bis(dimethylarsine)] associates strongly with halide and thiocyanate ions in solution,[9] and halide ions occupy axial positions in the crystalline solid.[10] No reports have been published of any interaction of such complexes with hydroxide, but it is not known whether this is because no such interaction takes place or just that the experiment has never been carried out.

It is of interest to note that, while there is considerable evidence for the interaction of hydroxide (and cyanide) ions with $[Pt(bpy)_2]^{2+}$, $[Pt(phen)_2]^{2+}$, and similar species (bpy = 2,2′-bipyridyl; phen = 1,10-phenanthroline), there is no evidence for interaction with chloride. This was interpreted in terms of addition of OH^- or CN^- to the heterocyclic base rather than to the metal,[11] but a recent critical review of the evidence[12] argues convincingly that both in the solid and in solution the hydroxide is bound to the metal. X-ray diffraction studies prove that, in $[Pt(phen)_2CN]^+$, the metal is square pyramidal with the cyanide in the basal plane.[13] Whether this can be taken as a precedent for the *cis*-$[Pt(Me_2S)_2(NH_3)_2]^{2+}$ system or whether its driving force is the provision of a means whereby the strong distortions due to the nonbonding repulsive interactions between the hydrogens on the phenanthrolines in the square-planar complex are regularized remains to be examined.

A mechanism reminiscent of that invoked to account for a similar higher order nucleophilic dependence in the displacement, by chloride, of 5-NO_2-phen from $[Au(5\text{-}NO_2\text{-}phen)Cl_2]^+$ is[14] shown in Scheme II. No attempt is made to distinguish between coordination and ion association, and the involvement of water in these axial positions is possible (in which case it is reminiscent of the early Basolo and Pearson mechanism for square planar substitution[15]). Likewise, no commitment is made as to the geometry of these five-coordinate species, or the location of the ligands within them. A square pyramid is just easier to draw.

Provided the reaction involving the association of OH^- and the subsequent proton-transfer processes are fast, the kinetics will be first order in [complex] and the observed first-order rate constants will be related to $[OH^-]$ by expressions of the sort

$$k_{obsd}(I,OH) = (k_1^{\circ} + k_1^{(1)}K_1[OH^-] + k_1^{(2)}K_1K_2[OH^-]^2)/(1 + K_1[OH^-] + K_1K_2[OH^-]^2)$$

This will reduce to the form $k_{obsd}(I,OH) = k_1^{\circ} + k_1^{(1)}[OH^-] + k_1^{(2)}K_1K_2[OH^-]^2$ provided $K_1[OH^-]$ and $K_1K_2[OH^-]^2$ are much less than unity. The scatter of the data does not allow us to detect the departures from the simplified relationship for $K_1 < 0.1$ although it is possible that the reduction in $k_{obsd}(I,OH)$ due to $K_1[OH^-]$ becoming significant compared to 1 is fortuitously compensated by a contribution from $k_1^{(2)}K_1K_2[OH^-]^2$, but this cannot allow for much larger values of K_1 and K_2. Comparison with the empirical rate law would make $k_1^{(1)}K_1 = k_a$ and $k_1^{(2)}K_1K_2 = k_b$. The smaller the values of K_1 and K_2, the larger will $k_1^{(1)}$ and $k_1^{(2)}$ have to be in order to compensate, and it remains necessary to explain why such new facile paths are available for entry of hydroxide alone. The lack of a second-order $[OH^-]$ dependence of the second stage of the reaction is perhaps consistent with the lower charge of the substrate and the small size of K_2 when OH^- is attached to an uncharged aggregate.

At this stage it is only possible to demonstrate the phenomenon of multiorder hydroxide dependence and to rule out certain of the possible explanations. We are now studying the factors that relate to the occurrence of this phenomenon and hope thereby to elucidate the cause.

Acknowledgment. We thank L. Gemelli for technical assistance and the Italian Council for Research (CNR, Rome) and the Ministero Pubblica Istruzione for financial support.

