Stereochemical Consequences of Chelated, Bridging Phosphino–Phosphido Ligands. Single-Crystal X-ray Diffraction and Multinuclear [^{1}H, ^{31}P{^{1}H}, ^{195}Pt{^{1}H}] NMR Studies on the Stereochemistry of Dichlorobis[(3-(di(cyclohexyl or phenyl)phosphino)propyl)phenylphosphido]diplatinum(II) Diastereomeric Complexes and Their Dipalladium(II) Analogues

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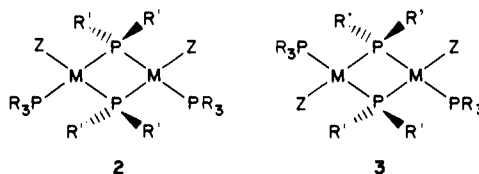
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Abstract: Tertiary–secondary diphosphine ligands of the type $R_2PCH_2CH_2CH_2P(Ph)H$ provide rational and controlled routes to phosphido-bridged bimetallic complexes. The ^{1}H, ^{31}P{^{1}H}, and ^{195}Pt{^{1}H} NMR data on a series of phosphido-bridged diplatinum(II) and dipalladium(II) complexes and the crystal and molecular structures of two phosphido-bridged diplatinum(II) complexes are reported. The compound *dl*-[PtCl{PhP(CH_2)_3P(C_6H_{11})_2}]_2 was synthesized from PtCl_2{Ph(H)-PCH_2CH_2CH_2P(C_6H_{11})_2} in THF and crystallized from dichloromethane/ethanol as chiral crystals belonging to the orthorhombic space group D_2^4-$P2_12_12_1$ in a cell of dimensions $a = 15.269$ (1) Å, $b = 17.119$ (2) Å, $c = 16.605$ (1) Å, with $Z = 4$ and $V = 4341$ (1) Å^3 at 148 K. The structure was refined to an R index on F of 0.027 for 4667 observed reflections ($F_o^2 \geq 3[\sigma(F_o^2)]$) and 368 variables. By use of the Bijvoet method, the data crystal was found to have the (S_m,S_n) absolute configuration. In the chiral diplatinum molecule, two nonbonded platinum atoms (Pt$\cdots$Pt = 3.5454 (5) Å) are bridged by two phosphido groups, the tetraatomic Pt-μP-Pt-μP core is bent [dihedral angle = 19.1(2)°], and the two phenyl groups are cis. The *meso*-[PtCl{PhP(CH_2)_3P(C_6H_{11})_2}]_2 crystallizes from dichloromethane/ethanol with $Z = 2$ in the monoclinic space group C_{2h}^5-$P2_1/n$ in a cell of dimensions $a = 11.1177$ (7) Å, $b = 12.466$ (1) Å, $c = 16.371$ (1) Å, $\beta = 99.751$ (1)°, with $V = 2236.1$ (3) Å^3 at 148 K. The structure was refined to an R index on F of 0.026 for 4365 observed reflections ($F_o^2 \geq 3[\sigma(F_o^2)]$) and 227 variables. In the *meso*-diplatinum complex, two nonbonded platinum atoms [Pt$\cdots$Pt = 3.5771 (2) Å] are bridged by two phosphido groups, the tetraatomic core is planar, and the two phenyl groups are trans. In a comparison of phosphido-bridged Pt(II) and Pd(II) dimers differing in core geometry, the δ_P value of the phosphido P atom is shifted −22 to −41 ppm in the planar diastereomer vis-à-vis the bent-core isomers. The magnitudes of some ^{31}P{^{1}H} and ^{195}Pt{^{1}H} NMR coupling constants (e.g., $^2J_{\mu P-\mu P}$, $^3J_{Pt-P}$, $^2J_{Pt-Pt'}$; $J_{meso} > J_{dl}$) appear to be sensitive to the planar-/bent-core stereochemistry. The platinum chemical shift of *meso*-[PtCl{PhP(CH_2)_3P(C_6H_{11})_2}]_2 is shielded +49 ppm relative to the value of the bent-core *dl* isomer. Comparisons of the ^{31}P{^{1}H} data between analogous Pt(II) and Pd(II) complexes, as well as with the planar Pt_2(μ-PPh_2)_2 core in other complexes, are presented.

Phosphido- and arsenido-bridged complexes of transition metals have attracted considerable attention recently on the reasonable assumption that the R_2As^-, RAs^{2-}, R_2P^-, and RP^{2-} groups would reduce undesirable fragmentation of cluster and bimetallic complexes.[2] Our results,[3] as well as recent reports by Carty,[4] Collman,[5] and Geoffroy,[6] indicate that organophosphido bridges between two metals may be more reactive than generally assumed. One might expect that the stability of the μ-PR_2 linkage could

be increased by incorporating it into a chelate ring. In contrast to the numerous examples of bis-PR_2-bridged bimetallic complexes of the general formula [MZ(PR_3)(μ-PR_2)]_2 (**1**), only two reports (besides ours) of an organophosphido group attached to a chelate chain have appeared to date.[7]

Phosphido-bridged complexes of planar metals [e.g., platinum(II), palladium(II), iridium(I), and rhodium(I)] of the general type **1** can be envisioned such that two Z ligands exhibit cis and trans dispositions (**2** and **3**, respectively) vis-à-vis the M_2(μ-PR_2)_2 core. Of the two isomeric forms, only the trans isomer **4** or **5**

2   **3**

is possible when the bridging phosphido group is linked to a terminal phosphino group via a chelate chain.

