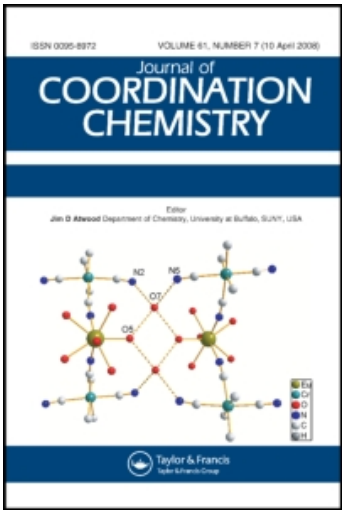

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AN OCTAPHENYL-SUBSTITUTED BICYCLIC ORGANOMETALLIC INCLUSION HOST

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AN OCTAPHENYL-SUBSTITUTED BICYCLIC ORGANOMETALLIC INCLUSION HOST†

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As part of a study involving design of new organometallic hosts, $Pd_2(dpm)_2Cl_2$ **5** was reacted with 4-isocyanoacetophenone **6** to produce the organometallic insertion product **7**. This forms an unstable ternary inclusion compound (**7**)·(chloroform)·(dimethyl sulfoxide) whose X-ray crystal structure [$C_{59}H_{51}Cl_2NOP_4Pd_2 \cdot CHCl_3 \cdot C_2H_6OS$, $P2_12_12_1$, a = 14.734(2), b = 15.782(2), c = 26.682(4) Å, Z = 4, R = 0.043] was determined. The host phenyl groups intermesh producing a helical arrangement of molecules of **7** generated by a 2_1 screw axis. Chloroform guests form a second helix intertwining that of the organometallic host through involvement in C=O···H-CCl_3 hydrogen bonds. The dimethyl sulfoxide guests exhibit no significant short intermolecular contacts.

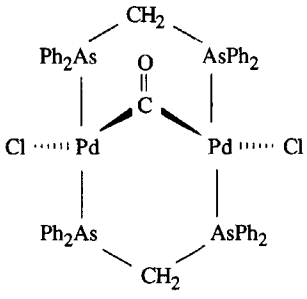
KEYWORDS: Palladium complexes, isonitrile insertion, chloroform guest, dimethyl sulfoxide guest, canal structure, helical structure

INTRODUCTION

The molecules **1–3** are examples[1–3] of a group of organometallic compounds which crystallize in the tetragonal space group $P4_1$ (or enantiomorph $P4_3$). Intermeshing of the phenyl groups results in the creation of parallel fourfold screw axes with individual molecules arranged as helices around small central canals. Since the types of metal atom, the electron-donating ligand atoms, and the molecular bridges have all been varied over structures **1–3**, it seemed reasonable to conclude that this type of lattice arrangement is due principally to the size and shape of the common octaphenyl-substituted bicyclic skeleton present in these organometallic compounds.

In some cases the canals present in such structures are sufficiently large to trap guest molecules and produce inclusion compounds.[4] Hence, for example, Colton[1] isolated **1** from hexane as the compound (**1**)·$(C_6H_{14})_3$. More remarkably, the host **4** crystallized with continuous parallel channels of diameter *ca.* 10 Å which resulted in solvent uptake during flotation density measurements.[5] The large substituent 'arms' present in structure **4** were disordered in the channels but were clearly not

* Author for correspondence.
† This paper is dedicated to Professor Toschitake Iwamoto in recognition of his major contributions to coordination and inclusion chemistry.



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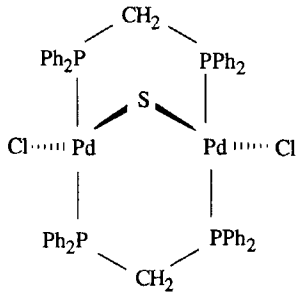

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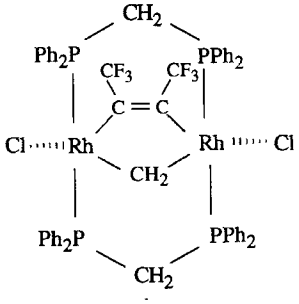

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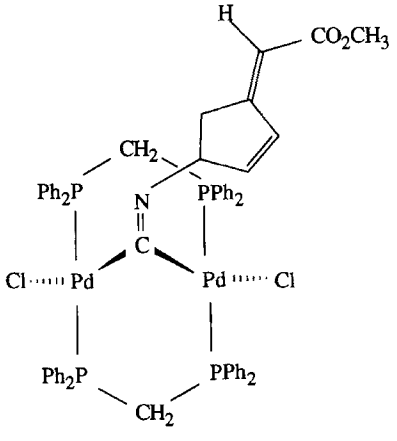