Registry No. *cis*-$[Pt(Me_2S)_2(NH_3)_2]^{2+}$, 90670-30-7.

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Bridged or Nonbridged Structures for Dinuclear Metal Complexes. The Case of Tetrakis(methyl isocyanide)dipalladium(I) Iodide: An Unbridged Compound

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The structure of $(CH_3NC)_4Pd_2I_2$ has been determined by X-ray diffraction. Molecules of the type $(RNC)_4Pd_2X_2$ were originally assigned a halide-bridged structure largely on the basis of infrared data. $(CH_3NC)_4Pd_2I_2$ crystallizes in the space group $P\bar{1}$ with cell dimensions (determined at 140 K) of $a = 7.188$ (2) Å, $b = 10.933$ (2) Å, $c = 12.803$ (4) Å, $\alpha = 80.58$ (2)°, $\beta = 75.45$ (2)°, $\gamma = 81.22$ (2)°, $Z = 2$, and $V = 954.3$ (4) Å^3. The structure was refined to a conventional R value of 0.039 from 2489 significant reflections. It has an unbridged structure with a linear I–Pd–Pd–I unit and two terminal isocyanide ligands on each palladium. The Pd–Pd and average Pd–I distances are 2.533 (1) and 2.698 (1) Å. The low-energy metal–halogen stretching vibrations, which caused the original structure misidentification, are discussed in the context of other compounds with linear X–M–M–X units.

Introduction

Polynuclear metal complexes continue to attract considerable attention both as models for catalysts and as actual catalyst precursors.[1] Binuclear complexes offer the simplest unit in which the important metal–metal interactions can be studied. Here, the relative energies of structural alternatives such as bridged vs. unbridged structures and the choice of bridging ligands are not readily predicted. Several theoretical articles dealing with the question of bridged vs. unbridged structures have appeared recently, and these articles recount the results of numerous experimental observations.[2-4]

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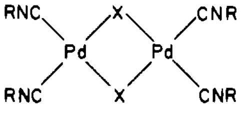
Binuclear compounds of Pd(I) and Pt(I) are remarkable for the range of bridging ligands that have been found. Among the bridging groups that have been characterized by X-ray diffraction to span isolated Pd_2 or Pt_2 units are π-allyl,[5] π-cyclopentadienide,[6] π-benzene,[7] carbonyl,[8] diene,[9] sulfide,[10] thiophosphinate,[11] halide (including iodide),[5,12] borane,[13] acetylene,[14] phosphide,[15] and diphosphine.[16] In addition, a number of bridged species also result from the insertion of various small molecules (including isocyanides[17,18] and carbon monoxide) into the metal–metal bonds of $M_2(\mu\text{-dpm})_2X_2$ (M = Pt, Pd; X = halide; dpm = bis(diphenylphosphino)methane).[19]

Here, we report on a structural study by X-ray diffraction of $(CH_3NC)_4Pd_2I_2$,[20] a member of a class of molecules that involves two ligands, both of which are capable of functioning as bridging ligands. Complexes of the type $(RNC)_4Pd_2X_2$ were first obtained by the conproportionation reaction between $(t\text{-BuNC})_4Pd$ and $(t\text{-BuNC})_4PdX_2$.[21] The diamagnetic, dimeric products were assigned a halide-bridged structure, **1**.



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Infrared spectra were interpreted in favor of such a structure. The isocyanide stretching frequencies fell in the region for terminal isocyanide ligands, and the metal–halogen stretching vibrations occurred at the low frequencies usually associated with bridging halide ligands. Subsequent work on these molecules reported other preparation methods and noted that the data available for metal–halide vibrations were not conclusive evidence in favor of the bridged structure.[20,22]

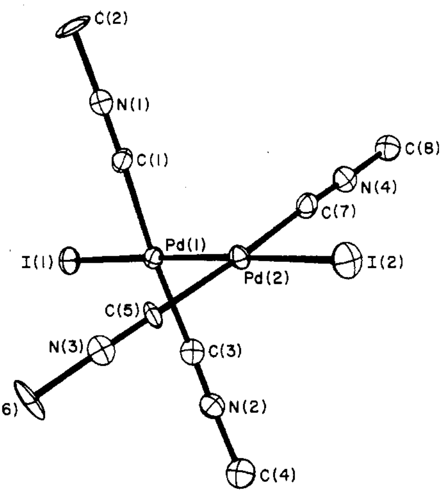


Figure 1. Perspective drawing of $(CH_3NC)_4Pd_2I_2$.