The tetraatomic core (M-μP-M-μP) must assume a planar

(1) On sabbatical leave of absence from the Department of Chemistry, Ben Gurion University of the Negev, Beersheva 84105, Israel.

(2) Recent papers that provide leading references to organophosphido bridging ligands are the following: (a) Fischer, K.; Vahrenkamp, H. *Z. Anorg. Allg. Chem.* **1981**, *475*, 109–115. (b) Braunstein, P.; Matt, D.; Bars, O.; Louer, M.; Grandjean, D.; Fischer, J.; Mitschler, A. *J. Organomet. Chem.* **1981**, *213*, 79–107. (c) Haines, R. J.; Steen, N. D. C. T.; English, R. B. *Ibid.* **1981**, *209*, C34. (d) Mays, M. J.; Raithby, P. R.; Taylor, P. L. *Ibid.* **1982**, *224*, C45. (e) Carty, A. J.; Hartstock, F.; Taylor, N. J. *Inorg. Chem.* **1982**, *21*, 1349–1354. (f) Jones, R. A.; Wright, T. C.; Atwood, J. L.; Hunter, W. E. *Organometallics* **1983**, *2*, 470.
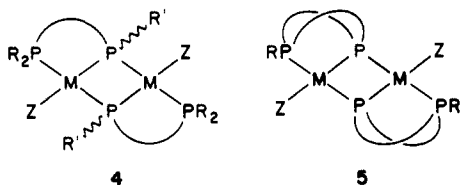
(3) (a) Kreter, P. E. Ph.D. Dissertation, The Ohio State University, Columbus, Ohio, 1981. (b) Kreter, P. E.; Meek, D. W. *Inorg. Chem.* **1983**, *22*, 319.

(4) Carty, A. J. *Pure Appl. Chem.* **1982**, *54*, 113–130.

(5) Collman, J. P.; Rothrock, R. K.; Finke, R. G.; Moore, E. J.; Rose-Munch, F. *Inorg. Chem.* **1982**, *21*, 146–156.
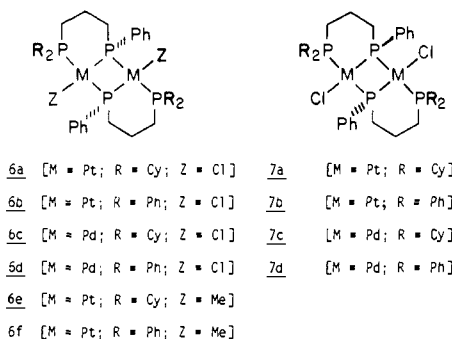
(6) (a) Harley, A. D.; Guskey, G. J.; Geoffroy, G. L. *Organometallics*, **1983**, *2*, 53–59. (b) Harley, A. D.; Whittle, R. R.; Geoffroy, G. L. *Ibid.* **1983**, *2*, 383–387.

(7) (a) Rafalko, J. J.; Watson, P. M.; Malueg, D. H.; Davis, E.; Gates, B. C. *Inorg. Chem.* **1981**, *20*, 3540. (b) Flood, T. C.; DiSanti, F. J.; Cambell, K. D. *Ibid.* **1978**, *17*, 1643–1646.

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4   **5**

geometry when at least one of three criteria is met: (1) the presence of a σ plane through all four atoms, **2** [with C_{2v} symmetry] and **3**, **5** [with C_{2h} symmetry]; (2) the presence of a C_2 axis through both phosphido phosphorus atoms, **2** [with C_2 symmetry]; (3) the presence of an inversion point at the center of the core, **3**, **4**, **5** [with C_i symmetry]. Only in the first case will each individual tetracoordinated platinum center also be ideally planar. Only in the third case may the phosphido phosphorus atoms exist as asymmetric P_{abcd} species.

Dichlorobis[(3-(dicyclohexylphosphino)propyl)phenyl-phosphido]diplatinum(II) complexes, [PtCl(μ-CyPP)]$_2$,[8] are examples of **4**; due to the presence of two stereogenic units [asymmetric phosphido phosphorus atoms], three stereoisomers are possible. Two isomers are chiral [C_2 symmetry] and together constitute a pair of enantiomers (**6a**, **6̄a**).[9a] The third isomer is diastereomeric to the two above-mentioned isomers and is a meso compound [C_i symmetry] (**7a**).

