

bidden for the trans isomer of the parent and very weak for the cis isomer) should remain quite weak in the product anion. Similarly, the observation of only one C-F stretch for each product anion argues for the bridged structure. If this structure is correct, then one would anticipate a stretching mode of the bridging fluorine for each anion. Previous studies¹⁶⁻¹⁸ of fluorine-bridged species have located this mode in the range 400-500 cm⁻¹. This model, of course, is *not* perfect in that, for the present system, C-C bond rupture did not occur. The pair of absorptions at 376 and 395 cm⁻¹ are likely candidates for this mode in each of the product anions. Their intensity ratio is comparable to the cis/trans ratio of the parent, and the separation (cis at 395 cm⁻¹ and trans at 376 cm⁻¹) is similar to the cis/trans separation for other vibrational modes (e.g., the 1456- and 1497-cm⁻¹ C-O stretches). The observation of these bands that may be assigned to the bridging fluorine (and have no other ready assignment) supports the possibility of a bridging structure for the two product anions.

Calculations

The interaction of a fluoride ion with oxalyl fluoride was also investigated in a series of calculations at the CNDO/S level, with complete geometry optimization for the ground state. Initial calculations focused on the trans isomer, and the geometry of F⁻ attack was varied over a wide range. Two local minima were found in the process, the first of which was a fluorine-bridged structure. The optimized geometry for this structure showed a lengthening

of the C-O, C-F, and C-C bonds relative to the parent and only a few degrees deviation from planarity. The fluoride ion was found to sit directly above this nearly planar oxalyl fluoride subunit, with equivalent C-F distances of 1.45 Å, which is quite reasonable for a bridging structure. The second local minimum corresponded to the unsymmetrical structure (2) above. While no reliable energy difference between the two isomeric forms of the anion could be determined, the calculations do demonstrate the stability of the bridged form and support the possibility of its formation. A similar set of calculations was then carried out with the cis isomer, and comparable results were obtained.

Further Considerations

The behavior of the matrix sample upon warming is of interest as well; while annealing to 35 K produced no distinct changes, after warming to room temperature the residue on the window exhibited broad absorptions near 1230, 1460, and 1710 cm⁻¹. These coincide well with the three most intense absorptions of the CF₃CO₂⁻ anion, which were observed at 1212, 1450, and 1680 cm⁻¹ in the sodium salt.¹⁵ These observations suggest that, upon warming and/or aggregation, rearrangement to the trifluoroacetate anion does occur and that this is the most stable structural form of the C₂F₃O₂⁻ anion. However, under matrix isolation conditions, this rearrangement does not have time to occur before condensation and isolation. These observations suggest that detection of the bridged form under normal laboratory conditions is quite unlikely. Consequently, the matrix isolation technique has provided the first, and perhaps only, spectroscopic identification and characterization of the intermediate, fluorine-bridged anion.

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Preparation and X-ray Structures of Compounds Containing the Tetrakis(methylhydroxypyridinato)- and Tetrakis(chlorohydroxypyridinato)dipalladium(II) Molecules

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The synthesis of [Pd₂L₄] compounds, where L = either the anion 6-methyl-2-hydroxypyridinate (mhp⁻) or 6-chloro-2-hydroxypyridinate (chp⁻), has been reinvestigated, with unexpected results. Three crystalline forms of the chp analogue were obtained. All three crystals contained virtually identical molecules, each having a Pd₂⁴⁺ unit bridged by four chp⁻ ligands, possessing *D*_{2d} symmetry. For compound **1**, [Pd₂(chp)₄].CHCl₃, the crystals are triclinic (*P* $\bar{1}$) with *a* = 10.407 (3) Å, *b* = 16.739 (3) Å, *c* = 8.811 (3) Å, α = 102.30 (2)°, β = 110.43 (2)°, γ = 79.04 (2)°, *V* = 1394.1 (12) Å³, and *Z* = 2 and have a Pd-Pd distance of 2.570 (1) Å. Compound **2**, [Pd₂(chp)₄], forms orthorhombic crystals (*Pnma*) that are isomorphous with those for [Pd₂(mhp)₄] previously obtained by Clegg et al. The crystals have *a* = 15.498 (8) Å, *b* = 16.012 (13) Å, *c* = 18.719 (8) Å, *V* = 4644 (5) Å³, and *Z* = 8 and a Pd-Pd separation of 2.563 (1) Å. Compound **3**, [Pd₂(chp)₄].0.5CHCl₃, forms triclinic crystals (*P* $\bar{1}$) with *a* = 11.167 (3) Å, *b* = 14.595 (4) Å, *c* = 16.895 (4) Å, α = 100.77 (2)°, β = 102.36 (2)°, γ = 101.21 (2)°, *V* = 2562.4 (12) Å³, and *Z* = 4 and has a Pd-Pd separation of 2.568 [4] Å. Crystallization of the intermediate compound in the preparation of the mhp analogue yielded triclinic crystals (*P* $\bar{1}$) with the composition [Pd₂(mhp)₄].6CHCl₃, compound **4**, which contain a mixture of two isomers of the [Pd₂(mhp)₄] molecule. Four of the molecules have *D*_{2d} symmetry, while the fifth has *C*_{2h} symmetry. The crystals have *a* = 12.944 (2) Å, *b* = 26.461 (4) Å, *c* = 11.390 (2) Å, α = 100.43 (1)°, β = 92.67 (1)°, γ = 78.68 (1)°, *V* = 3761.8 (9) Å³, and *Z* = 5. The cisoid molecule of [Pd₂(mhp)₄] in compound **4** is the first example of a cisoid (*C*_{2h}) isomer of an [M₂(xhp)₄] molecule.

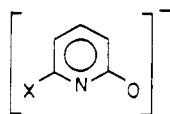
Introduction

In 1982, Clegg, Garner, and Al-Samman¹ reported the preparation and structural characterization of the compound [Pd₂(mhp)₄] in an unsolvated, orthorhombic crystal form. Compounds of the type [M₂(xhp)₄], where xhp is a generic abbreviation for

6-X-2-hydroxypyridinate anions, I, have played a very important role in developing the chemistry of metal-metal bonds, ranging from quadruple (for Cr, Mo, W) to single (for Rh, Pt).² The structure of Clegg et al.'s¹ [Pd₂(mhp)₄] was of the type previously displayed by all unsolvated, neutral [M₂(xhp)₄] molecules, namely,

(1) Clegg, W.; Garner, C. D.; Al-Samman, M. H. *Inorg. Chem.* **1982**, *21*, 1897.

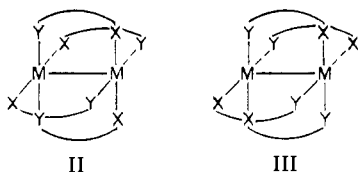
(2) Cotton, F. A.; Walton, R. A. "Multiple Bonds Between Metal Atoms"; Wiley: New York, 1982.



I

mhp⁻: X = CH₃
 chp⁻: X = Cl
 fhf⁻: X = F
 hp⁻: X = H

the isomer having idealized D_{2d} symmetry, II. In this case, all



M-N and M-O bonds are trans to bonds of the same kind. There is, however, an alternative isomer, having idealized C_{2h} symmetry, III, where like bonds are cis to each other. The C_{2h} structure has been found for other $[M_2(XYZ)_4]$ molecules with unsymmetrical bridging ligands but not for those containing xhp⁻ ligands.

The palladium compound was unique among $[M_2(xhp)_4]$ molecules in having a formal Pd-Pd bond order of 0, if the conventional method of assessing such bond orders, entirely in terms of d-d overlaps, is employed. For this reason, as well as for others, we decided to pursue the structural chemistry of $[Pd_2(xhp)_4]$ compounds further. We have therefore reexamined the mhp compound, with unexpected results, and also prepared the chp analogue in three crystalline forms.

Experimental Section

Palladium acetate was purchased from Johnson-Matthey Inc. and was used without further purification. Sodium salts of chp⁻ and mhp⁻ were prepared by the stoichiometric reaction of NaOCH₃ in methanol with Hchp and Hmhp, respectively. Solvents were predried and distilled under N₂ prior to use.