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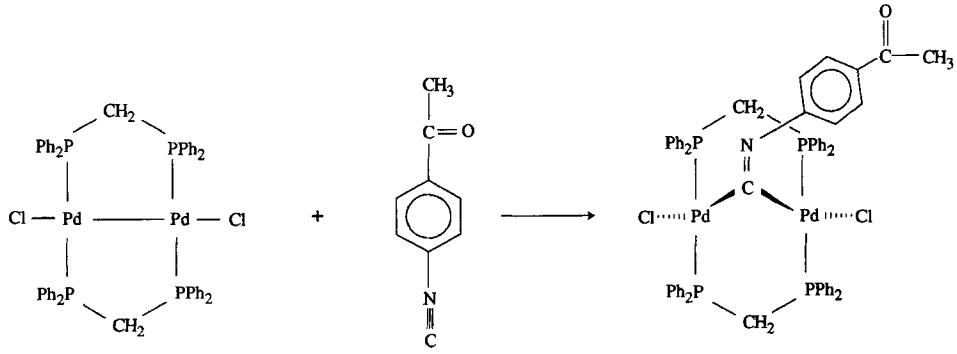
an impediment to retention of the general type of molecular assembly in space group $P4_1$ produced by the less complex analogues **1–3**.

Organometallic compounds of this type therefore appear to have considerable potential in the deliberate design of new host-guest systems. In particular we are interested in the possibility of creating large parallel canals where the subtended arms contain substituents of moderate polarity which would associate weakly with the guest molecules. Variation of the structure of the arm should also allow control of the canal dimensions. Such a host arrangement would have many common structural features with certain antibiotic compounds which are known to self-assemble as *trans*-membrane ion channels and this approach therefore might provide a convenient entry to new synthetic analogues.[6]

In our preliminary study we chose to commence with the phosphine-bridged Pd(I) dimer $Pd_2(dpm)_2Cl_2$ [**5**, dpm = bis(diphenylphosphino)methane] because of its availability and since organic isonitriles are known to insert into the Pd—Pd

bond producing molecules of the required type in one step.[4,5] Thus various organic isonitriles could allow ready synthesis of a series of model organometallics related to **1–4** but with side arms of differing size, flexibility, and functionality. For the initial study reported here 4-isocyanoacetophenone **6** was used since this would provide a semi-rigid arm with moderate polarity in the resulting product **7**.



5 6 7

EXPERIMENTAL

General Procedures

IR spectra were recorded on a Perkin-Elmer 298 spectrometer, with significant peaks being expressed as strong (s), medium (m), weak (w) and broad (br). NMR spectra were recorded on a Bruker AM-500 instrument (^{1}H 500 MHz; ^{13}C 126 MHz) and are reported as chemical shifts δ relative to $SiMe_4$. Because of poor solubility, the ^{13}C NMR spectrum for adduct **7** was recorded as an overnight run. Substitution of carbon atoms was determined using the DEPT procedure. The proton decoupled ^{31}P NMR spectrum was recorded on a Bruker AM-500 instrument using 85% H_3PO_4 as external reference. R_f values were determined on thin layer plates using silica gel type $60GF_{254}$ (Merck) and eluting with chloroform. Melting point values were obtained with a Kofler instrument and are uncorrected. Microanalyses were carried out at UNSW by Dr. H.P. Pham.

Synthetic Considerations

The formamide precursor for **6** was prepared from 4-aminoacetophenone by standard procedures. ^{1}H and ^{13}C NMR spectra of the product indicated a mixture of both *syn* and *anti* isomers resulting from restricted rotation around the amide CO–NH bond at ambient temperatures. This phenomenon has been investigated thoroughly by previous workers.[7-9]

Of the many methods available for preparation of isonitriles,[10,11] the most convenient is usually the dehydration of a suitable formamide precursor. Here we

employed the dehydrating agent chlorodimethylformiminium chloride (Vilsmeier reagent), prepared *in situ* from thionyl chloride and *N,N*-dimethylformamide (DMF), as described by Walborsky and Niznik.[12] The required isonitrile **6** was obtained as an odorous oil in 62% yield.

Reaction of the palladium dimer **5** with the isonitrile **6** in acetonitrile solution at room temperature rapidly afforded the complex **7** in 73% yield.

Dichlorobis-μ-[methylenebis(diphenylphosphine)] dipalladium(I) (Pd-Pd) **5**

The palladium dimer **4** was prepared from bis(benzonitrile)dichloropalladium(II)[13], [tris(1,5-diphenyl-1,4-pentadien-3-one)dipalladium(0)]·(chloroform)[14], and bis-(diphenylphosphino)methane as described by Balch and Benner.[15] Yield 58% (lit.[15] 80%), m.p. 200–204 °C (decomp.), R_f 0.37. IR (paraffin mull): $\nu_{max.}$ 1590 (w,br), 1440 (s), 1100 (m), 1030 (w), 1000 (w), 785 (m), 740 (s), 695 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.50–7.48 (16H, m), 7.33–7.28 (8H, m), 7.17–7.12 (16H, m), 4.17–4.12 (4H, quintet, *J* 4.11 Hz). ^{13}C NMR ($CDCl_3$): δ 133.6 (CH), 133.2 (C), 130.0 (CH), 128.1 (CH), 39.2 [quintet, CH_2, *J* (CP) 10.2 Hz]; ^{31}P NMR ($CDCl_3$): δ −2.39 (s) (lit.[15] −2.50).