6a	[M = Pt; R = Cy; Z = Cl]	**7a**	[M = Pt; R = Cy]
6b	[M = Pt; R = Ph; Z = Cl]	**7b**	[M = Pt; R = Ph]
6c	[M = Pd; R = Cy; Z = Cl]	**7c**	[M = Pd; R = Cy]
6d	[M = Pd; R = Ph; Z = Cl]	**7d**	[M = Pd; R = Ph]
6e	[M = Pt; R = Cy; Z = Me]		
6f	[M = Pt; R = Ph; Z = Me]		

By the use of symmetry arguments,[9a] it can be shown that the diplatinum(II) complexes **6a**|**6̄a** fulfill none of the three above-mentioned requisites for an ideally planar-core geometry; thus, a bent-core geometry **8** is expected both in the solid state and in solution. By similar reasoning, the meso complex **7a** is expected to exhibit a planar-core geometry **9** by virtue of its inversion center.[9b]


8   **9**
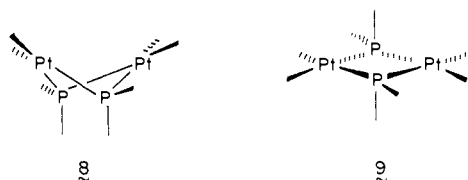
On this basis, we expected that some of the proton, phosphorus-31, and platinum-195 NMR spectral parameters would show a correlation with the bent-/planar-core geometry of the complex. This paper reports the syntheses and multinuclear NMR spectra of diplatinum(II) complexes **6a**, **7a**[10] (all with R = C_6H_{11}) as well as the corresponding diphenylphosphino analogues **6b**, **7b** (all with R = C_6H_5). The analogous dipalladium(II) complexes **6c**, **7c** (all with R = C_6H_{11}) and **6d**, **7d** (all with R = C_6H_5) were synthesized

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(8) Where CyPPH = $(C_6H_{11})_2PCH_2CH_2CH_2P(C_6H_5)H$, PPH = $(C_6H_5)_2PCH_2CH_2CH_2P(C_6H_5)H$, and dppe = $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$.

(9) (a) In the C_2 symmetry conformation of **6a**|**6̄a**, the C_2 axis passes neither through both phosphido phosphorus atoms nor through both platinum atoms. (b) In addition, Dr. C. Pierpont, University of Colorado, has pointed out to us that: "If the molecule is located about an inversion center the core is required to be planar, but there is no requirement that a meso isomer must have an inversion center. Also, C_2 isomers with the rotational axis perpendicular to the plane, while not ideally planar, could have dihedral angles which are close to 0°."

(10) For simplicity, chiral molecules [e.g., **6a–f** or **6̄a–f**] will be designated by an italicized descriptor [e.g., **6a–f**] when we do not desire to specify their absolute configuration.
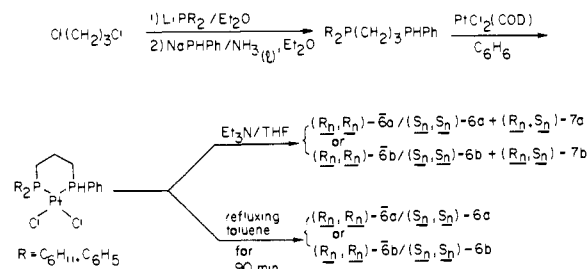
for comparison of the phosphorus-31 NMR spectra with the corresponding diplatinum(II) complexes. In addition, the solid-state stereochemistry of **6a** and **7a**—based on single-crystal X-ray diffraction—will be discussed and compared with that of the dimethyl analogue **6f**.[11]

Results and Discussion

Scheme I shows the syntheses of the phosphido-bridged *dl*- and *meso*-platinum(II) complexes utilizing (±)-1-(dicyclohexyl-phosphino)-3-(phenylphosphino)propane (CyPPH) (**10**) or (±)-1-(diphenylphosphino)-3-(phenylphosphino)propane (PPH) (**11**). The [PtCl(μ-CyPP)]$_2$ diastereomers showed separate spots on silica gel plates (R_f 0.70 and 0.53; 2:1 CH$_2$Cl$_2$/petroleum ether) and were separated via fractional crystallization. Only the *dl* complexes were found in the reaction products of the thermal route.

X-ray Diffraction Studies. Although the [PtCl(μ-CyPP)]$_2$ isomers exhibited different proton and phosphorus-31 NMR chemical shift values for the absorbances arising from the phenyl ring protons and the bridging (phosphido) phosphorus atoms, the spectral data did not provide an unequivocal characterization of the diastereomers. Accordingly, a single-crystal X-ray diffraction study was undertaken to provide the definitive characterization and to determine the solid-state stereochemistry. The separated [PtCl(μ-CyPP)]$_2$ diastereomers (TLC R_f 0.70 and 0.53 in CH$_2$Cl$_2$/petroleum ether) gave single crystals which belonged to orthorhombic $P2_12_12_1$ ($Z = 4$) and monoclinic $P2_1/n$ ($Z = 2$) space groups, respectively. The determination of the crystal structures unequivocally characterized the crystals of the TLC R_f 0.53 diastereomer as those formed by the meso isomer **7a**, which has a planar core and *trans*-phenyl groups.[12] Now, the chiral $P2_12_12_1$ crystals containing the TLC R_f 0.70 diastereomer are assumed to be a *conglomerate* of **6a** and **6̄a** (bent core/*cis*-phenyls) crystals. Such an example of *spontaneous resolution*[13] is in contrast to the behavior of the analogous enantiomeric complex [PtCH$_3$(μ-PP)]$_2$ (**6f**/**6̄f**) (bent core/cis-phenyls) which formed a *racemic compound*[13] upon crystallization.[11] By *conglomerate* we mean a mechanical mixture of **6a** crystals and **6̄a** crystals of pure enantiomers, whereas the racemic compound has both enantiomers present in equal quantity and in specific geometrical positions in the crystal unit cell.[13] These racemic crystals belong to the monoclinic $P2_1/n$ ($Z = 4$) space group.[11]