Preparation of $[Pd_2(chp)_4] \cdot nCHCl_3$, $n = 0, 0.5, 1$. A mixture of palladium acetate (0.50 g, 0.74 mmol) and Na(chp) (0.67 g, 4.45 mmol) was dissolved in 50 mL of CH₂Cl₂. These quantities give a chp/Pd mole ratio of 2.00, since palladium(II) acetate is trinuclear.^{3,6} The reaction mixture was stirred at room temperature for 48 h and subsequently was filtered to remove a small quantity of insoluble material. The dark red-orange solution was then evaporated to dryness in vacuum to give an orange solid. A small portion of the orange solid was dissolved in CHCl₃, and from this solution large, orange-brown crystals of $[Pd_2(chp)_4] \cdot CHCl_3$, compound 1, formed together with some decomposition products after several days.

The rest of the reaction mixture was stirred with 15 mL of methanol at room temperature for 24 h. During this time the initially dark red-orange solution became dark brown and a green-brown precipitate formed. The precipitate was then filtered and washed with small portions of methanol and dried under vacuum. This precipitate was dissolved in the minimal quantity of CH₂Cl₂, and crystals of the composition $[Pd_2(chp)_4]$, compound 2, were grown by slow diffusion of hexane into the concentrated CH₂Cl₂ solution.

Crystals of composition $[Pd_2(chp)_4] \cdot 0.5CHCl_3$, compound 3, were obtained after an unsuccessful attempt to add CH₃I oxidatively to the dimeric complex. They were grown by slow evaporation of a CHCl₃ solution in air over the course of several days.

Preparation of $[Pd_2(mhp)_4] \cdot 1.2CHCl_3$ (4). A mixture of palladium acetate (0.50 g, 0.74 mmol) and Na(mhp) (0.58 g, 4.45 mmol) in 50 mL of CH₂Cl₂ was stirred at room temperature for 48 h. A small amount of solid was removed by filtration through Celite, and the solution was evaporated to dryness in vacuum. The orange solid remaining was then divided into two portions. One portion was dissolved in 30 mL of CHCl₃ and filtered through Celite. Crystals of the composition $[Pd_2(mhp)_4] \cdot 1.2CHCl_3$, compound 4, were obtained by slow evaporation of this solution over the course of several days.

The second portion of orange solid was treated with 15 mL of methanol at room temperature for 24 h. During this time, the solution, which was initially dark red-orange, became dark brown. After approximately 1 h a dark green-brown solid precipitated from the solution. The precipitate was subsequently filtered, washed with small portions of dry methanol, and dried under vacuum. Crystals of $[Pd_2(mhp)_4]$, compound 5, with orthorhombic symmetry were grown by slow diffusion of hexane into a concentrated CH₂Cl₂ solution of the dark solid obtained from methanol.

X-ray Crystallography for $[Pd_2(chp)_4] \cdot CHCl_3$ (1). Preliminary examination of the crystal showed it to have triclinic symmetry, and the space group was assumed to be $P\bar{1}$. Unit cell dimensions and other pertinent crystal data are included in Table I. Lorentz, polarization, and absorption corrections were applied.⁷ No decay of the crystal due to the loss of lattice solvent was observed during the course of data collection. The palladium atom positions were obtained from the Patterson function. Alternating difference Fourier maps and least-squares cycles revealed the remaining non-hydrogen atoms as well as a CHCl₃ molecule of solvation. Logical hydrogen atom positions for several of the pyridine ring hydrogen atoms were obtained from one of the final difference maps. The remaining hydrogen atom positions were calculated. All hydrogen atoms were subsequently refined with isotropic thermal parameters. All other atoms were refined with anisotropic thermal parameters. Full-matrix least-squares refinement converged to final residuals of $R = 0.025$ and $R_w = 0.038$. The largest peak in the final difference map was ca. $0.6 e/\text{\AA}^3$.

X-ray Crystallography for $[Pd_2(chp)_4]$ (2). Preliminary examination of the crystal showed it to have a primitive orthorhombic lattice with the unit cell parameters listed in Table I. Lorentz, polarization, and absorption corrections (by the ψ -scan method) were applied. The structure was successfully refined in the space group $Pbca$, which was determined from the systematic absences. The structure is isomorphous with that of $[Pd_2(mhp)_4]$ characterized by Clegg et al.¹ and the metal atom positions were taken from that structure. The remaining non-hydrogen atoms were located from alternating difference Fourier maps and least-squares cycles. No attempts were made to locate the hydrogen atoms. All atoms were refined with anisotropic thermal parameters. Full-matrix least-squares refinement converged to final residuals of $R = 0.039$ and $R_w = 0.051$. The largest peak in the final difference map was ca. $1.0 e/\text{\AA}^3$ and was located near one of the palladium atom positions.

X-ray Crystallography for $[Pd_2(chp)_4] \cdot 0.5CHCl_3$ (3). Preliminary examination of the crystal showed it to have triclinic symmetry, and the space group was assumed to be $P\bar{1}$. Unit cell dimensions and other pertinent crystal parameters are included in Table I. Lorentz, polarization, and absorption corrections were applied. The crystal showed no decay due to possible loss of lattice solvent during the course of data collection. The four heavy-atom positions for the two independent Pd_2L_4 molecules in the asymmetric unit were obtained from the direct methods program MULTAN 11/82. Alternating difference maps and least-squares cycles revealed the remaining non-hydrogen atoms as well as a CHCl₃ molecule of solvation. All atoms were refined with anisotropic thermal parameters with full-matrix least-squares refinement converging to residuals of $R = 0.042$ and $R_w = 0.053$. The largest peak in the final difference map was ca. $0.8 e/\text{\AA}^3$.

X-ray Crystallography for $[Pd_2(mhp)_4] \cdot 1.2CHCl_3$ (4). Preliminary examination of the crystal showed that it had triclinic symmetry with the unit cell parameters as listed in Table I. Lorentz, polarization, and absorption corrections were applied. An additional correction for isotropic crystal decay, which probably occurred from the loss of lattice solvent, was also applied. The structure was successfully refined in the triclinic space group $P\bar{1}$. The unit cell packing is unusual in that it contains five dinuclear molecules and six CHCl₃ molecules of solvation. The five independent palladium atom positions were obtained from the direct-methods program MULTAN 11/82. The remaining non-hydrogen atoms were located from alternating difference Fourier maps and least-squares cycles. The methylhydroxypyridine carbon atoms, with the exception of the bridgehead carbon atoms, were refined with isotropic thermal parameters in order to preserve a favorable data to parameter ratio. The solvent carbon atoms were also refined in a similar manner. All other atoms were refined with anisotropic thermal parameters. Full-matrix least-squares refinement converged to residuals of $R = 0.059$.

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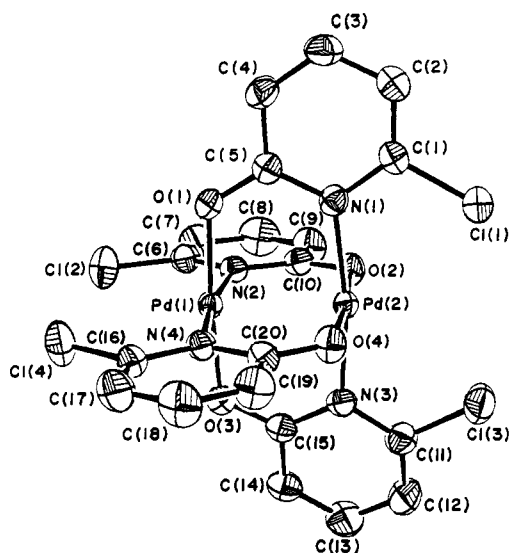
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(7) All calculations were carried out on PDP 11/60 or VAX 11/780 computers with use of the Enraf-Nonius CAD 4-SDP-PLUS programs. This crystallographic computing package is described by: Frenz, B. A. In "Computing in Crystallography"; Schenk, H., Olthof-Hazekamp, R., van Koningsveld, H., Bassi, G. C., Eds.; Delft University Press: Delft, Holland, 1978; pp 64-71. "Structure Determination Package and SDP-Plus User's Guide"; B. A. Frenz & Associates, Inc.: College Station, TX, 1982.