Table I. Atom Coordinates ($\times 10^4$) and Temperature Factors ($\times 10^3$) for $(CH_3NC)_4Pd_2I_2 \cdot CH_2Cl_2$

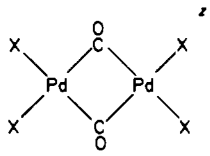
atom	*x*	*y*	*z*	*U*,[a] Å^2
Pd(1)	2892 (1)	2384 (1)	2703 (1)	16 (1)*
Pd(2)	4633 (1)	2516 (1)	4165 (1)	16 (1)*
I(1)	1137 (1)	2313 (1)	1085 (1)	24 (1)*
I(2)	6460 (1)	2709 (1)	5722 (1)	27 (1)*
Cl(1)	7186 (5)	1256 (4)	9215 (3)	60 (1)*
Cl(2)	7291 (4)	3962 (3)	8868 (3)	58 (1)*
N(1)	5907 (12)	119 (8)	2079 (7)	26 (3)*
N(2)	191 (11)	4701 (7)	3518 (7)	23 (3)*
N(3)	6662 (11)	4446 (7)	2371 (7)	22 (3)*
N(4)	1984 (11)	612 (7)	5647 (7)	22 (3)*
C(1)	4810 (14)	952 (9)	2329 (8)	21 (4)*
C(2)	7253 (15)	−946 (10)	1727 (10)	38 (4)*
C(3)	1189 (14)	3847 (10)	3245 (8)	20 (4)*
C(4)	−1094 (15)	5784 (10)	3926 (10)	33 (3)
C(5)	5958 (13)	3742 (9)	3024 (8)	18 (3)*
C(6)	7530 (16)	5379 (10)	1495 (9)	35 (4)*
C(7)	2953 (14)	1295 (9)	5089 (8)	21 (4)*
C(8)	674 (14)	−265 (9)	6322 (9)	26 (2)
C(9)	6641 (17)	2640 (11)	9844 (10)	42 (5)*

[a] Asterisks denote cases where the equivalent isotropic *U* value is defined as one-third of the trace of the orghogonalized U_{ij} tensor.

Table II. Bond Lengths (Å) for $(CH_3NC)_4Pd_2I_2 \cdot CH_2Cl_2$

Pd(1)–Pd(2)	2.533 (1)		
Pd(1)–I(1)	2.699 (1)	Pd(2)–I(2)	2.697 (1)
Pd(1)–C(1)	1.959 (9)	Pd(2)–C(5)	1.972 (9)
Pd(1)–C(3)	1.969 (10)	Pd(2)–C(7)	1.974 (9)
C(1)–N(1)	1.142 (12)	C(5)–N(3)	1.115 (12)
C(3)–N(2)	1.133 (12)	C(7)–N(4)	1.135 (12)
N(1)–C(2)	1.450 (13)	N(3)–C(6)	1.468 (13)
N(2)–C(4)	1.468 (13)	N(4)–C(8)	1.468 (12)
Cl(1)–C(9)	1.775 (13)		
Cl(2)–C(9)	1.786 (12)		

Recent theoretical calculations, which compared the carbonyl- and halide-bridged structures **2** and **3** (and its cis isomer), concluded that the carbonyl-bridged structure, **2**, is favored over the halide-bridged structure, **3**, for Pd(I) (z = 2−) but that the reverse is true for Pd(II) (z = 1−).[23] These



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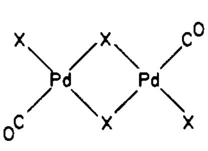