By use of the Bijvoet method,[14] the absolute configuration of the **6a** molecule within the examined crystal was determined to be that of the **6a** model rather than the **6̄a** model. The absolute configuration of each stereogenic unit [i.e., the bridging phosphorus atom] in **6a** may be denoted by assigning a Cahn–Ingold–Prelog descriptor according to the recently revised sequence subrule 3.[15] While no descriptor can be specified by using the original subrule

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(11) Meek, D. W.; Waid, R.; Tau, K. D.; Kirchner, R. M.; Morimoto, C. N. *Inorg. Chim. Acta* **1982**, *64*, L221–L223.

(12) The asymmetric unit in the $P2_1/n$ unit cell consists of one-half of a molecule, since two molecules in the unit cell can only be realized if the crystallographic inversion center is imposed on a molecular inversion center.

(13) Jacques, J.; Collet, A.; Wilen, S. H. "Enantiomers, Racemates, and Resolutions"; Wiley-Interscience: New York, 1981; pp 4 and 5.

(14) Bijvoet, J. M.; Reesdeman, A. F.; van Bommel, A. J. *Nature (London)* **1957**, *168*, 271–272.

(15) Prelog, V.; Helmchen, G. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 567–583.

Table I. Crystallographic Details for **7a** and **6a**

	(R_n,S_n)-$Pt_2Cl_2P_4C_{42}H_{66}$	(S_n,S_n)-$Pt_2Cl_2P_4C_{42}H_{66}$
fw, amu	1155.98	1155.98
space group	C_{2h}^5-$P2_1/n$	D_2^4-$P2_12_12_1$
a, Å	11.1177 (7)	15.269 (1)
b, Å	12.466 (1)	17.119 (2)
c, Å	16.371 (1)	16.605 (1)
β, deg	99.751 (1)	
V, Å³	2236	4341
Z	2	4
ρ_c, g/cm³	1.72[a]	1.77[a]
ρ_{obsd}, g/cm³	1.71[b]	1.76[b]
linear abs coeff, cm⁻¹	66.0	68.0
transmission coeff[c]	0.228–0.407	0.241–0.427
bounding crystal faces	{011}, {101}, {110}, {10Ī}	{101}, (1Ī1), (ĪĪ1), (010)
temp, K	148 (1)	148 (1)
radiation	graphite-monochromated Mo Kα (λ(Kα₁) = 0.70926 Å)	same
collection range	±h,k,l	+h,+k,+l
2θ limits	4.0 ≤ 2θ ≤ 57.0°	4.0 ≤ 2θ ≤ 55.0°
scan type	ω–2θ	same
scan width	1.0° below Kα₁ to 1.2° above Kα₂	same
scan speed	2.0° min⁻¹ to 24.0° min⁻¹	same
background time/ scan time	0.5	same
unique data	5706	5535
unique data with $F_o^2 \geq 3\sigma(F_o^2)$	4365	4667
no. of variables	227	368
isotropic extinc coeff	6.2 (1) × 10⁻⁸	8 (1) × 10⁻⁹
R(F)	0.026	0.027
$R_w(F)$	0.027	0.027

[a] Calculated at 148 K. [b] Measured by buoyancy method at 298 K. [c] Analytical absorption correction was applied.

3[16] (ordering by stereochemical differences), the modified subrule now bases cis/trans isomerism relative to the stereogenic unit itself. Thus, the two four-coordinate platinum atoms can now be distinguished geometrically by comparing the highest priority atom (chlorine) positions relative to the stereogenic phosphido phosphorus atoms, such that a cis position has precedence over a trans position.[15] In this manner, isomer **6a** is given the configurational description (S_n,S_n) while its enantiomer $\overline{6}a$ becomes (R_n,R_n).