Table I. Crystal Data

	$[Pd_2(chp)_4] \cdot CHCl_3$ (1)	$[Pd_2(chp)_4]$ (2)	$[Pd_2(chp)_4] \cdot 0.5CHCl_3$ (3)	$[Pd_2(mhp)_4] \cdot 1.2CHCl_3$ (4)
fw	846.33	726.96	780.60	788.54
space group	$P\bar{1}$	$Pbca$	$P\bar{1}$	$P\bar{1}$
systematic absences	none	$0kl, k = 2n + 1; hOl, l = 2n + 1; hko, h = 2n + 1$	none	none
$a, \text{\AA}$	10.407 (3)	15.492 (8)	11.167 (3)	12.944 (2)
$b, \text{\AA}$	16.739 (3)	16.012 (13)	14.595 (4)	26.461 (4)
$c, \text{\AA}$	8.811 (2)	18.719 (8)	16.895 (4)	11.390 (2)
α, deg	102.30 (2)	90.0	100.77 (2)	100.43 (1)
β, deg	110.43 (2)	90.0	102.36 (2)	92.67 (1)
γ, deg	79.04 (2)	90.0	101.21 (2)	78.68 (1)
$V, \text{\AA}^3$	1394 (1)	4643.5 (5)	2562 (1)	3761.8 (9)
Z	2	8	4	5
$d_{\text{calcd}}, \text{g/cm}^3$	2.016	2.080	2.023	1.740
cryst size, mm	$0.3 \times 0.4 \times 0.5$	$0.5 \times 0.5 \times 0.4$	$0.4 \times 0.4 \times 0.3$	$0.3 \times 0.4 \times 0.4$
$\mu(\text{Mo}, K\alpha), \text{cm}^{-1}$	19.873	20.305	20.00	15.385
data collecn instrument	CAD-4	Syntax P3	Syntax P3	Syntax P3
radiation (monochromated in incident beam)	Mo $K\alpha$ ($\lambda = 0.71073 \text{\AA}$)	d	d	d
orientation reflcns: no.; range (2θ), deg	25; 22–29	25; 15–24	25; 20–30	25; 20–29
temp, $^\circ\text{C}$	25	25	25	25
scan method	$\theta-2\theta$	$\theta-2\theta$	$\theta-2\theta$	$\theta-2\theta$
data collecn range, 2θ , deg	4.0–50.0	3.0–45.0	4.0–45.0	4.0–45.0
no. of unique data, total with $F_o^2 > 3\sigma(F_o^2)$	3881, 3610	2292, 1855	5591, 3743	4632, 4288
no. of parameters refined	395	307	649	624
transmission factors: max, min, %	99.87, 85.20	99.80, 76.11	99.92, 84.75	99.78, 91.07
R^a	0.025	0.039	0.042	0.059
R_w^b	0.038	0.051	0.053	0.090
quality of fit indicator ^c	1.231	1.17	1.005	1.878
largest shift/esd, final cycle	0.14	0.00	0.10	0.05
largest peak, $e/\text{\AA}^3$	0.605	1.029	0.795	2.889

^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^b $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_c|)$. ^c Quality of fit = $[\sum w(|F_o| - |F_c|)^2 / (N_{\text{observns}} - N_{\text{parameters}})]^{1/2}$. ^d As for compound 1.

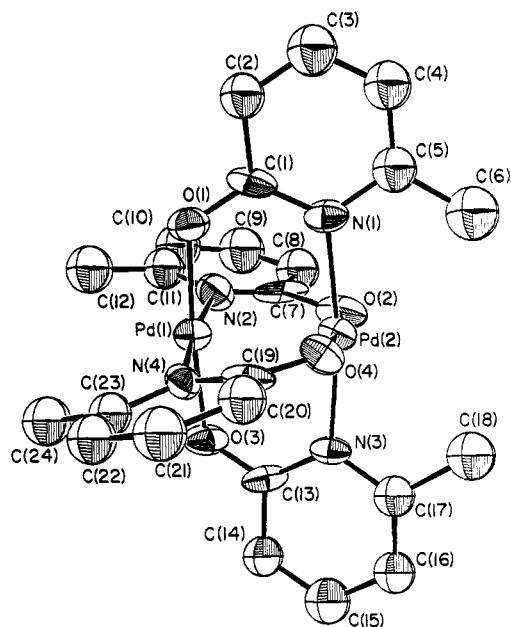
Figure 1. ORTEP view of $[Pd(chp)_4]$.

and $R_w = 0.090$. The largest peak in the final difference map was ca. $2.9 e/\text{\AA}^3$ and was located near one of the Pd atoms.

Results

Structures of the $[Pd_2(chp)_4] \cdot nCHCl_3$ Compounds, 1–3. Figure 1 shows a representative ORTEP view of the dinuclear unit. Tables II–IV contain final positional and thermal parameters for the three structures. Tables V and VI list some selected bond lengths and angles, respectively. All three structures contain virtually the same dinuclear Pd(II) molecule residing in each case on a general position.

The dinuclear unit is of type II with virtual D_{2d} symmetry, and the Pd–Pd distances range from 2.563 (1) to 2.570 (1) \AA , with a mean value of 2.567 [2] \AA . All other bond lengths and the various bond angles are identical within experimental error in all three compounds. The average Pd–N and Pd–O bond lengths are 2.043 [14] and 2.013 [10] \AA , respectively. The ligand chlorine

Figure 2. ORTEP view of $trans-[Pd_2(mhp)_4]$.

atoms at each end of the dimeric molecule effectively block the axial positions, preventing the binding of additional axial ligands to the metal atoms. The fact that, depending upon the method of crystallization, 0, 0.5, or 1 molecule of crystallization solvent was present per $[Pd_2(chp)_4]$ molecule is clearly of no chemical importance.

Structure of $[Pd_2(mhp)_4] \cdot 1.2CHCl_3$ (4). Table VII contains final positional and thermal parameters. Figure 2 shows an ORTEP view of one of the two D_{2d} dinuclear molecules, and Tables V and VI list selected bond lengths and angles.

The unit cell contains five dinuclear Pd(II) molecules with four of the five molecules residing on general positions in the crystal lattice. The fifth molecule resides on an inversion center. Four of the five molecules are related in pairs by inversion centers, so

Table II. Positional and Thermal Parameters for $[\text{Pd}_2(\text{chp})_4]\cdot\text{CHCl}_3$