4-Isocyanoacetophenone **6**

4-Aminoacetophenone (15.00 g, 0.11 mol), 90% formic acid (12.70 g, 0.25 mol) and toluene (36 mL) were placed in a flask fitted with a Dean-Stark trap. The mixture was stirred and heated at reflux till water ceased to be collected (4.5 h), then evaporated to dryness under reduced pressure. The crude solid was recrystallized from toluene to give *N*-4-formamidoacetophenone as a yellow solid (17.55 g, 96%), m.p. 101–103 °C, (lit.[16] 102–103 °C). IR (paraffin mull): $\nu_{max.}$ 3320 (s), 1705 (s), 1670 (s), 1595 (s), 1530 (s), 1410 (s), 1400 (m), 1365 (m), 1320 (s), 1275 (s), 1260 (m), 1180 (m), 1145 (m), 965 (w), 870 (w), 845 (m), 665 (w) cm^{-1}. ^1H NMR ($CDCl_3$) δ 8.87 (1H, d, *J* 11.1 Hz, CHO)*, 8.80 (1H, br d, *J* 11.1 Hz, NH)*, 8.44 (1H, s, CHO), 8.15 (1H, br s, NH), 7.96 (2H, d, *J* 8.5 Hz, Ar-H)*, 7.93 (2H, d, *J* 8.6 Hz, Ar-H), 7.67 (2H, d, *J* 8.6 Hz, Ar-H), 7.18 (2H, d, *J* 8.5 Hz, Ar-H)*, 2.58 (3H, s, CH_3)*, 2.57 (3H, s, CH_3). ^{13}C NMR ($CDCl_3$): δ 197.2 (C), 196.6 (C)*, 162.0 (CH)*, 159.3 (CH), 141.4 (C), 141.2 (C)*, 133.7 (C)*, 133.2 (C), 130.4 (CH)*, 129.8 (CH), 119.3 (CH), 117.2 (CH)*, 26.5 (2 CH_3). [Addition of C_6D_6 resolved the latter peak into 26.92 (CH_3) and 26.89 (CH_3)*. Peaks marked * are due to the minor amide isomer].

To a flask fitted with a condenser, a dropping funnel, a low temperature thermometer, and protected by drying tubes, was added *N*-4-formamido-acetophenone (8.15 g, 49.9 mmol) and freshly distilled *N,N*-dimethylformamide (DMF; 100 mL). The stirred solution was cooled to −50 °C, and then a solution of freshly distilled thionyl chloride (6.25 g, 52.5 mmol) in DMF (15 mL) was added dropwise over *ca.* 1 h such that the temperature of the solution never exceeded −50°C. Removal of the cooling bath allowed the temperature of the mixture to rise to −40°C for about 10 min. Upon renewed cooling to −50 °C, anhydrous sodium carbonate (11.70 g, 0.11 mol) was added with stirring. The temperature was maintained at this value for *ca.* 10 min. after the addition, then the bath was removed and the solution allowed to warm to room temperature. After

being stirred overnight, the mixture was diluted with cold water (350 mL) and extracted several times with diethyl ether. The combined ethereal extracts were washed with water several times to remove DMF and then dried ($CaCl_2$). Ether was distilled from the filtrate yielding the isonitrile **7** as a foul-smelling brown liquid (4.50 g, 62%), b.p. 75–79°C/*ca.* 30 mm Hg, (lit.[17] 80–81°C/30 mm Hg). IR (film): $\nu_{max.}$ 2135 (s), 1695 (s), 1605 (s), 1580 (m), 1500 (w), 1430 (m), 1410 (s), 1360 (s), 1300 (m), 1265 (s), 1170 (s), 1110 (m), 1075 (w), 1015 (m), 965 (m), 840 (s), 795 (w), 655 (w) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.95 (2H, d, *J* 8.5 Hz), 7.43 (2H, d, *J* 8.5 Hz), 2.58 (3H, s). ^{13}C NMR ($CDCl_3$): 196.3 (C), 167.1 (C), 137.2 (C), 129.7 (C), 129.4 (CH), 126.5 (CH), 26.5 (CH_3).