Note Added in Proof: It has been suggested by J. E. Blackwood at Chemical Abstracts that the Rule for Equivalent Centers[16] be used in the assignment of configurational descriptors for compounds **6**. In such a case, the absolute configuration of the molecule in the **6a** data crystal may be described as (S,S), rather than as (S_n,S_n). We agree in the case of symmetrical complexes like **6a**; however, we believe that the use of the Rule for Equivalent Centers for dimetallic complexes like **6a** is less preferable, since it is conditional on the presence of symmetry-related chiral centers and ligands like the chelating phosphino–phosphido ligands. The absence of either one or both of these two structural features in complexes similar to **6** voids the use of the Rule of Equivalent Centers, whereas the modified subrule 3[15] is still applicable. Therefore, modified subrule 3 is appropriate for a larger, more general class of compounds still exhibiting the same type of isomerism found in **6**, rather than being restricted narrowly to a smaller subgroup of molecules. For example, modified subrule 3 may still be used with arsino–phosphido bridged analogues of **6**, or unsymmetrically substituted phosphido (PR'R'') analogues of **3**, whereas the Rule for Equivalent Centers may not. The greater generality of modified subrule 3, for describing the type of stereoisomerism exemplified by **6** and **7**, makes its use preferred.

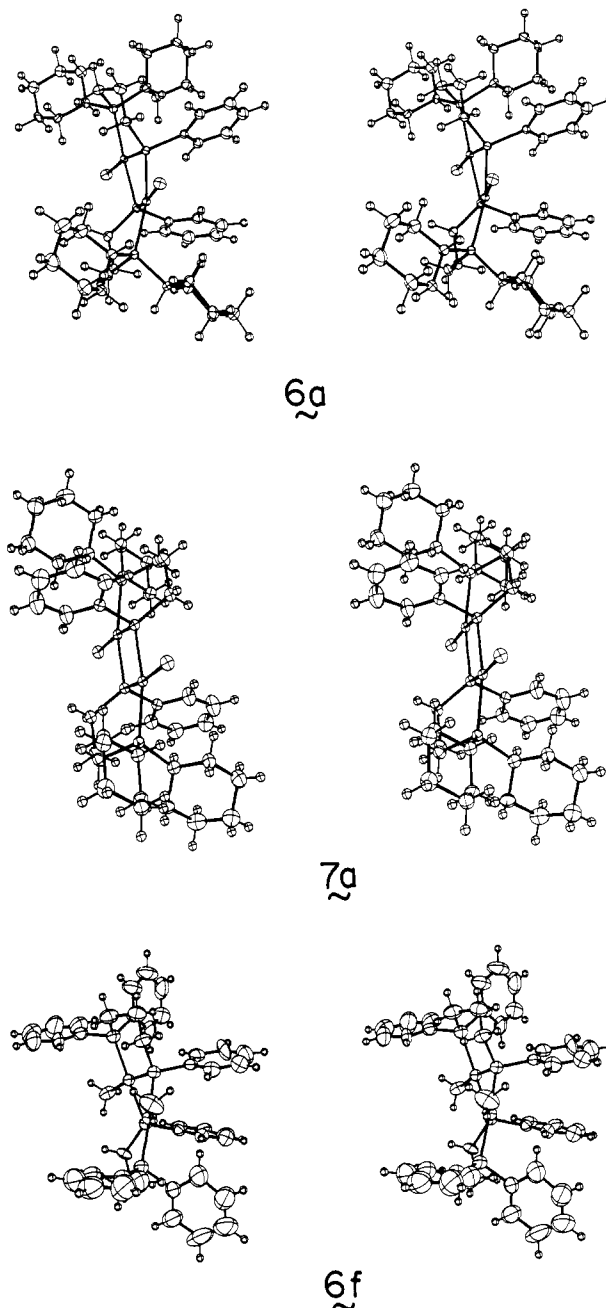(16) Cahn, R. S.; Ingold, C.; Prelog, V. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 385–415.

Figure 1. Stereoviews of **6a**, **7a**, and **6f** drawn with the thermal ellipsoids at 50% probability for the non-hydrogen atoms; for clarity the hydrogens are assigned $B = 1.0$ Å².

While only one crystal belonging to space group $P2_12_12_1$ was examined on the diffractometer, we assume that the enantiomeric (R_n,R_n)-$\overline{6}a$ complex was also formed in the non-asymmetric synthesis of the complexes. Kress et al.[17] have noted that hemihedral faces for crystal class 222 must be of order (111) or higher. A careful morphological investigation of these crystals (222 crystal class) under a microscope showed that some crystals had developed the complete set of faces for the hemihedral form {ĪĪĪ}.[18] However, the angles between the faces of the holohedral {101} form are very close to 90°, resulting in approximate *mm* symmetry for the crystal. So using only a microscope, it is not possible to

(17) Kress, R. B.; Duesler, E. N.; Etter, M. C.; Paul, I. C.; Curtin, D. Y. *J. Am. Chem. Soc.* **1980**, *102*, 7709–7714.

(18) The chiral crystal used for data collection was cut from a larger clump of crystals. It was a clear, colorless rod with well-formed faces: (101), (10Ī), (Ī0Ī), (Ī01), (1Ī1), (Ī Ī 1), and (010) (which was the cut face). The complete hemihedral form {ĪĪĪ} was not observed since the crystal had been cut along the (010).