atom	x	y	z	$B,^a \text{ \AA}^2$
Pd(1)	0.34492 (2)	0.33120 (1)	0.05789 (2)	2.072 (5)
Pd(2)	0.54361 (2)	0.21515 (1)	0.14104 (2)	2.079 (5)
Cl(1)	0.86287 (9)	0.17062 (6)	0.2125 (1)	4.11 (2)
Cl(2)	0.1302 (1)	0.39989 (6)	-0.2516 (1)	4.27 (2)
Cl(3)	0.6048 (1)	0.04044 (6)	0.2468 (1)	4.69 (2)
Cl(4)	0.1839 (1)	0.48627 (7)	0.2114 (1)	4.53 (2)
Cl(5)	0.7430 (1)	0.16581 (8)	0.7525 (1)	6.36 (3)
Cl(6)	0.9094 (2)	0.2613 (1)	0.6883 (2)	8.87 (4)
Cl(7)	0.9429 (2)	0.0867 (1)	0.5943 (2)	12.32 (6)
O(1)	0.4872 (2)	0.3972 (1)	0.0555 (2)	2.73 (5)
O(2)	0.5048 (2)	0.1726 (1)	-0.1002 (2)	2.81 (5)
O(3)	0.2157 (2)	0.2559 (1)	0.0589 (2)	2.90 (5)
O(4)	0.5674 (2)	0.2650 (2)	0.3757 (2)	3.01 (5)
N(1)	0.6686 (3)	0.2922 (2)	0.1273 (3)	2.49 (5)
N(2)	0.3250 (3)	0.2773 (2)	-0.1784 (3)	2.45 (5)
N(3)	0.3946 (3)	0.1500 (2)	0.1365 (3)	2.58 (5)
N(4)	0.3872 (3)	0.3709 (2)	0.3053 (3)	2.61 (5)
C(1)	0.8052 (3)	0.2676 (2)	0.1542 (4)	2.76 (7)
C(2)	0.8949 (3)	0.3110 (2)	0.1371 (4)	3.29 (8)
C(3)	0.8407 (4)	0.3878 (2)	0.0891 (4)	3.68 (8)
C(4)	0.7043 (4)	0.4160 (2)	0.0628 (4)	3.17 (7)
C(5)	0.6157 (3)	0.3679 (2)	0.0823 (3)	2.45 (6)
C(6)	0.2245 (3)	0.3088 (2)	-0.3051 (4)	2.88 (7)
C(7)	0.1947 (4)	0.2734 (3)	-0.4645 (4)	4.3 (1)
C(8)	0.2755 (5)	0.1997 (3)	-0.5000 (4)	4.7 (1)
C(9)	0.3778 (4)	0.1656 (3)	-0.3774 (4)	3.87 (9)
C(10)	0.4048 (3)	0.2058 (2)	-0.2125 (3)	2.70 (7)
C(11)	0.4287 (4)	0.0722 (2)	0.1698 (4)	3.21 (7)
C(12)	0.3370 (4)	0.0196 (2)	0.1453 (5)	4.26 (9)
C(13)	0.1995 (4)	0.0483 (2)	0.0830 (5)	4.32 (9)
C(14)	0.1584 (3)	0.1266 (2)	0.0494 (4)	3.36 (8)
C(15)	0.2580 (3)	0.1799 (2)	0.0807 (3)	2.62 (7)
C(16)	0.3136 (3)	0.4392 (2)	0.3619 (4)	2.90 (7)
C(17)	0.3338 (4)	0.4706 (3)	0.5213 (4)	4.01 (9)
C(18)	0.4411 (4)	0.4317 (3)	0.6370 (4)	4.15 (9)
C(19)	0.5179 (4)	0.3624 (2)	0.5869 (4)	3.70 (9)
C(20)	0.4924 (3)	0.3309 (2)	0.4187 (3)	2.66 (7)
C(21)	0.8277 (5)	0.1731 (3)	0.6171 (5)	4.7 (1)
H(1)	-0.006 (4)	0.290 (2)	0.154 (4)	3.8 (8)*
H(2)	0.909 (5)	0.417 (3)	0.068 (5)	6 (1)*
H(3)	0.659 (4)	0.464 (2)	0.034 (4)	3.9 (9)*
H(4)	0.121 (4)	0.297 (3)	-0.559 (4)	5 (1)*
H(5)	0.240 (6)	0.179 (4)	0.397 (6)	9 (2)*
H(6)	0.425 (5)	0.108 (3)	-0.418 (5)	6 (1)*
H(7)	0.349 (4)	0.982 (2)	0.145 (4)	3.7 (8)*
H(8)	0.138 (5)	0.022 (3)	0.059 (5)	8 (1)*
H(9)	0.064 (4)	0.150 (3)	0.002 (4)	5 (1)*
H(10)	0.271 (4)	0.515 (3)	0.543 (4)	5 (1)*
H(11)	0.461 (4)	0.447 (3)	0.733 (4)	5 (1)*
H(12)	0.596 (4)	0.340 (3)	0.670 (4)	5 (1)*
H(13)	0.738 (4)	0.191 (2)	0.517 (4)	4.1 (9)*

^a Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $\frac{1}{3}[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos \gamma)\beta_{12} + ac(\cos \beta)\beta_{13} + bc(\cos \alpha)\beta_{23}]$.

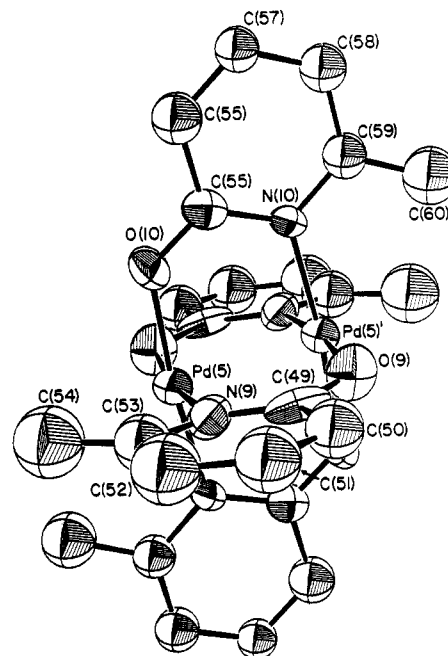
that there are two independent molecules on general positions. Two, which are essentially identical with only minor, insignificant differences in the bond lengths and angles, possess approximate D_{2d} symmetry, II, with slight distortions caused by a small torsional twist about the metal-metal axis. The average Pd-Pd separation is 2.547 [6] Å, and the average Pd-N and Pd-O bond distances are 2.050 [15] and 2.005 [11] Å, respectively. The ligand methyl groups effectively block the axial positions, preventing the coordination of axial ligands to the metal atoms.

The molecule residing on the inversion center is qualitatively different from the other four. It has the C_{2h} arrangement, III, of bridging ligands, as shown in Figure 3. The Pd-Pd distance, 2.559 (3) Å, is slightly longer than the distance in the other molecules. Other selected bond lengths and bond angles for this molecule are listed in Tables V and VI. The average Pd-N and Pd-O bond distances are 2.024 [13] and 1.998 [6] Å, respectively. The axial positions are unoccupied, presumably because of steric interference from the ligand methyl groups.

Table III. Positional and Thermal Parameters for $[\text{Pd}_2(\text{chp})_4]$

atom	x	y	z	$B,^a \text{ \AA}^2$
Pd(1)	0.12789 (5)	0.16280 (4)	0.06697 (4)	2.59 (1)
Pd(2)	0.12428 (5)	0.20742 (5)	0.19840 (4)	2.88 (1)
Cl(1)	0.6142 (3)	0.3680 (2)	0.2063 (2)	6.61 (9)
Cl(2)	0.3953 (2)	0.6292 (2)	0.3509 (1)	5.71 (7)
Cl(3)	0.5091 (2)	0.4091 (2)	0.0512 (1)	3.73 (6)
Cl(4)	0.2477 (2)	0.3445 (2)	0.4340 (1)	5.94 (8)
O(1)	0.2536 (4)	0.2159 (4)	0.1920 (3)	3.5 (1)
O(2)	0.1046 (4)	0.2832 (4)	0.0409 (3)	3.4 (1)
O(3)	-0.0031 (4)	0.1955 (5)	0.1971 (3)	3.5 (1)
O(4)	0.1547 (4)	0.0465 (4)	0.1013 (4)	3.6 (2)
N(1)	0.2559 (5)	0.1861 (5)	0.0705 (4)	2.8 (2)
N(2)	0.1125 (5)	0.3262 (5)	0.1594 (4)	3.2 (2)
N(3)	-0.0016 (5)	0.1426 (5)	0.0795 (4)	2.7 (2)
N(4)	0.1353 (5)	0.0809 (5)	0.2195 (4)	3.4 (2)
C(11)	0.2961 (6)	0.2077 (5)	0.1329 (5)	2.7 (2)
C(12)	0.3893 (6)	0.2223 (6)	0.1340 (6)	3.6 (2)
C(13)	0.4343 (7)	0.2151 (6)	0.0709 (6)	4.2 (3)
C(14)	0.3936 (6)	0.1937 (6)	0.0055 (6)	4.1 (3)
C(15)	0.3065 (7)	0.1814 (6)	0.0096 (6)	3.6 (2)
C(21)	0.1070 (6)	0.3417 (6)	0.0879 (5)	3.3 (2)
C(22)	0.1009 (7)	0.4243 (7)	0.0624 (6)	4.7 (3)
C(23)	0.1004 (9)	0.4903 (7)	0.1101 (7)	5.7 (3)
C(24)	0.1051 (8)	0.4750 (7)	0.1829 (6)	5.5 (3)
C(25)	0.1091 (7)	0.3931 (7)	0.2032 (5)	4.1 (2)
C(31)	-0.0430 (6)	0.1617 (6)	0.1427 (5)	3.4 (2)
C(32)	-0.1342 (6)	0.1449 (7)	0.1483 (6)	4.0 (2)
C(33)	-0.1760 (7)	0.1081 (8)	0.0927 (6)	4.5 (3)
C(34)	-0.1341 (6)	0.0903 (7)	0.0290 (6)	4.5 (3)
C(35)	-0.0484 (6)	0.1091 (6)	0.0260 (5)	3.2 (2)
C(41)	0.1486 (6)	0.0244 (6)	0.1678 (5)	3.3 (2)
C(42)	0.1602 (8)	-0.0614 (7)	0.1843 (6)	5.0 (3)
C(43)	0.1524 (8)	-0.0865 (8)	0.2541 (7)	5.9 (3)
C(44)	0.1328 (8)	-0.0278 (8)	0.3087 (6)	5.6 (3)
C(45)	0.1257 (6)	0.0535 (7)	0.2884 (5)	4.1 (2)