Dichloro{μ-[4-acetophenylcarbonimidoyl]}bis{μ-[methylenebis(diphenyphosphine)-P:P']}dipalladium(I) **7**

To a stirred suspension of the palladium(I) dimer **5** (0.20 g, 0.185 mol) in acetonitrile (10 mL) was added excess 4-isocyanoacetophenone **6** dropwise. The solid dissolved giving first a bright yellow solution and then a yellow/orange precipitate which was filtered off after *ca.* 10 min. The filtrate was diluted with diethyl ether producing a second crop of solid. The combined precipitates were dried in air, then recrystallized from chloroform yielding complex **7** as a fine orange powder (0.16 g, 73%), m.p. 228–230°C (from chloroform), R_f 0.39. *Anal.* Calcd. for $C_{59}H_{51}Cl_2NOP_4Pd_2$ (%): C, 59.17; H, 4.29; N, 1.17. Found: C, 59.14; H, 4.54, N, 1.26. IR (paraffin mull): $\nu_{max.}$ 1725 (s), 1675 (m), 1625 (w br), 1585 (s br), 1410 (w), 1345 (w), 1275 (s br), 1165 (w), 1130 (m), 1100 (s), 1030 (w), 850 (w), 795 (m), 780 (m), 745 (s), 730 (s), 695 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.76–7.71 (8H, m), 7.71–7.65 (8H, m), 7.33–7.18 (20H, m), 7.11–7.05 (8H, m), 2.64 (1H, quintet, *J* 2.8 Hz), 2.61 (1H, quintet, *J* 2.6 Hz), 2.48–2.38 (2H, m), 2.36 (3H, s). ^{13}C NMR ($CDCl_3$): δ 196.9 (C), 135.2 (CH), 133.7 (C), 133.0 (C), 132.9 (C), 132.8 (C), 132.3 (CH), 130.7 (CH), 130.1 (CH), 129.2 (CH), 128.8 (C), 128.7 (C), 128.5 (CH), 128.3 (CH), 120.6 (CH), 16.4 (CH_3), 19.4 (CH_2-P, further coupling to triplet).

Solution and Refinement of the Structure (7)·(chloroform)·(dimethyl sulfoxide)

The crystals of **7** initially lost chloroform guest molecules rapidly to give an orange powder fully characterized by the methods above as the solvent-free structure. Crystals of this rather insoluble compound were grown from a mixture of chloroform and dimethyl sulfoxide (DMSO) and the X-ray structural determination was carried out on one such crystal mounted in a sealed capillary tube containing a small amount of the mother liquor. This material proved to have the ternary composition (**7**)·(chloroform)·(dimethyl sulfoxide).

Data were recorded using an Enraf-Nonius CAD4 X-ray diffractometer. Data collection and processing procedures have been described previously.[18] The positions of Pd atoms were located using direct methods (MULTAN).[19] Coordinates of the remaining non-hydrogen atoms of both the organometallic host and of the lattice solvent molecules of chloroform and dimethylsulfoxide were determined using Fourier syntheses. Some full matrix least squares refinement (BLOCKLS)[20] with the Pd, Cl, and P atoms anisotropic and all other atoms isotropic gave R = 0.060. However, there was insufficient data to complete anisotropic refinement for

the whole structure. Refinement was therefore completed using the program RAELS[21] which allowed rigid body refinement. Each of the phenyl rings was included in the refinement as a rigid group of *mm2* symmetry. The position and orientation of each of the rings was allowed to vary. The thermal motion of each ring was described by a 12 parameter TL model (where T is the translation tensor and L is the libration tensor), with the origin of libration fixed on the P (or N) atom to which the ring was attached. The remainder of the structure was refined anisotropically in the usual way, except that the three C-Cl distances of the chloroform molecule were slack constrained to be equal. Refinement converged with $R = 0.043$, with R for the other enantiometer being 0.044. The largest peaks in the final difference Fourier map were up to 1.7 e Å^{-3} and were in the vicinity of the Pd atoms.

The numbering system for the atoms of the molecular structure of host **7** is indicated in Figure 1. Aromatic rings were numbered C(XN), X = 1 to 6, for each of the nine rings (N = 1–9). The atom labels for the chloroform guest molecule are prefixed with C, while those of the DMSO guest are prefixed with D. There is one close contact between the keto group and the carbon atom of the chloroform molecule O$\cdots$CC^{a} = 3.037 Å (a = $-x$, $-1/2 + y$, $1\frac{1}{2} - z$).

Numerical details of the solution and refinement of this structure are shown in Table 1. Positional parameters for the non-hydrogen atoms are listed in Table 2; bond lengths and angles are given in Tables 3 and 4.