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Table II. Selected Bond and Nonbond Distances (Å) for (R_n,S_n)-**7a**, (S_n,S_n)-**6a**, and dl-**6f**/**6f**

distance	(R_n,S_n)-**7a**	(S_n,S_n)-**6a**	dl-**6f**/**6f**
Pt1···Pt2	3.5771 (2)	3.5454 (5)	3.5206 (9)
P1···P3/ P1···P1'	2.8270 (13)	2.827 (3)	2.815 (7)
Pt1–P1	2.2470 (9)	2.243 (2)	2.305 (5)
Pt2–P3		2.255 (2)	2.319 (5)
Pt1–P3/ Pt1–P1'	2.3119 (10)	2.330 (2)	2.324 (4)
Pt2–P1		2.316 (2)	2.330 (5)
Pt1–Z1	2.3782 (9)^a	2.377 (2)^a	2.08 (2)^b
Pt2–Z2		2.386 (2)^c	2.14 (8)^d
Pt1–P2	2.2970 (10)	2.306 (2)	2.266 (5)
Pt2–P4		2.310 (2)	2.278 (5)
P1–C1	1.817 (4)	1.836 (9)	1.89 (2)
P3–C4		1.821 (8)	1.87 (2)
P1–C11	1.824 (4)	1.831 (5)	1.83 (2)
P3–C41		1.841 (5)	1.88 (2)
P2–C3	1.829 (4)	1.831 (9)	1.84 (2)
P4–C6		1.845 (9)	1.81 (2)
P2–C21	1.844 (4)	1.844 (8)	1.87 (2)
P4–C51		1.849 (8)	1.77 (2)
P2–C31	1.833 (4)	1.841 (8)	1.80 (2)
P4–C61		1.842 (8)	1.84 (2)
C11···C41/ C11···C11'	>5	4.327 (7)	3.649 (28)
Pt1···C2	3.818 (4)	3.836 (8)	3.809 (21)
Pt2···C5		3.792 (8)	3.795 (19)
P1···P2	3.2967 (13)	3.287 (3)	3.393 (6)
P3···P4		3.427 (3)	3.418 (7)
C11···C21	3.688 (6)	3.59 (1)	4.70 (2)
C41···C51		4.80 (1)	4.585 (24)
C11···H21	2.840 (4)	2.701 (5)	
C41···H51		>5	

^{a} Z1 = C11. ^{b} Z1 = C7. ^{c} Z2 = C12. ^{d} Z2 = C8.

Table III. Selected Angles (deg) for (R_n,S_n)-**7a**, (S_n,S_n)-**6a**, and dl-**6f**/**6f**

angle	(R_n,S_n)-**7a**	(S_n,S_n)-**6a**	dl-**6f**/**6f**
Pt1–P1–Pt2/ Pt1–P1–Pt1'	103.37 (4)	102.08 (8)	98.8 (2)
Pt1–P3–Pt2		101.28 (8)	98.6 (2)
P1–Pt1–P3/ P1–Pt1–P1'	76.33 (3)	76.30 (7)	74.9 (2)
P1–Pt2–P3		76.36 (7)	74.5 (2)
P3–Pt1–Z1/ P1'–Pt1–Z1	94.04 (3)^a	94.59 (7)^a	96.0 (5)^b
P1–Pt2–Z2		93.62 (7)^c	95.9 (6)^d
Z1–Pt1–P2	96.78 (3)^a	96.74 (7)^a	93.0 (5)^b
Z2–Pt2–P4		92.75 (7)^c	93.3 (6)^d
P1–Pt1–P2	93.02 (4)	92.50 (7)	95.9 (2)
P3–Pt2–P4		97.32 (7)	96.1 (2)
P1–Pt1–Z1	169.93 (4)	170.48 (8)	170.4 (5)
P3–Pt2–Z2		169.90 (7)	169.9 (6)
P2–Pt1–P3/ P2–Pt1–P1'	166.30 (4)	168.44 (7)	169.8 (2)
P1–Pt2–P4		166.44 (8)	170.1 (2)
P3–P1–C11/ P1'–P1–C11	119.65 (14)	114.04 (18)	103.3 (7)
P1–P3–C41		114.20 (19)	102.7 (6)
P3–P1–C1/ P1'–P1–C1	133.95 (13)	140.72 (28)	153.7 (7)
P1–P3–C4		141.17 (28)	153.7 (7)
P2–P1–C11	95.14 (13)	95.12 (19)	110.6 (5)
P4–P3–C41		105.47 (20)	107.9 (5)
P1–P2–C21	97.06 (13)	94.13 (27)	110.8 (6)
P3–P4–C51		118.30 (26)	109.3 (7)
Pt1–P2–C3	110.68 (14)	111.18 (26)	113.7 (5)
Pt2–P4–C6		113.75 (27)	114.4 (5)
P2–C3–C2	116.12 (29)	115.43 (59)	112.3 (1.4)
P4–C6–C5		118.61 (55)	113.5 (1.3)
C3–C2–C1	115.28 (32)	115.76 (66)	112.8 (1.6)
C6–C5–C4		113.92 (67)	112.4 (1.5)
C2–C1–P1	116.32 (30)	116.10 (58)	111.1 (1.3)
C5–C4–P3		114.45 (54)	111.7 (1.2)
C1–P1–Pt1	113.46 (12)	114.70 (28)	117.8 (5)
C4–P3–Pt2		113.34 (26)	116.1 (6)

^{a} Z1 = C11. ^{b} Z1 = C7. ^{c} Z2 = C12. ^{d} Z2 = C8.