^a Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $\frac{1}{3}[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos \gamma)\beta_{12} + ac(\cos \beta)\beta_{13} + bc(\cos \alpha)\beta_{23}]$.

**Figure 3.** ORTEP view of *cis*- $[\text{Pd}_2(\text{mhp})_4]$.

In addition to the five Pd(II) molecules, the unit cell contains six molecules of CHCl_3 present as solvent molecules of crystallization. There are no special or close contacts with the five dinuclear molecules.

Discussion

Preparative Procedures. The preparative method originally reported by Clegg et al.¹ does indeed lead to the observed product,

Table IV. Positional and Thermal Parameters for [Pd₂(chp)₄] \cdot 0.5CHCl₃

atom	x	y	z	B, ^a Å ²	atom	x	y	z	B, ^a Å ²
Pd(1)	0.37058 (8)	0.25754 (7)	0.35895 (5)	2.35 (2)	C(6)	0.384 (1)	0.6383 (9)	0.5265 (7)	3.0 (3)
Pd(2)	0.54902 (8)	0.17108 (7)	0.35379 (6)	2.47 (2)	C(7)	0.305 (1)	0.559 (1)	0.4607 (9)	4.7 (4)
Pd(3)	0.27104 (8)	0.28382 (7)	0.84627 (5)	2.33 (2)	C(8)	0.181 (1)	0.562 (1)	0.430 (1)	5.5 (4)
Pd(4)	0.05917 (8)	0.33195 (7)	0.81739 (6)	2.67 (2)	C(9)	0.135 (2)	0.641 (1)	0.457 (1)	6.4 (5)
Cl(1)	0.2178 (3)	0.3747 (3)	0.2612 (2)	5.28 (9)	C(10)	0.216 (1)	0.714 (1)	0.5193 (8)	4.0 (3)
Cl(2)	0.1688 (4)	0.8147 (3)	0.5605 (3)	6.3 (1)	C(11)	0.415 (1)	0.1366 (8)	0.4807 (7)	2.7 (3)
Cl(3)	0.1695 (3)	0.2927 (3)	0.4545 (2)	4.34 (9)	C(12)	0.397 (1)	0.1009 (8)	0.5520 (7)	3.0 (3)
Cl(4)	0.3927 (3)	0.0044 (3)	0.7562 (2)	4.63 (9)	C(13)	0.310 (1)	0.1282 (9)	0.5925 (8)	3.7 (3)
Cl(5)	0.5119 (3)	0.2904 (3)	0.7801 (2)	5.3 (1)	C(14)	0.236 (1)	0.1884 (9)	0.5646 (8)	3.9 (3)
Cl(6)	0.0644 (3)	0.5000 (3)	0.1362 (3)	5.5 (1)	C(15)	0.256 (1)	0.2197 (9)	0.4942 (8)	3.1 (3)
Cl(7)	0.4277 (3)	0.1743 (3)	0.9581 (2)	5.2 (1)	C(16)	0.290 (1)	0.0677 (9)	0.2466 (7)	2.9 (3)
Cl(8)	0.2218 (3)	0.7427 (3)	0.2905 (3)	5.9 (1)	C(17)	0.199 (1)	-1.0128 (8)	0.1921 (8)	3.2 (3)
Cl(9)	0.0644 (5)	0.8668 (5)	0.7669 (4)	13.2 (2)	C(18)	0.235 (1)	0.909 (1)	0.153 (1)	4.7 (4)
Cl(10)	0.1122 (5)	0.6861 (5)	0.7774 (5)	15.3 (3)	C(19)	0.368 (1)	0.910 (1)	0.1660 (9)	4.4 (4)
Cl(11)	0.2523 (6)	0.8477 (6)	0.9043 (4)	12.8 (2)	C(20)	0.447 (1)	-1.0100 (9)	0.2221 (7)	3.0 (3)
O(1)	0.4108 (7)	0.7601 (6)	0.7336 (5)	3.3 (2)	C(21)	0.224 (1)	0.4005 (9)	0.7180 (8)	3.6 (3)
O(2)	0.4974 (7)	0.6329 (6)	0.5586 (5)	3.4 (2)	C(22)	0.261 (1)	0.454 (1)	0.6595 (9)	4.9 (4)
O(3)	0.4964 (7)	0.1116 (6)	0.4439 (5)	3.3 (2)	C(23)	0.370 (1)	0.455 (1)	0.6401 (9)	5.3 (4)
O(4)	0.2516 (7)	0.1384 (6)	0.2796 (5)	3.2 (2)	C(24)	0.457 (1)	0.404 (1)	0.6762 (8)	4.6 (4)
O(5)	0.1143 (8)	0.3947 (6)	0.7307 (5)	3.7 (2)	C(25)	0.418 (1)	0.3564 (9)	0.7330 (8)	3.4 (3)
O(6)	0.3423 (7)	0.4089 (6)	0.9323 (5)	3.0 (2)	C(26)	0.275 (1)	0.4708 (8)	0.9452 (7)	2.7 (3)
O(7)	0.0216 (7)	0.2677 (6)	0.9082 (5)	3.3 (2)	C(27)	0.335 (1)	0.5578 (9)	0.0073 (7)	3.4 (3)
O(8)	0.1825 (7)	0.1600 (6)	0.7588 (5)	3.2 (2)	C(28)	0.269 (1)	0.624 (1)	0.0253 (9)	4.8 (4)
N(1)	0.4167 (8)	0.3072 (7)	0.2624 (6)	2.7 (2)	C(29)	0.138 (1)	0.608 (1)	-1.0185 (9)	4.5 (4)
N(2)	0.3373 (9)	0.7144 (8)	0.5565 (6)	3.4 (3)	C(30)	0.091 (1)	0.5254 (9)	0.9222 (8)	3.8 (3)
N(3)	0.3442 (9)	0.1975 (7)	0.4548 (6)	2.9 (2)	C(31)	0.101 (1)	0.2310 (9)	0.9514 (8)	3.1 (3)
N(4)	0.4131 (9)	0.0651 (7)	0.2629 (6)	3.0 (2)	C(32)	0.068 (1)	0.195 (1)	0.0197 (8)	4.0 (3)
N(5)	0.3052 (9)	0.3511 (7)	0.7542 (6)	3.2 (3)	C(33)	0.145 (1)	0.154 (1)	0.0666 (9)	5.4 (4)
N(6)	0.1515 (8)	0.4561 (7)	0.9052 (6)	2.7 (2)	C(34)	0.261 (1)	0.143 (1)	-0.9513 (9)	4.8 (4)
N(7)	0.2125 (9)	0.2232 (7)	0.9351 (6)	2.8 (2)	C(35)	0.286 (1)	0.1795 (9)	-1.0166 (8)	3.4 (3)
N(8)	-0.0096 (9)	0.2016 (7)	0.7319 (6)	3.2 (3)	C(36)	0.066 (1)	0.1417 (9)	0.7190 (7)	2.9 (3)
C(1)	0.519 (1)	0.2921 (8)	0.2342 (7)	2.9 (3)	C(37)	-0.018 (1)	0.9448 (9)	0.3418 (8)	3.7 (3)
C(2)	0.451 (1)	0.667 (1)	0.8299 (7)	3.7 (3)	C(38)	0.107 (1)	0.970 (1)	0.388 (1)	5.5 (4)
C(3)	0.477 (1)	0.384 (1)	0.1322 (8)	4.2 (4)	C(39)	0.184 (2)	0.907 (1)	0.375 (1)	6.3 (5)
C(4)	0.368 (1)	0.399 (1)	0.1592 (8)	4.4 (4)	C(40)	0.132 (1)	0.823 (1)	0.3136 (8)	4.0 (3)
C(5)	0.346 (1)	0.359 (1)	0.2236 (7)	3.5 (3)	C(41)	0.180 (1)	0.808 (1)	0.796 (1)	8.5 (5)