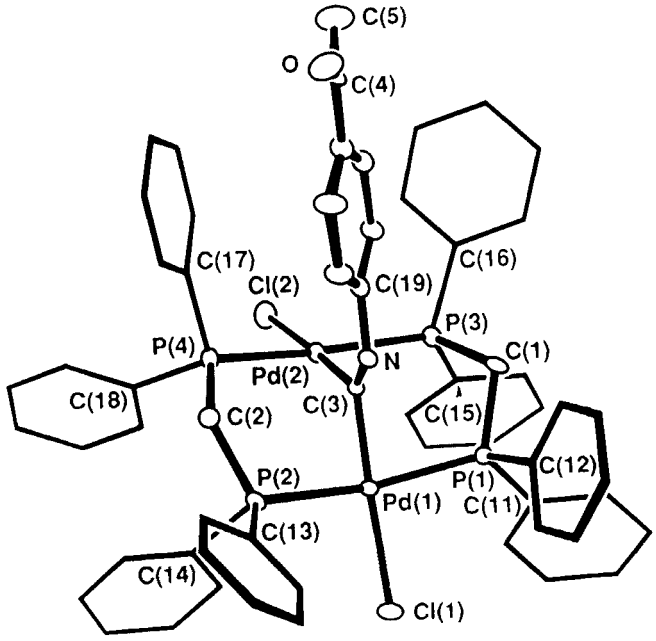


Figure 1 Molecular structure of the organometallic host **7** in the inclusion compound showing the crystallographic numbering system used. For clarity, only the first carbon atom of each aromatic ring is numbered and hydrogen atoms are omitted.

Table 1 Numerical details of the solution and refinement of the structure (**7**)·(chloroform)·(dimethyl sulfoxide)

Formula	$C_{59}H_{51}Cl_2NOP_4Pd_2 \cdot CHCl_3 \cdot C_2H_6OS$
Formula mass	1395.2
Crystal description	{101}{10-1}{011}{01-1}
Space group	$P2_12_12_1$
a/Å	14.734(2)
b/Å	15.782(2)
c/Å	26.682(4)
V/Å^3	6204(1)
Temp./°C	21(1)
Z	4
$D_{calc.}$/g cm^{-3}	1.49
Radiation, λ/Å	Mo$K\alpha$, 0.7107
μ/cm^{-1}	9.65
Crystal dimensions/mm	~0.2 × 0.1 × 0.1
Scan mode	$\theta/2\theta$
$2\theta_{max}$/°	40
ω scan angle	(0.45 + 0.35 tanθ)
No. of intensity measurements	6061
Criterion for observed reflection	$I/\sigma(I)>3$
No. of independent obsd. reflections	3600
No. of reflections (m) and variables (n) in final refinement	3600, 370
$R = \Sigma^m \lvert \Delta F \rvert / \Sigma^m \lvert F_o \rvert$	0.043
$R_w = [\Sigma^m{}_w \lvert \Delta F \rvert^2 / \Sigma^m{}_w \lvert Fo \rvert^2]^{1/2}$	0.048
$s = [\Sigma^m{}_w \lvert \Delta F \rvert^2/(m-n)]^{1/2}$	1.38
Crystal decay	1 to 0.94
Max., min. transmission coefficients	0.91, 0.87

RESULTS AND DISCUSSION

The X-ray determination confirms that the isonitrile insertion product has the anticipated structure 7 where the two Pd atoms are linked by two bis(diphenylphosphino)methane ligands and a 4-acetophenylcarbonimidoyl bridge. Approximately square planar coordination around each Pd atom is completed by the bridgehead-substituted chlorine atom. The Pd-Cl bond lengths average 2.43 Å, the Pd-P average 2.34 Å, and the Pd-C distances average 2.98 Å; the Cl-Pd-C angles are 177° and the P-Pd-P angles average 167°.

The principal difference of this structure from its progenitors **1-4** is the switch from a tetragonal space group ($P4_1$) to an orthorhombic one ($P2_12_12_1$) which results in an inherently more complex structure. There are four molecules in the unit cell. The ring skeleton adopts the twin-twist boat conformation similar to previously described organometallic complexes of this type, but in marked contrast to the behaviour of its carbocyclic analogue (the bicyclo[3.3.1]nonane system) where this conformation is uncommon.[22,23]

Viewed down the long cell dimension, c (Figure 2), the 8-membered Pd-P-C-P-Pd-P-C-P ring is almost edge-on and shows a slight curvature. It has what might be termed a concave and a convex surface. The 4-acetophenylcarbonimidoyl bridge extends from the concave surface, the Cl atoms protrude from the convex surface, four phenyl rings extend nearly vertically and four horizontally outward from the convex surface. There are three intramolecular pairs of phenyl rings which may be

Table 2 Fractional coordinates for the non-hydrogen atoms of the structure (7)·(chloroform)·(dimethyl sulfoxide)