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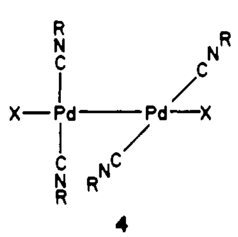
Table III. Bond Angles (deg) for $(CH_3NC)_4Pd_2I_2 \cdot CH_2Cl_2$

Pd(2)-Pd(1)-I(1)	177.5 (1)	Pd(1)-Pd(2)-I(2)	178.8 (1)
I(1)-Pd(1)-C(1)	94.0 (3)	I(2)-Pd(2)-C(5)	97.5 (3)
I(1)-Pd(1)-C(3)	94.8 (3)	I(2)-Pd(2)-C(7)	94.6 (3)
Pd(2)-Pd(1)-C(1)	86.0 (3)	Pd(1)-Pd(2)-C(5)	81.8 (3)
Pd(2)-Pd(1)-C(3)	85.1 (3)	Pd(1)-Pd(2)-C(7)	86.0 (3)
C(1)-Pd(1)-C(3)	171.1 (5)	C(5)-Pd(2)-C(7)	167.7 (5)
Pd(1)-C(1)-N(1)	177.6 (10)	Pd(2)-C(5)-N(3)	178.1 (9)
Pd(1)-C(3)-N(2)	177.3 (10)	Pd(2)-C(7)-N(4)	177.9 (11)
C(1)-N(1)-C(2)	177.5 (12)	C(5)-N(3)-C(6)	178.0 (11)
C(3)-N(2)-C(4)	177.2 (10)	C(7)-N(4)-C(8)	177.0 (11)
Cl(1)-C(9)-Cl(2)	110.6 (7)		

calculations were in accord with the known structural data which show that $(CO)_2Pd_2Cl_4^{2-}$ has the carbonyl-bridged structure, **2**,[8] while spectroscopic data suggest that $(OC)_2Pd_2Cl_4$ has the halide-bridged structure, **3**.[24] These observations cast further doubt in our minds on the hypothesis that the $(RNC)_4Pd_2X_2$ class would contain a halide-bridged structure. To settle these matters, the structural study reported here was undertaken. Together with the infrared data, it shows that the $(RNC)_4Pd_2X_2$ class has the unbridged structure, **4**.



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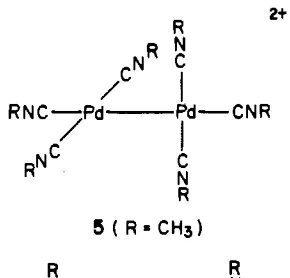
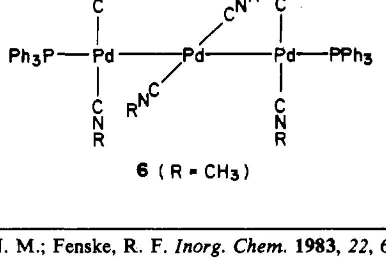
Results

Molecular Structure of $(CH_3NC)_4Pd_2I_2$. The compound $(CH_3NC)_4Pd_2I_2$ crystallizes with one molecule of the palladium complex and one molecule of dichloromethane in the asymmetric unit and no unusual intermolecular contacts. A perspective drawing of the molecule is presented in Figure 1, which also gives the numbering scheme used. Final atomic coordinates and thermal parameters are given in Table I. Tables II and III give selected interatomic distances and angles, respectively. The molecule has no crystallographically imposed symmetry, but its idealized symmetry is D_{2d}.