^a Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $\frac{1}{3}[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos \gamma)\beta_{12} + ac(\cos \beta)\beta_{13} + bc(\cos \alpha)\beta_{23}]$.

Table V. Selected Bond Distances (Å)

compd	Pd-Pd	Pd-O	Pd-N	O-C	N-C	X-C
[Pd ₂ (chp) ₄] \cdot CHCl ₃	2.570 (1)	2.012 [6]	2.045 [5]	1.293 [3]	1.360 [8]	1.732 [9]
[Pd ₂ (chp) ₄]	2.563 (1)	2.007 [17]	2.046 [22]	1.296 [9]	1.363 [16]	1.729 [12]
[Pd ₂ (chp) ₄] \cdot CHCl ₃	2.568 [4]	2.015 [7]	2.041 [14]	1.29 [1]	1.36 [1]	1.72 [1]
<i>cis</i> -[Pd ₂ (mhp) ₄]	2.559 (3)	1.999 [6]	2.024 [13]	1.26 [1]	1.36 [2]	1.44 [2]
<i>trans</i> -[Pd ₂ (mhp) ₄]	2.547 [6]	2.005 [11]	2.050 [15]	1.31 [4]	1.37 [3]	1.51 [3]

Table VI. Selected Bond Angles (deg)

angle	compd				
	1	2	3	<i>cis</i> -4	<i>trans</i> -4
O-Pd-O	174.8 [2]	175.3 [4]	174.0 [4]	88.7 (7)	174.8 [3]
N-Pd-N	171.4 [1]	170.8 [9]	171.7 [1]	94.8 (7)	172.5 [10]
O-Pd-N (<i>cis</i>)	89.8 [12]	89.8 [10]	89.8 [8]	87.8 [1]	89.8 [14]
O-Pd-N (<i>trans</i>)				172.4 [4]	
Pd-N-C	120.8 [5]	121.1 [10]	120.6 [12]	119 [4]	120 [1]
Pd-O-C	122.7 [6]	122.4 [10]	122.4 [10]	124 [1]	122 [2]
O-C-N	122.4 [4]	122.1 [7]	122 [1]	125 [1]	123 [1]
X-C-N	115.0 [4]	114.2 [13]	115 [1]	117 [1]	116 [1]

[Pd₂(mhp)₄]. Under similar conditions the chp analogue can also be prepared. In both cases, the orange-brown intermediate smoothly reacts with methanol, in the manner indicated, giving the respective products. It is important to note, however, that care must be taken to control the reaction conditions when the intermediate is reacted with methanol. Substantial reduction of the complexes to elemental palladium tended to occur if longer times than indicated were used or if heat was applied to the reaction mixture. The products obtained are similar, both containing a Pd₂⁴⁺ unit bridged by four anionic ligands, which have the type II arrangement, with D_{2d} symmetry. We have found that, in both cases, the preparative procedure is improved by using only the stoichiometrically necessary quantity of Na(chp) or Na(mhp).

The use of an excess seems only to make product purification more difficult.

One of the puzzling observations of Clegg et al.¹ was that in preparing [Pd₂(mhp)₄] they first obtained an orange or orange-brown intermediate, for which they proposed the formula Na₂Pd(mhp)₃(O₂CCH₃), on the basis of elemental analyses. This was transformed to [Pd₂(mhp)₄] simply by stirring it with methanol for 24 h at room temperature. This seemed to us to be somewhat odd, and we devoted considerable attention to this aspect of the procedure. In preparing [Pd₂(mhp)₄], we obtained the orange intermediate, as described by Clegg et al.,¹ and found that it was indeed transformed to [Pd₂(mhp)₄] essentially as they reported. We found that a similar orange intermediate was formed

Table VII. Positional and Thermal Parameters for $[\text{Pd}_2(\text{mhp})_4] \cdot 1.2\text{CHCl}_3$