Atom	*x*	y	z		x	y	z
Pd(1)	0.40037(6)	0.23419(5)	0.66994(3)	C(52)	0.0826(5)	0.3253(6)	0.7084(2)
Pd(2)	0.48737(6)	0.13465(5)	0.58029(3)	C(62)	0.1684(4)	0.3301(5)	0.6863(2)
Cl(1)	0.4176(3)	0.3582(2)	0.7235(1)	C(13)	0.4179(1)	0.1155(2)	0.7806(1)
Cl(2)	0.6216(2)	0.1348(2)	0.5276(1)	C(23)	0.3680(4)	0.1817(3)	0.8016(2)
P(1)	0.2987(2)	0.2995(2)	0.6158(1)	C(33)	0.3190(4)	0.1685(5)	0.8457(2)
P(2)	0.4787(1)	0.1402(2)	0.7234(1)	C(43)	0.3199(4)	0.0891(6)	0.8688(2)
P(3)	0.4030(2)	0.2241(2)	0.5269(1)	C(53)	0.3699(5)	0.0229(4)	0.8477(2)
P(4)	0.5444(2)	0.0314(2)	0.6342(1)	C(63)	0.4189(4)	0.0361(2)	0.8036(2)
C(1)	0.2923(7)	0.2531(7)	0.5527(3)	C(14)	0.5912(1)	0.1700(2)	0.7446(1)
C(2)	0.4936(9)	0.0323(6)	0.6966(4)	C(24)	0.6231(3)	0.2504(2)	0.7317(2)
C(3)	0.3813(7)	0.1353(6)	0.6262(4)	C(34)	0.7093(3)	0.2763(4)	0.7472(3)
N	0.3157(5)	0.0858(5)	0.6316(3)	C(44)	0.7635(2)	0.2219(5)	0.7756(2)
C(4)	0.2135(9)	-0.2187(9)	0.5311(5)	C(54)	0.7315(2)	0.1415(5)	0.7885(2)
O	0.1673(8)	-0.2678(6)	0.5537(4)	C(64)	0.6453(3)	0.1156(3)	0.7730(2)
C(5)	0.2425(12)	-0.2349(11)	0.4798(6)	C(15)	0.4554(3)	0.3237(2)	0.5090(2)
CC	0.0091(19)	0.2514(6)	0.8886(4)	C(25)	0.4080(3)	0.3825(3)	0.4799(2)
CC1(1)	0.0473(7)	0.3251(4)	0.9291(3)	C(35)	0.4492(5)	0.4588(3)	0.4664(2)
CC1(2)	0.0628(7)	0.1580(5)	0.8956(3)	C(45)	0.5377(5)	0.4764(3)	0.4819(3)
CC1(3)	-0.0050(7)	0.2872(7)	0.8298(3)	C(55)	0.5851(4)	0.4175(4)	0.5110(3)
DS	-0.0879(5)	0.5165(5)	0.7706(3)	C(65)	0.5439(3)	0.3412(3)	0.5245(2)
DO	-0.1262(14)	0.4363(9)	0.7561(6)	C(16)	0.3728(3)	0.1768(3)	0.4672(1)
DC(1)	-0.0044(17)	0.5522(18)	0.7251(8)	C(26)	0.4311(4)	0.1145(4)	0.4486(2)
DC(2)	-0.1702(15)	0.5941(15)	0.7553(10)	C(36)	0.4122(6)	0.0753(5)	0.4029(3)
C(19)	0.2927(3)	0.0125(3)	0.6047(3)	C(46)	0.3350(6)	0.0984(5)	0.3757(2)
C(29)	0.2532(5)	-0.0538(4)	0.6316(2)	C(56)	0.2768(5)	0.1607(5)	0.3943(2)
C(39)	0.2287(5)	-0.1285(4)	0.6071(3)	C(66)	0.2957(4)	0.1999(4)	0.4401(2)
C(49)	0.2436(5)	-0.1369(3)	0.5557(3)	C(17)	0.5204(2)	-0.0741(2)	0.6108(2)
C(59)	0.2831(5)	-0.0706(4)	0.5288(2)	C(27)	0.4858(5)	-0.1401(3)	0.6399(2)
C(69)	0.3076(4)	0.0041(4)	0.5533(3)	C(37)	0.4696(5)	-0.2193(3)	0.6183(3)
C(11)	0.3091(5)	0.4113(2)	0.6013(2)	C(47)	0.4880(5)	-0.2324(3)	0.5676(3)
C(21)	0.2347(4)	0.4542(4)	0.5811(3)	C(57)	0.5227(5)	-0.1664(4)	0.5385(2)
C(31)	0.2416(5)	0.5403(4)	0.5697(3)	C(67)	0.5389(4)	-0.0873(3)	0.5601(2)
C(41)	0.3227(6)	0.5835(2)	0.5785(3)	C(18)	0.6650(2)	0.0299(5)	0.6473(1)
C(51)	0.3970(5)	0.5405(4)	0.5987(3)	C(28)	0.7158(5)	0.1041(5)	0.6421(3)
C(61)	0.3902(4)	0.4544(4)	0.6101(2)	C(38)	0.8087(5)	0.1035(7)	0.6521(3)
C(12)	0.1850(3)	0.2889(3)	0.6409(2)	C(48)	0.8511(2)	0.0286(8)	0.6674(3)
C(22)	0.1160(4)	0.2429(5)	0.6176(2)	C(58)	0.8003(5)	-0.0456(6)	0.6727(3)
C(32)	0.0302(4)	0.2381(6)	0.6397(3)	C(68)	0.7073(5)	-0.0449(4)	0.6626(3)
C(42)	0.0135(3)	0.2793(6)	0.6851(3)				

