those of *4* while the Pd–I–Pd angle has opened up to accommodate the longer Pd–Pd separation. The dimensions of these molecules may also be compared to *5* which has a Pd–Pd single bond distance of 2.609(1) Å [21].



5

The Pd–C distance, 2.28(4) Å, is longer than that found for other palladium–carbon bonds. Comparable Pd–C(sp^3) distances include 2.025(12) in $[C_5(CH_3)_5(CH(p\text{-tolyl})CH_2Pd(acac)]$ [22] and 2.038(4) in $LPd(\mu\text{-}Cl)_2PdL$ ($L = -CCl(CO_2Me) \cdot C_5(CO_2Me)_4C(OMe){:}O^-$) [23]. The length of the Pd–C bond in $Ph_2(dpm)_2(\mu\text{-}I)(CH_3)I^+$ is clearly an artifact of the disorder found in cation A. This disorder may also be responsible for the apparent shortness of the terminal Pd–I bond since partial averaging of the methyl and iodide positions will produce an apparent shortening of the Pd–I bond and a lengthening of the Pd–C bond.

The geometry of the phenyl groups of the bis(diphenylphosphino)methane ligands is unexceptional. The Pd–P and P–C distances are normal and within the error limits. These values are the same for the two molecules. The non-bonded P···P separation within each diphosphine ligand is *ca.* 0.1 Å longer than our previous correlation between P···P separation and metal–metal separation would have predicted [24]. The present structure maintains a feature common to all other molecular A-frames which have been structurally characterized: the IPd_2P_2C rings possess the boat conformation.

The external disposition of the phenyl rings in $[Pd_2(dpm)_2(\mu\text{-}I)(CH_3)I]^+$ and the relative orientation of the *trans* P–Pd–P units are twisted so that this complex takes on a shape like that found for $Rh_2(dpm)_2(\mu\text{-}S)(CO)_2$. For the more regular A-frame structures of $Pd_2(dpm)_2(\mu\text{-}SO_2)Cl_2$, $Pd_2(dpm)_2(\mu\text{-}S)Cl_2$, $Pd_2(dpm)_2(\mu\text{-}CNCH_3)(CNCH_3)_2^+$ and $Rh_2(dpm)_2(\mu\text{-}Cl)(CO)_2^+$, the *trans*-P–M–P units are nearly parallel to one another. This is reflected in small torsional angles for the PMMP unit. For example in $Rh_2(dpm)_2(\mu\text{-}Cl)(CO)_2^+$ the PRhRhP torsional angles are 0.16(6)° and 3.70(5)° [7]. For these structures four of the phenyl group lie in between the legs of the A in the endo pocket between the metals. In contrast in $Pd_2(dpm)_2(\mu\text{-}I)(CH_3)I^+$ and in $Rh_2(dpm)_2(\mu\text{-}S)(CO)_2$ only two phenyl groups occupy the endo space between the metals and the PMMP torsional angles are larger. These angles are 14° and 12° in $Pd_2(dpm)_2(\mu\text{-}I)(CH_3)I^+$ complex ion A while in B it is 20°. In $Rh_2(dpm)_2(\mu\text{-}S)(CO)_2$ the PRhRhP torsional angle is 20.19°(9) [10].

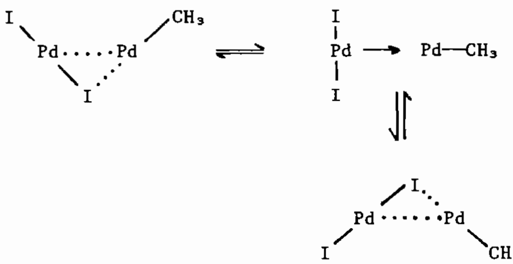
The structural parameters for the tetrahedral tetrafluoroborate anion are entirely normal. These tetrafluoroborate ions are well separated from the cations, with fluorine atoms approaching phenyl carbon atoms at distances in some cases in the range of 3.12–3.21 Å and iodine atoms at distances of 3.57–3.70 Å. The shortest distance between carbon atoms of adjacent molecules is 3.40(1) Å between C(23) and C(25).

Discussion

The structural study confirms the conversion of the methylene bridge of *2* into a terminal methyl group and reveals the basic A-frame geometry of the cationic product of equation 1. The cation *3* is isoelectronic with several other previously characterized molecular A-frames including $Pd_2(dpm)_2(\mu\text{-}S)Cl_2$ [6], $Rh_2(dpm)_2(\mu\text{-}S)(CO)_2$ [10] and $Rh_2(dpm)_2(\mu\text{-}Cl)(CO)_2^+$ [7]. All of these have metal-metal separations of 3.15 Å or greater. We believe that the decreased Pd–Pd separation in $Pd_2(dpm)_2(\mu\text{-}I)(CH_3)I^+$ is a consequence of the asymmetry of the complex and results from a degree of dative bonding between the two palladium ions so that Pd(2) acts as partial donor toward Pd(I). As a result of this dative Pd–Pd bonding, the Pd(I)–I(1) distance is longer than the Pd(2)–I distance of the Pd–I distance in *4*.

In terms of electron counting we can begin by considering each palladium as a d^8, Pd(II). Pd(2) achieves a normal sixteen electron count by accepting eight electrons in pairs from the two phosphine ligands and the two iodide ligands. Pd(1) accepts four electrons from its two phosphine ligands and two more from the methyl ligand. This brings its electron count to fourteen. Its electron count could be brought to sixteen if the bridging iodide donated a pair of electrons to Pd(1). However if this were the only other source of electron donation to Pd(1), a more regular A-frame structure should be found with a larger Pd···Pd separation, similar to that found in the isoelectronic $Pd_2(dpm)_2(\mu\text{-}S)Cl_2$. Consequently we propose that Pd(2) also acts as an electron donor toward Pd(1). Donation of a full electron pair from Pd(2) to Pd(1) raises the electron count on Pd(1) to eighteen without affecting the electron count at Pd(2). However the lengths of the Pd(1)–Pd(2) and Pd(1)–I(1) internuclear distances suggest that each of these is weaker than a normal two electron bond.

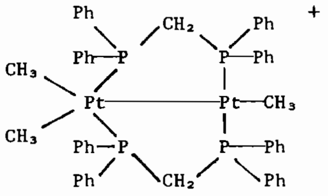
Further evidence for the presence of dative Pd–Pd bonding in *3* comes from the nmr observations reported elsewhere [11], which show that the ion is fluxional. At 25° in dichloromethane solution the two methylene protons of the bis(diphenylphosphino)methane ligands are magnetically equivalent while at –90 °C they are inequivalent, a characteristic of molecular A-frames. The fluxional process appears to be adequately described by equation 2 which



(2)

shows only the in-plane ligands and omits the bridging diphosphine ligands which lie above and below the planar unit shown. This process switches the terminal and bridging iodide ligands and renders both methylene protons of the bridging dpm ligands equivalent.

In the absence of donors like iodide, which can act as bridging ligands, the dative metal–metal bonding in a complex of the composition $M_2(dpm)_2L_3$ should be strengthened. An example exists in the structure of $Pt_2(dpm)_2(CH_3)_3^+$ *6* recently reported [25].



6

While this structure has an uncharacteristic *cis* arrangement of the phosphorus donors at one of the two platinum ions, it also has a short Pt–Pt (2.769(1) Å) separation which has been ascribed to a dative Pt–Pt single bond.

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