Table IV. Selected Torsion Angles (deg) for the Heterocyclic Six-Membered Rings of (R_n,S_n)-**7a**, (S_n,S_n)-**6a**, and dl-**6f**/**6f**

torsion angle	(R_n,S_n)-**7a**	(S_n,S_n)-**6a**	dl-**6f**/**6f**
P1–P2–C21–H21	−5.6 (6)	−6.7 (8)	
P3–P4–C51–H51		−123.6 (8)	
C3–P2–C31–H31	−179.3 (5)	+177 (1)	
C6–P4–C61–H61		+174 (1)	
Pt1–P2–C21–H21	−47 (1)	−48 (1)	
Pt2–P4–C51–H51		−171 (1)	
Pt1–P1–C11–C12	31.4 (5)	−30.2 (5)	+21 (2)
Pt2–P3–C41–C42		−18.4 (6)	0 (3)

distinguish this crystal form from the enantiomer crystal wherein the {101} and {111} forms are fully developed.

Crystallographic details for **7a** and **6a** are contained in Table I. Selected bonded and nonbonded distances for **7a**, **6a**, and **6f** are compared in Table II. Likewise, Table III contains selected angles and Table IV contains selected torsion angles for the six-membered heterocyclic rings. The stereoviews of **6a**, **7a**, and **6f** are shown in Figure 1.

The meso diastereomer **7a** has a crystallographically imposed planar-core structure, whereas the chiral (S_n,S_n)-diastereomer (**6a**) possesses a bent (19.1 (2)°) $Pt_2(\mu\text{-PRR}')_2$ core.[19] The dimethyl–diplatinum complex **6f** shows an analogous bending of 34.6 (3)°.[20] In the three diplatinum complexes, the long metal–metal separations show the absence of metal–metal bonding (cf. Pt–Pt = 2.628 (1) Å in $[Pt(dppe)]_2^{21}$). The phosphido-phosphido distance is invariant for all three complexes. The three Pt–Pt distances are all comparable to two other planar-core, phosphido-bridged diplatinum complexes that were reported recently (i.e., Pt–Pt = 3.585 (1) Å in *trans*-$[PtCl(PHPh_2)(\mu\text{-PPh}_2)]_2$ (**17**) and 3.639 (1) Å in $[Pt(\mu\text{-PPh}_2)(dppe)]_2Cl_2$ (**18**)).[2e] Increased bending of the $Pt_2(\mu\text{-PR}_2)_2$ core can cause substituents on the bridging phosphorus atom to become more axial-like [angle P3–P1–C11/P1–P3–C41], while the methylene substituent (C1/C4) on the phosphido group assumes a more equatorial disposition [angle P3–P1–C1/P1–P3–C4] (see Figure 5).

As the bending of the core increases and the Pt–Pt distance decreases, the Pt1–P1–Pt2/Pt1–P3–Pt2 angle decreases more than the angle P1–Pt1–P3/P1–Pt2–P3. With the exception of the $[Pt(CH_3)(\mu\text{-PP})]_2$ dimer **6f**, these $Pt\text{-}\mu P\text{-}Pt$ and $\mu P\text{-}Pt\text{-}\mu P$ angles are comparable to those observed in other phosphido-bridged diplatinum complexes such as **17** and **18** [angle $Pt\text{-}\mu P\text{-}Pt = 102.7$

(1)° in **17** and 103.9 (1)° in **18**; angle $\mu P\text{-}Pt\text{-}\mu P = 77.3$ (1)° in **17** and 76.1 (1)° in **18**].[2e] The $Pt\text{-}\mu P$ bond lengths trans to the dicyclohexyl-substituted phosphorus are longer than those trans to chlorine and reflect the weaker trans influence of the chloro ligand. This phenomenon is also seen in the molecular structure of *trans*-$[PtCl(PHPh_2)(\mu\text{-PPh}_2)]_2$ (**17**), wherein the $Pt\text{-}\mu P$ bond trans to phosphorus has a length of 2.329 (3) Å while that trans to chlorine is 2.260 (3) Å.[2e] The Pt–Cl bond lengths and the lengths of the Pt–P bond trans to the phosphido phosphorus are also comparable to those found in **17** [2.379 (4) and 2.313 (3) Å, respectively].[2e]

The coordination geometry about the platinum atoms is essentially "square-planar" except for the pinched nature of the $\mu P\text{-}Pt\text{-}\mu P$ angle. In the case of both the (S_n,S_n)-**6a** and (R_n,S_n)-**7a** diastereomers, the chloro- and dicyclohexyl-substituted phosphino ligands are distorted to opposite sides of a reference plane defined by the platinum and the two phosphido phosphorus atoms. The chloro atom is on the same side of the reference plane as a phenyl group, while the dicyclohexylphosphino group is on the opposite side. Thus, the coordination plane is distorted, and this results

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(19) The core bending (absolute value) is defined as the supplementary angle of the torsion angle Pt1–P1–P3–Pt2.