atom	x	y	z	$B, \text{\AA}^2$	atom	x	y	z	$B, \text{\AA}^2$
Pd(1)	0.1035 (1)	0.24426 (7)	0.0123 (2)	3.16 (4)	C(16)	0.395 (2)	0.3463 (9)	0.260 (2)	4.1 (5)*
Pd(2)	0.0955 (1)	0.29668 (7)	0.2232 (2)	3.08 (4)	C(17)	0.298 (2)	0.3349 (9)	0.277 (2)	4.0 (5)*
Pd(3)	0.7458 (1)	0.03263 (6)	0.3659 (1)	2.38 (4)	C(18)	0.248 (2)	0.348 (1)	0.403 (2)	5.3 (6)*
Pd(4)	0.7163 (1)	0.06596 (6)	0.1681 (1)	2.32 (4)	C(19)	0.208 (2)	0.1900 (8)	0.204 (2)	3.7 (6)
Pd(5)	0.4449 (1)	0.49790 (7)	0.9036 (2)	3.23 (4)	C(20)	0.261 (2)	0.1467 (9)	0.256 (2)	4.4 (6)*
Cl(1)	0.7883 (7)	0.1582 (3)	0.7979 (7)	7.6 (2)	C(21)	0.315 (2)	0.104 (1)	0.176 (2)	5.4 (6)*
Cl(2)	0.5744 (7)	0.2044 (4)	0.7537 (8)	8.6 (3)	C(22)	0.313 (2)	0.101 (1)	0.055 (2)	4.8 (6)*
Cl(3)	0.7410 (7)	0.2137 (3)	0.6033 (7)	9.8 (2)	C(23)	0.258 (2)	0.1457 (9)	0.010 (2)	3.8 (5)*
Cl(4)	0.8553 (7)	0.6679 (4)	0.3147 (8)	10.0 (3)	C(24)	0.745 (2)	0.852 (1)	0.124 (2)	5.3 (6)*
Cl(5)	0.6333 (7)	0.6886 (5)	0.2902 (9)	12.7 (3)	C(25)	0.576 (1)	-0.0024 (7)	0.202 (2)	2.3 (5)
Cl(6)	0.737 (1)	0.7743 (5)	0.375 (1)	15.0 (4)	C(26)	0.492 (2)	0.9704 (8)	0.171 (2)	3.0 (5)*
Cl(7)	0.5329 (8)	0.5554 (4)	0.4562 (9)	9.8 (3)	C(27)	0.460 (2)	0.9379 (9)	0.244 (2)	4.7 (6)*
Cl(8)	0.4259 (8)	0.6585 (4)	0.4436 (9)	10.5 (3)	C(28)	0.518 (2)	0.9324 (9)	0.353 (2)	4.3 (5)*
Cl(9)	0.3110 (8)	0.5759 (5)	0.4215 (9)	10.8 (3)	C(29)	0.600 (2)	0.9599 (8)	0.382 (2)	3.1 (5)*
O(1)	-0.024 (1)	0.2176 (5)	0.050 (1)	3.7 (4)	C(30)	0.667 (2)	0.9549 (9)	0.494 (2)	4.1 (5)*
O(2)	0.023 (1)	0.3589 (5)	0.151 (1)	4.7 (4)	C(31)	0.590 (2)	0.1306 (8)	0.373 (2)	3.3 (5)
O(3)	0.228 (1)	0.2765 (6)	-0.013 (1)	3.8 (4)	C(32)	0.516 (2)	0.1717 (9)	0.434 (2)	3.7 (5)*
O(4)	0.165 (1)	0.2307 (5)	0.281 (1)	3.3 (4)	C(33)	0.461 (2)	0.2099 (9)	0.368 (2)	4.5 (6)*
O(5)	0.601 (1)	0.0251 (5)	0.134 (1)	2.7 (3)	C(34)	0.479 (2)	0.2068 (9)	0.245 (2)	3.9 (5)*
O(6)	0.641 (1)	0.0959 (5)	0.437 (1)	3.0 (3)	C(35)	0.552 (2)	0.1657 (8)	0.190 (2)	3.3 (5)*
O(7)	0.833 (1)	0.1053 (5)	0.218 (1)	2.7 (3)	C(36)	0.574 (2)	0.1563 (9)	0.059 (2)	4.4 (6)*
O(8)	0.849 (1)	-0.0279 (5)	0.282 (1)	3.3 (4)	C(37)	0.884 (2)	0.1041 (8)	0.318 (2)	2.7 (5)
O(9)	0.432 (1)	0.4857 (6)	0.170 (1)	4.8 (4)	C(38)	0.967 (2)	0.1337 (9)	0.345 (2)	3.7 (5)*
O(10)	0.486 (1)	0.5779 (6)	0.129 (1)	4.4 (4)	C(39)	0.022 (2)	0.1329 (9)	0.454 (2)	4.1 (5)*
N(1)	-0.045 (1)	0.2736 (6)	0.237 (2)	3.2 (4)	C(40)	0.001 (2)	0.8961 (9)	0.470 (2)	3.9 (5)*
N(2)	0.003 (1)	0.3061 (7)	0.964 (2)	4.0 (5)	C(41)	0.919 (2)	0.0753 (8)	0.506 (2)	3.1 (5)*
N(3)	0.241 (1)	0.3107 (6)	0.187 (1)	2.9 (4)	C(42)	0.109 (2)	0.9587 (9)	0.414 (2)	3.7 (5)*
N(4)	0.203 (1)	0.1872 (6)	0.083 (1)	2.9 (4)	C(43)	0.871 (2)	0.9669 (8)	0.167 (2)	3.0 (5)
N(5)	0.627 (1)	-0.0076 (6)	0.313 (2)	3.0 (4)	C(44)	0.946 (2)	0.9217 (8)	0.120 (2)	3.1 (5)*
N(6)	0.608 (1)	0.1264 (6)	0.256 (1)	2.9 (4)	C(45)	0.028 (2)	0.0861 (9)	-0.003 (2)	4.0 (5)*
N(7)	0.863 (1)	0.0761 (6)	0.401 (1)	2.8 (4)	C(46)	0.079 (2)	0.0496 (9)	0.069 (2)	4.2 (5)*
N(8)	0.825 (1)	0.0007 (6)	0.098 (1)	2.7 (4)	C(47)	0.150 (2)	0.0049 (8)	0.019 (2)	2.9 (5)*
N(9)	0.666 (1)	0.5221 (7)	0.004 (1)	3.9 (5)	C(48)	0.205 (2)	0.9656 (9)	0.090 (2)	3.7 (5)*
N(10)	0.609 (1)	0.4237 (6)	0.050 (1)	2.8 (4)	C(49)	0.350 (2)	0.4770 (7)	0.113 (2)	3.8 (6)
C(1)	0.922 (2)	0.2373 (8)	0.146 (2)	3.7 (6)	C(50)	0.272 (2)	0.462 (1)	0.183 (2)	5.6 (7)*
C(2)	0.827 (2)	0.2181 (9)	0.158 (2)	4.4 (6)*	C(51)	0.188 (2)	0.447 (1)	0.120 (3)	6.5 (7)*
C(3)	0.771 (2)	0.239 (1)	0.263 (2)	5.6 (7)*	C(52)	0.174 (2)	0.446 (1)	-0.006 (3)	7.6 (8)*
C(4)	0.805 (2)	0.275 (1)	0.353 (2)	5.0 (6)*	C(53)	0.750 (2)	0.540 (1)	0.066 (2)	5.5 (6)*
C(5)	0.897 (2)	0.2934 (9)	0.340 (2)	4.5 (6)*	C(54)	0.752 (3)	0.544 (1)	0.195 (3)	8.9 (9)*
C(6)	0.941 (2)	0.334 (1)	0.432 (2)	6.4 (7)*	C(55)	0.420 (2)	0.5997 (8)	0.060 (2)	3.4 (5)
C(7)	0.015 (2)	0.6495 (9)	0.962 (2)	4.2 (6)	C(56)	0.376 (2)	0.656 (1)	0.097 (2)	4.8 (6)*
C(8)	0.920 (2)	0.398 (1)	0.007 (2)	5.5 (6)*	C(57)	0.689 (2)	0.3165 (9)	0.979 (2)	3.7 (5)*
C(9)	0.121 (2)	0.608 (1)	0.107 (2)	6.4 (7)*	C(58)	0.717 (2)	0.3425 (9)	0.090 (2)	4.4 (6)*
C(10)	0.108 (2)	0.654 (1)	0.182 (2)	6.2 (7)*	C(59)	0.672 (2)	0.3957 (9)	0.124 (2)	4.0 (5)*
C(11)	0.043 (2)	0.6972 (9)	0.144 (2)	4.6 (6)*	C(60)	0.686 (2)	0.420 (1)	0.244 (3)	6.5 (7)*
C(12)	0.020 (2)	0.749 (1)	0.223 (2)	6.2 (7)*	C(61)	0.696 (2)	0.1730 (9)	0.684 (2)	5.2 (7)
C(13)	0.278 (2)	0.2987 (8)	0.073 (2)	3.3 (5)	C(62)	0.429 (2)	0.591 (1)	0.389 (2)	6.2 (8)
C(14)	0.378 (2)	0.3101 (9)	0.051 (2)	4.0 (5)*	C(63)	0.741 (2)	0.719 (2)	0.284 (3)	11 (1)
C(15)	0.434 (2)	0.335 (1)	0.144 (2)	5.2 (6)*					

*Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $\frac{1}{3}[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos \gamma)\beta_{12} + ac(\cos \beta)\beta_{13} + bc(\cos \alpha)\beta_{23}]$.

in the preparation of $[\text{Pd}_2(\text{chp})_4]$. In both cases we failed to recrystallize these intermediates from CH_2Cl_2 , obtaining only powders in each case.

Recrystallization from chloroform was then tried in each case, and each time we obtained crystals of composition $[\text{Pd}_2\text{L}_4] \cdot n\text{CHCl}_3$, where $\text{L} = \text{mhp}$ or chp . With chp , we obtained two crystallographically different solvates, **1** and **3**, with $n = 1$ and 0.5 , respectively. Both of these contained only molecules of type II that were essentially identical with each other and with the $[\text{Pd}_2(\text{chp})_4]$ molecules in **2**, obtained by treating the orange intermediate with methanol. Moreover, compound **2** is crystallographically isomorphous with Clegg et al.'s¹ $[\text{Pd}_2(\text{mhp})_4]$ (**5**).