As can be seen from Figure 1, there are no bridging ligands present. The dimeric unit is held together by a direct Pd-Pd bond. Its bond length (2.533 (1) Å) is similar to that of the only other crystallographically characterized, unbridged Pd(I) dimer, $[(CH_3NC)_6Pd_2]^{2+}$ (**5**), which has a Pd–Pd length of 2.5310 (9) Å.[25,26] Likewise, the related unbridged trinuclear cation, $[(Ph_3P)_2(CH_3NC)_6Pd_3]^{2+}$ (**6**), has a Pd–Pd separation of 2.5921 (5) Å.[27] The Pd–Pd bond length in $(CH_3NC)_4Pd_2I_2$ is shorter than the Pd–Pd distance found in palladium metal (2.751 Å).[28] It is also shorter than the corresponding distances in bridged binuclear Pd(I) complexes where the Pd–Pd separations range from 2.57 Å in $Pd_2(\mu\text{-}\pi\text{-}C_6H_6)_2(AlCl_4)_2$[9] to 2.697 Å in $[Pd_2(\mu\text{-}CO)_2Cl_4]^{2-}$.[10] However, it is interesting to note that a Pd(II) dimer, dipalladium(II) tetrakis(6-methyl-2-oxypyridine), has a similarly short but *nonbonded* Pd···Pd distance of 2.546 (1) Å.[29]



5 (R = CH_3)



6 (R = CH_3)

The coordination about each palladium is planar. The dihedral angle between the two coordination planes is 85.3°. The basic structure is similar to the arrangement in $[(CH_3NC)_6Pd_2]^{2+}$ where that angle is 86.4° and in $[(Ph_2P)_2(CH_3NC)_6Pd_3]^{2+}$ where the coordination planes meet at an angle of 74.5°. In unbridged $Pt_2(CO)_2Cl_4^{2-}$ the corresponding dihedral angle is much less, 60°,[30] while in the diphosphine-bridged complexes of the type $Pd_2(\mu\text{-dpm})_2X_2$, which also have square coordination at each metal, these dihedral angles are in the vicinity of 40°.[16,31] For the three isocyanide complexes the interplanar orientations are largely dictated by steric considerations that are minimized when the coordination planes are perpendicular. However, in solution evidence has been presented that indicates that there is a low barrier to rotation about the Pd–Pd bond in $[(CH_3CN)_6Pd_2]^{2+}$ and $[(Ph_3P)Pd_2(CNCH_5)_5]^{2+}$.[20] In $Pd_2(\mu\text{-dpm})_2X_2$ the interplanar angle is subject to the constraint of the bridging ligands. For $Pt_2(CO)_2Cl_4^{2-}$ it has been suggested that interaxial repulsions between filled d orbitals of the two platinum atoms are responsible for the unusual interplanar angle. Such repulsions would be expected to be smaller in $[(CH_3NC)_6Pd_2]^{2+}$, $[(CH_3NC)_8Pd_3]^{2+}$, and $(CH_3NC)_4Pd_4I_2$, which possess more π-accepting ligands than $Pt_2(CO)_2Cl_4^{-}$ and have neutral or cationic character that should result in contraction of the d orbitals. Moreover, repulsions between filled d orbitals are likely to be lower for palladium than for platinum due to the lower d-orbital radial extension for the second-row element. Indeed, this effect may have a major consequence in explaining why $[(CH_3NC)_6Pd_2]^{2+}$ undergoes rapid axial/equatorial isocyanide exchange whereas $[(CH_3NC)_6Pt_2]^{2+}$ is nonfluxional.[20] Since free rotation about the M–M bond is required for the proposed mechanism of this fluxional process, repulsion between the filled Pt d orbitals of $[(CH_3NC)_6Pt_2]^{2+}$ may contribute to a larger barrier to rotation.

The I–Pd–Pd–I unit is nearly linear. The I–Pd–Pd angles are 177.5 (1) and 178.8 (1)°. The Pd–I bond lengths (2.697 (1) and 2.699 (1) Å) are unusually long for terminal Pd–I bonds. In comparison, the following terminal Pd–I distances have been observed: 2.601 (2) (trans to N) and 2.624 (2) Å (trans to S) in diiodo(5-methyl-1-thia-5-azacyclooctane)palladium(II),[32] 2.638 (3) and 2.619 (3) Å (trans to I) in the red isomer of *trans*-$(Me_2PhP)_2PdI_2$, 2.59 (3) Å[33] (trans to I) in the yellow isomer of $(Me_2PhP)_2PdI_2$,[33] and 2.577 (6) Å (trans to I) in $[Pd_2(\mu\text{-dpm})_2(\mu\text{-}I)(CH_3)I]^+$.[34] We ascribe this