Table 3 Bond lengths (Å) for the structure (7)·(chloroform)·(dimethyl sulfoxide)

Cl(1)-Pd(1)	2.437(3)	Cl(2)-Pd(2)	2.428(3)
P(1)-Pd(1)	2.323(3)	P(2)-Pd(1)	2.358(3)
P(3)-Pd(2)	2.359(3)	P(4)-Pd(2)	2.331(3)
C(1)-P(1)	1.837(9)	C(1)-P(3)	1.829(11)
C(2)-P(2)	1.861(11)	C(2)-P(4)	1.824(11)
C(3)-Pd(1)	1.969(10)	C(3)-Pd(2)	1.986(10)
N-C(3)	1.252(11)	O-C(4)	1.195(14)
C(5)-C(4)	1.456(18)	CCl(1)-CC	1.685(8)
CCl(2)-CC	1.684(8)	CCl(3)-CC	1.681(8)
DO-DS	1.439(14)	DC(2)-DS	1.771(23)
C(19)-N	1.401(9)	C(49)-C(4)	1.515(13)

Table 4 Bond angles (°) for the structure (7)·(chloroform)·(dimethyl sulfoxide)

Cl(1)-Pd(1)-P(1)	94.3(1)	Cl(1)-Pd(1)-P(2)	95.7(1)
Cl(1)-Pd(1)-C(3)	177.7(3)	P(1)-Pd(1)-P(2)	166.1(1)
P(1)-Pd(1)-C(3)	83.8(3)	P(2)-Pd(1)-C(3)	85.9(3)
Cl(2)-Pd(2)-P(3)	94.5(1)	Cl(2)-Pd(2)-P(4)	93.7(1)
Cl(2)-Pd(2)-C(3)	177.3(3)	P(3)-Pd(2)-P(4)	168.8(1)
P(3)-Pd(2)-C(3)	87.4(3)	P(4)-Pd(2)-C(3)	84.6(3)
Pd(1)-P(1)-C(1)	115.2(4)	Pd(1)-P(2)-C(2)	113.7(3)
Pd(2)-P(3)-C(1)	113.1(3)	Pd(2)-P(4)-C(2)	114.2(4)
P(1)-C(1)-P(3)	113.5(5)	P(2)-C(2)-P(4)	113.9(5)
Pd(1)-C(3)-Pd(2)	104.9(5)	Pd(1)-C(3)-N	122.5(8)
Pd(2)-C(3)-N	132.5(8)	C(3)-N-C(19)	130.0(8)
O-C(4)-C(5)	121.9(14)	O-C(4)-C(49)	120.0(12)
C(5)-C(4)-C(49)	118.1(12)	CCl(1)-CC-CCl(2)	112.1(9)
CCl(1)-CC-CCl(3)	114.1(9)	CCl(2)-CC-CCl(3)	117.2(10)
DO-DS-DC(2)	106.1(12)	N-C(19)-C(29)	117.1(6)
N-C(19)-C(69)	122.9(6)	C(4)-C(49)-C(39)	117.5(7)
C(4)-C(49)-C(59)	122.5(7)		

considered to take part in an offset face-to-face interaction. One involves the phenyl ring of the 4-acetophenylcarbonimidoyl bridge and one of the horizontal phenyl rings and has an interplanar distance of about 3.6 Å. The two other pairs involve the four phenyl rings which protrude vertically from the convex surface, the