When the orange intermediate in the preparation of $[\text{Pd}_2(\text{mhp})_4]$ was recrystallized from chloroform, we obtained compound **4**, $[\text{Pd}_2(\text{mhp})_4] \cdot 6\text{CHCl}_3$, which contains a mixture of two isomers of the $[\text{Pd}_2(\text{mhp})_4]$ molecule. Four of them have the D_{2d} structure II, while the other one has the C_{2h} structure III.

We are led by this last observation to speculate that perhaps the orange intermediates in these preparations might be the cisoid (C_{2h}) type $[\text{Pd}_2\text{L}_4]$ molecules, which then rearrange upon treatment with methanol or other solvents. This hypothesis is consistent with the rather mild conditions under which the D_{2d} $[\text{Pd}_2\text{L}_4]$

products are obtained from the intermediates. The true identity of the orange intermediates is a subject requiring further study.

Structural Comparisons. The $[\text{Pd}_2(\text{chp})_4]$ and $[\text{Pd}_2(\text{mhp})_4]$ molecules of type II are very similar, but there is a difference of ca. 0.020 \AA in the Pd-Pd bond distances. It is interesting to note that essentially the same difference was found in comparing the $[\text{Mo}_2(\text{chp})_4]$ and $[\text{Mo}_2(\text{mhp})_4]$ molecules.⁸ In view of the fact that the molybdenum compounds have strong quadruple bonds while the palladium compounds have, as already noted, formal bond orders of zero, the basis of this similarity is not immediately obvious.

It can be seen in Table V that the two isomers of $[\text{Pd}_2(\text{mhp})_4]$ have very similar bond lengths. Even the apparent differences in the Pd-Pd distances, $0.012 (7) \text{ \AA}$, is barely, if at all, significant.

Finally, it should be noted that there are small torsional angles in all of the $[\text{Pd}_2\text{L}_4]$ molecules, as indicated in Table VIII. These probably arise because, in the absence of any barrier to such rotation in the Pd...Pd interaction, such as that may be, some relief of nonbonded (repulsive) contacts between pairs of methyl groups

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Table VIII. Selected Mean Torsional Angles (deg)

compd	mean O-Pd-Pd-N
[Pd ₂ (chp) ₄].CHCl ₃ (1)	0.4 [3]
[Pd ₂ (chp) ₄] (2)	6 [1]
[Pd ₂ (chp) ₄].0.5CHCl ₃ (3a) ^a	5 [1]
[Pd ₂ (chp) ₄].0.5CHCl ₃ (3b) ^a	0.2 [8]
<i>trans</i> -[Pd ₂ (mhp) ₄] (4a)	-11 [2]
<i>trans</i> -[Pd ₂ (mhp) ₄] (4b)	0 [1]
<i>cis</i> -[Pd ₂ (mhp) ₄] (4c)	2.92 [6]

^aCrystallographically independent molecules in the same crystal lattice.

or Cl atoms is achieved. Additionally, it should be noted that the torsional angles in compounds 3 and 4 are different for each of the two independent, but otherwise identical, molecules in the respective cells. These differences can probably be attributed to relief of intermolecular strain arising from crystal-packing forces. This type of behavior was observed in one other case,⁹ however,

with only one example it was not clear whether this was unusual or not. We can now ascertain that this type of behavior is not unusual and should be expected in the future.

In closing, we note again that the *cisoid* molecule of [Pd₂(mhp)₄] in compound 4 is the first observed example of a *cisoid* (C_{2h}) isomer of an [M₂(xhp)₄] molecule, although a few other *cisoid* [M₂(XYZ)₄] type molecules with other bridging ligands have been observed.²

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Supplementary Material Available: Tables of bond distances, bond angles, anisotropic thermal parameters, torsional angles, and observed and calculated structure factors (102 pages). Ordering information is given on any current masthead page.

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Reactions of Small Molecules with Re₂Cl₄(PEt₃)₄. 1. Structural and Spectroscopic Studies of Several Products Resulting from the Reaction with Carbon Monoxide

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The reaction of carbon monoxide at about 120 atm pressure with Re₂Cl₄(PEt₃)₄ in dichloromethane solution has been found to yield several products. The structures of four of them, *all-trans*-Re(CO)₂Cl₂(PEt₃)₂ (1), *mer*-Re(CO)₃Cl(PEt₃)₂ (2), *cis*-Re(CO)₄Cl(PEt₃) (3), and *trans*-ReCl₄(PEt₃)₂ (4), have been determined by single-crystal X-ray diffraction methods. The structure of the dicarbonyl compound is the first reported for the general class of 17-electron Re(II) compounds Re(CO)₂X₂(PR₃)₂. Infrared spectra were measured and Cotton-Kraihanzel calculations carried out on the carbonyl compounds. The combined structural and spectroscopic results are shown to exhibit the correlations expected for low-valent rhenium carbonyls. The salient data for each compound are as follows. 1: IR 1912 cm⁻¹; space group P2₁/c; unit cell *a* = 7.521 (1) Å, *b* = 10.853 (1) Å, *c* = 14.853 (2) Å, β = 118.25 (4)°, *V* = 1068 (1) Å³, *Z* = 2. 2: IR 2045, 1887, 1940 cm⁻¹; space group P1; unit cell *a* = 7.971 (1) Å, *b* = 9.107 (2) Å, *c* = 7.624 (2) Å, α = 95.25 (1)°, β = 92.23 (2)°, γ = 107.68 (1)°, *V* = 523.9 (3) Å³, *Z* = 1. 3: IR 2102, 1997, 1987, 1942 cm⁻¹; space group P2₁/n; unit cell *a* = 6.422 (1) Å, *b* = 14.761 (1) Å, *c* = 15.778 (2) Å, β = 94.80 (2)°, *V* = 1490.4 (6) Å³, *Z* = 4. 4: space group P1; unit cell *a* = 8.395 (8) Å, *b* = 8.698 (6) Å, *c* = 7.508 (7) Å, α = 96.19 (4)°, β = 93.04 (2)°, γ = 71.54 (3)°, *V* = 516.8 (6) Å³, *Z* = 1. The infrared spectra and CO stretching force constants are shown to correlate with the structures.

Introduction

It is now well-known that the reactions of π-acid ligands such as carbon monoxide, nitric oxide, and isocyanides with compounds containing triply and quadruply bonded dimetal cores characteristically afford products in which metal-metal bond rupture has occurred,^{2a} although in special cases bond retention occurs.^{2b} Not infrequently reduction accompanies this bond scission.³ We have undertaken a detailed study of the reactions of small molecules with the dimer Re₂Cl₄(PEt₃)₄ and have found that several products are formed in the reaction of this species with CO. Walton and co-workers have already pioneered the study of the reactions of CO with Re₂X₄(PR₃)₄ compounds,^{4,5} but their work

employed CO at atmospheric pressure only, whereas in this research we have carried out reactions with CO at pressures of about 120 atm. This has led to differences in product distribution, favoring higher CO content and more reduction.

We have used single-crystal X-ray diffraction methods to determine the structures of four of the compounds produced in the reaction of CO with the title compound, namely *all-trans*-Re(CO)₂Cl₂(PEt₃)₂ (1), *mer*-Re(CO)₃Cl(PEt₃)₂ (2), *cis*-Re(CO)₄Cl(PEt₃) (3), and *trans*-ReCl₄(PEt₃)₂ (4). The structure of the 17-electron dicarbonyl (a member of a class of compounds first reported by Walton and co-workers⁴) is the first one reported for a compound of the general formula Re(CO)₂X₂(PR₃)₂. The structure determination for *mer*-Re(CO)₃(PEt₃)₂Cl (2) entailed the resolution of a disorder between a Cl and a CO ligand. The molecule *trans*-ReCl₄(PEt₃)₂ (4) was found to be similar to ReCl₄(PMe₂Ph)₂, previously described by Mason and co-workers.⁶

The infrared spectra in the carbonyl stretching region have been measured for 1, 2, and 3, and force constant (Cotton-Kraihanzel) calculations⁷ have been carried out. For *cis*-Re(CO)₄(PEt₃)Cl, which possesses local C_s symmetry, a secular equation not reported

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