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Table IV. Far-Infrared Spectra for Molecules with Linear X-M-M-X Units

compd	ν(CN), cm^{-1}	ν_{as}(M-X), cm^{-3}	ref
$(CH_3NC)_4Pd_2I_2$	2165	139	this work
$(CH_3NC)_4Pd_2Cl_2$	2218	250	20, 22
$(t\text{-}C_4H_9NC)_4Pd_2I_2$		160	this work
	2166	164	21
$(t\text{-}C_4H_9NC)_4Pd_2Br_2$	2170	185	21
$(t\text{-}C_4H_9NC)_4Pd_2Cl_2$	2178	259	21
$(\mu\text{-dpm})_2Pd_2Cl_2$		249	18
$(\mu\text{-dpm})_2Pd_2Br_2$		185	this work
$(\mu\text{-dpm})_2Pd_2I_2$		160	this work
$(\mu\text{-dpm})_2Pt_2Cl_2$		249	36
$[(OC)_2Pt_2Cl_4]^{2-}$		269	37
Hg_2Cl_2		250	38

elongation to the high trans effect of the Pd–Pd bond on the Pd–I bond. Similar lengthening of terminal halide metal bonds trans to metal–metal bonds has been seen before.[35] Notice, however, that although the Pd–Pd bond exerts a significant effect on the bond lengths of trans ligands, there is no reciprocal effect. The Pd–Pd distances in $[(CH_3NC)_6Pd_2]^{2+}$ and $(CH_3NC)_4Pd_2I_2$ are the same within experimental error even though two very different terminal ligands are present.

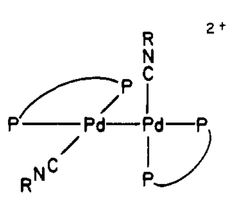
The terminal isocyanide ligands are linearly coordinated to the palladium atoms and are trans to one another. The average of the Pd–C–N angles is 177.7°, and of the C–N–C angles it is 177.4°. The isocyanide ligands are slightly bent toward the Pd–Pd bond. Thus, the C–Pd–C angles are 171.1 (5) and 176.7 (5)°, and the average of the Pd–Pd–C angles is 84.7° while the average of the I–Pd–C angles is 95.2°. Similar bending is found in $[(CH_3NC)_6Pd_2]^{2+}$ where the average of the Pd–Pd–C angles is 85.0°[25] and in $[(Ph_3P)_2(CH_3NC)_6Pd_3]^{2+}$ where the average (80.0°) indicates greater bending.[27] An explanation of this bending has been presented.[26]

Infrared Spectra. The Pd–X stretching frequencies for $(CH_3NC)_4Pd_2I_2$ and a number of related species[36-38] that are known to contain linear X–M–M–X units are collected in Table IV. In all cases, these vibrations occur at unusually low energies for terminal M–X stretching vibrations as a result of two factors: the high trans effect of the M–M bond and the fact that it is the asymmetrical stretch that is being observed. As a consequence, they have been mistaken for bridging M–X–M stretching vibrations.

Discussion

Our results show that $(CH_3NC)_4Pd_2I_2$ exists in the unbridged form. Such unbridged Pd(I) dimers are relatively rare. In addition to $[(CH_3NC)_6Pd_2]^{2+}$, the only other types of Pd(I) dimers that have been shown spectroscopically to exist in unbridged forms are the bis(phosphine) complexes, 7 (where the bis(phosphine) can be $Ph_2P(CH_2)_nPPh_2$ (n = 2–4) or *cis*-$Ph_2PCHCHPPh_2$)[39] and $[(Ph_3P)_nPd_2(CNCH_3)_{6-n}]^{2+}$ (n = 1 or 2).[20]