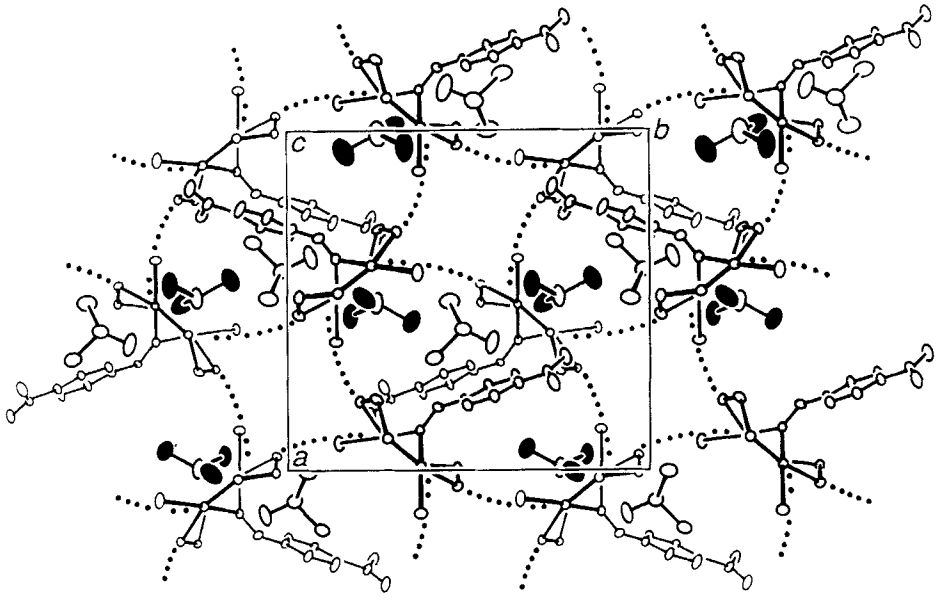


Figure 2 View down *c* showing the three components of (7)·(chloroform)·(dimethyl sulfoxide). The chlorine atoms of the chloroform molecules are filled to distinguish these from the DMSO guests. To simplify the figure, hydrogen atoms and the phenyl rings on phosphorus atoms have been omitted. The curved profile of the Pd-P-C-P-Pd-P-C-P ring which is nearly edge-on is clearly seen. Each partially-filled helical channel is outlined by a dotted line. This shows their oval cross-sectional shape and also the adjacent zones of square cross-section which are filled by the phenyl substituents.

interplanar distances being 3.3 and 3.4 Å. Four molecules of the host **7** form a helical arrangement, with alternate pairs related by a 2_1 screw axis. Around the helix, molecules are alternately concave surface in and concave surface out, so that for one turn of the helix only two 4-acetophenylcarbonimidoyl bridges extend towards the central area of the helix. Each of these partially-filled helical channels has an oval cross-section as shown in Figure 2 and in stereoview Figure 3.

The helical tubes abut orthogonally leaving approximately square channels in between which are filled primarily with phenyl rings. This region has approximate 4_1 symmetry, with four phenyl rings layered around the middle of the channel, nearly in the *ab* plane and separated by about 6.7 Å (*c*/4). Other phenyl rings protrude into the area to a small extent. The shortest intermolecular phenyl-phenyl interaction has C···C = 3.57 Å.

This new organometallic inclusion host has the stoichiometry (**7**)·(chloroform)·(dimethyl sulfoxide). There is a short CH···O contact of 2.09 Å between the chloroform hydrogen and the carbonyl oxygen of the 4-acetophenylcarbonimidoyl bridge. The chloroform molecules could therefore be described as being arranged in a second helix which intertwines the first. The DMSO guest molecules do not take part in intermolecular contacts under 3.5 Å.

As planned in the original concept, the octaphenyl-substituted bicyclic skeleton of **7** does act as an inclusion host, and does indeed assemble in the solid state as a helical structure. In addition, the moderately polar carbonyl group of the host arm also interacts with guest molecules by means of a relatively weak interaction. Therefore these three key features of the molecular design have been successfully achieved and provide strong encouragement that the crystal engineering ideas involved are sound. Unfortunately, the complete design has failed in that a 2_1 screw axis has replaced the required 4_1 type in this structure, thereby causing partial filling of the helical canals. This outcome is probably not due to the actual size of the subtended arm of **7**, since this is fairly close to that present in **4**. More probably it is due to either the chemical nature of the arm or the linear nature of the *para*-substituted group present. The aromatic face···face interaction discussed

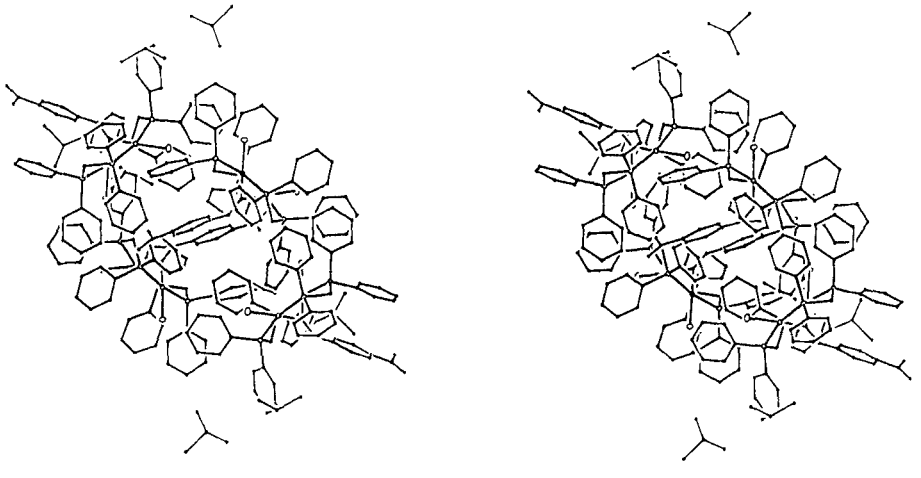


Figure 3 A stereoscopic view along *c* of one helical channel of (**7**)·(chloroform)·(dimethyl sulfoxide).

earlier may also be significant in this regard. Further work is therefore in progress on analogues of this first compound to assess the importance of these structural features towards channel formation.

SUPPLEMENTARY MATERIAL

Atomic thermal parameters, fractional coordinates for the hydrogen atoms, torsional angles, and structure factors are available on request from the authors.

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