The fact that $(CH_3NC)_4Pd_2I_2$ exists in a nonbridged form is entirely in accord with theoretical predictions. Were it to assume the bridged structure 1, this would require that the strongly antibonding b_{1g} orbital shown in 8 would be doubly



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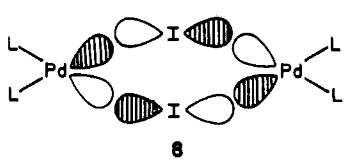
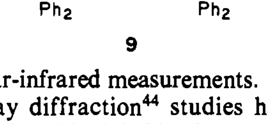


8

occupied. According to the Kostic/Fenske calculations, this orbital would be the HOMO and its occupancy would lead to weakening of the bridge bonding.[23] In contrast in 2 (the actual structure for $[(CO)_2Pd_2Cl_4]^{2-}$) this orbital is empty as a consequence of the fact that carbon monoxide has available empty π^* orbitals for bridge bonding. Thus, for carbonyl (or presumably for isocyanide) a bridged structure does not suffer instability due to occupation of the molecular orbital shown in 8. However, since halide ions possess filled orbitals of π symmetry, a halide-bridged structure for $(RNC)_4PdX_2$ would suffer from this instability. In electron-counting terms, the hypothetical halide-bridged structure 1 with a Pd–Pd bond would give each palladium an 18-electron count. However, the true structure 4 results in a 16-electron count for each palladium. This structure then conforms to the type found for many Pd(I) dimers that have two coordinatively unsaturated centers joined by a metal–metal bond.

The infrared spectra of the $(RNC)_4Pd_2X_2$ class of molecules are consistent with the unbridged structure. For each molecule of this type, only a single isocyanide stretching vibration is observed and it falls into the region of terminal isocyanide absorptions. The single infrared-active, palladium–halide stretching vibration is what is expected for a linear X–Pd–Pd–X chain. In contrast, the D_{2h} structure, 1, predicts two infrared-active, stretching vibrations of the Pd_2X_2 unit and two infrared-active, isocyanide stretching absorptions.[40]

However, the low energies of the palladium–halogen stretching frequencies are unusual and fall into the range where bridging palladium–halogen stretches frequently occur.[41] The low energy of the stretching vibrations undoubtedly is caused by the trans effect of the metal–metal bond that has been shown to lengthen and therefore weaken metal–halogen bonds.[34] This is not the first case where these low-energy metal–halogen stretching vibrations have been mistaken for the vibrations of a halogen bridge. $Pt_2(\mu\text{-dpm})_2Cl_2$ was originally assigned[42] a halogen-bridged structure, 9, on the basis



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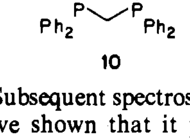

10

of far-infrared measurements. Subsequent spectroscopic[43] and X-ray diffraction[44] studies have shown that it possesses a bis(phosphine)-bridged structure, 10. We suspect that the

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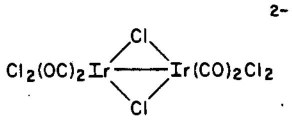
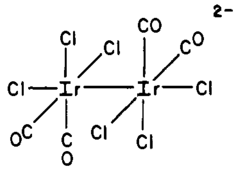
Table V. Summary of Crystal Data, Data Collection, and Refinement

formula	$Pd_2I_2C_8N_4H_{12}\cdot CH_2Cl_2$
fw	715.75
space group	$P\bar{1}$
a, Å	7.188 (2)
b, Å	10.933 (2)
c, Å	12.803 (4)
α, deg	80.58 (2)
β, deg	75.45 (2)
γ, deg	81.22 (2)
V, Å^3	954.3 (4)
Z	2
temp, K	140
ρ_{calcd}(140 K), g cm^{-3}	2.49
cryst dimens, mm	0.12 × 0.27 × 0.37
radiation	Mo Kα (graphite monochromator; λ = 0.710 69 Å
μ(Mo Kα), cm^{-1}	53.4
range abs cor factors	2.06–4.33
scan method	ω
$2\theta_{max}$, deg	45
diffractometer	$P2_1$
octants collcd	$h,\pm k,\pm l$
no. of reflcns measd	2521
no. of unique data	2489 (R(merge) = 0.037)
no. of data with $I > 2\sigma(I)$	2060
R	0.039
R_w	0.043
no. of parameters refined	162
mean shift/esd, last cycle	0.005

observation of low-energy metal–halide vibrations has led to other structural misidentifications. For example, the chloro-bridged structure, **11**, has been proposed[45] for $[Ir_2(CO)_4Cl_6]^{2-}$. The unbridged structure, **12**, appears a more reasonable alternative. Unlike **11**, which, with the proposed Ir–Ir bond, has 20 electrons per iridium, **12** conforms to the 18-electron rule.



11



12

Experimental Section

Preparation of Compounds. $(CH_3NC)_4Pd_2I_2$,[20] $(t\text{-}C_4H_9NC)_4Pd_2I_2$,[21] and $Pd_2(\mu\text{-dpm})_2X_2$[18] were obtained by previously reported procedures.

Infrared Spectroscopy. Far-infrared spectra were recorded on a Perkin-Elmer 180 spectrometer with the solid sample suspended in a mineral oil mull and supported on parafilm sheet.

X-ray Crystallography. Yellow needles were obtained by diffusion of diethyl ether into a dichloromethane solution of $(CH_3NC)_4Pd_2I_2$. Details of the crystal structure determination are summarized in Table V. The crystal was mounted with its long axis parallel to ϕ on a Syntex $P2_1$ diffractometer. The temperature of the crystal was maintained at 140 K by using a locally modified LT-1 low-temperature apparatus. From the automatic indexing feature of the diffractometer software and axial photographs, the crystal lattice was found to be triclinic. All crystallographic computations, except the Patterson map, were carried out with the SHELXTL, version 3, 1981 integrated package (Nicolet Instrument Corp., Madison, WI). An empirical absorption correction was applied to the data by using the program XEMP. The Patterson map and its solution were obtained by using the FMAP8 routine of SHELXTL, version 4, 1983. Scattering factors and corrections for anomalous dispersion were taken from a standard source.[46] No attempt was made to locate hydrogen atoms. Blocked-cascade least-squares refinement was carried out with all atoms, except for C(4) and C(8), and assigned anisotropic thermal parameters. In the case of C(4) and C(8), nonpositive definite anisotropic thermal parameters were obtained; thus, the isotropic thermal parameters were retained. Although the magnitudes of the isotropic thermal parameters for C(4) and C(8) are typical for other atoms in the structure and the computed C-N bond distances are reasonable, the disklike shape of the anisotropic thermal ellipsoids indicates some dynamic disorder is present. This is also visible in the anisotropic thermal ellipsoids of the other two methyl carbon atoms, C(2) and C(6), in Figure 1. A static disorder was ruled out by examination of difference electron density maps viewed down the isocyanide axis. In addition, the possibility that the behavior of the methyl groups was an artifact of the absorption correction was ruled out by application of an entirely different absorption correction procedure that obtains an empirical absorption tensor from an expression relating F_o and F_c.[47] The problem persisted. Therefore, refinement was continued with the original absorption-corrected data. Refinement converged at a conventional R of 0.039 (R_w = 0.043). A test for extinction showed that no measurable extinction was present. No features larger than a hydrogen atom were present on the final difference map. Table I contains the final atomic coordinates.

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Registry No. 4·CH_2Cl_2 (R = CH_3, X = I), 91230-83-0; 4 (R = CH_3, X = I), 91230-82-9; 4 (R = $t\text{-}C_4H_9$, X = I), 91265-28-0; $(\mu\text{-dpm})_2Pd_2Br_2$, 60482-68-0; $(\mu\text{-dpm})_2Pd_2I_2$, 67477-87-6.

Supplementary Material Available: Listings of anisotropic temperature factors and structure factor amplitudes (14 pages). Ordering information is given on any current masthead page.

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