(20) Meek, D. W.; Waid, R.; Tau, K. D.; Kirchner, R. M.; Morimoto, C. N., unpublished data.

(21) Arnold, D. P.; Bennett, M. A.; Bitton, M. S.; Robertson, G. B. *J. Chem. Soc., Chem. Commun.* **1982**, 115–116.

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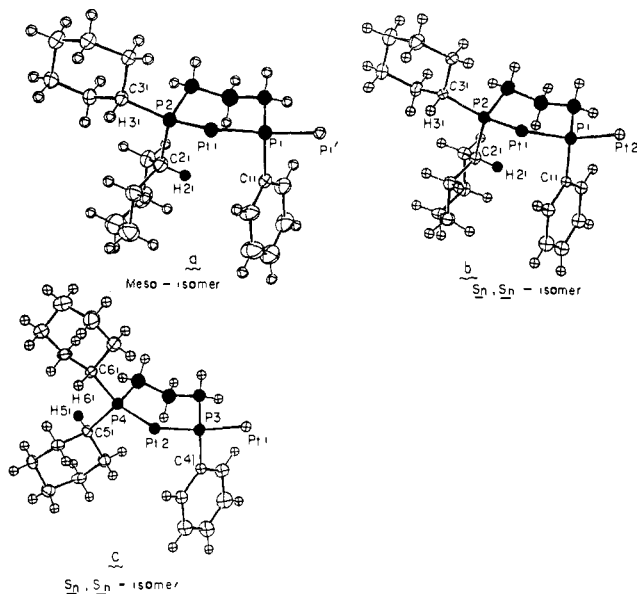
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Figure 2. Comparison of the similar chair conformations of the heterocyclic six-membered chelating rings in the complexes **7a** and **6a**, respectively, with the distorted twisted-chair chelating ring in complex **6a**. The tertiary proton [H21(H51)] on the *pro-R*-cyclohexyl group is shaded darker for clarity.

in a slight tetrahedral distortion about the platinum atoms. On the other hand, in the case of the dimethyl complex, **6f**, both the chloro and the diphenylphosphino ligands are located on the same side of the Pt,μP,μP reference plane [toward the side opposite the phenyl group]; this results in a slight pyramidal distortion of the pseudoplanar platinum atoms. The torsion angles P2–Pt1–P1–P3/P4–Pt2–P3–P1 and P1–P3–Pt1–Z1/P3–P1–Pt2–Z2, as well as the deviations from the best plane through the metal and its four ligands, are listed in Tables V and VI (supplementary material), respectively. The labeling schemes for the atoms in the structures of **6a** and **7a** are given in Figure 5.

In Figure 2a the heterocyclic six-membered ring in **7a** is in a chair conformation, in which the *pro-R*-cyclohexyl and phenyl ring substituents exhibit a 1,3-*cis*-diaxial orientation, whereas the *pro-S*-cyclohexyl ring occupies an equatorial position. In the **6a** structure, the two six-membered heterocycles (nonsymmetry related in the solid state) show different conformations. One is very similar to that found in *meso*-**7a**, whereas the other one is a slightly distorted chair that is somewhat flattened in the region of the platinum atom. This flattening causes the 1,3-cis substituents to twist away from each other in Figure 2c vs. the axial orientation in Figure 2b. In the **6f** structure, which has the largest bending of the three Pt$_2$(μ-PR$_2$)$_2$ cores, both six-membered heterocyclic rings show this flattened chair distortion. The situation is most evident in the angle P2–P1–C11/P4–P3–C41 and in the angle P1–P2–C21/P3–P4–C51, both of which should be 90° in the classical chair conformation of cyclohexane (Table III). A more sterically demanding conformation for the axial (*pro-R*) cyclohexyl group would place the small tertiary proton (H21/H51) facing outward from the axial phenyl group across the ring. To minimize the increased 1,3-*cis* steric interactions resulting from pushing part of the bulky cyclohexyl group inward toward the axial phenyl, it is expected that the chair conformation will be distorted by twisting the diaxial substituents away from each other. This situation is observed in the second hexagonal chelating ring of **6a** as shown in the P1–P2–C21–H21/P3–P4–C51–H51 torsion angles (Tables IV) of the chair conformation of **7a** (Figure 2a), the chair ring of **6a** (Figure 2b), and the twisted-chair ring of **6a** (Figure 2c). The C11⋯H21 distance between the tertiary proton (H21) pointing toward the tertiary aromatic carbon atom C11 is 2.8 and 2.7 Å for the **7a** and **6a** chair rings, respectively. These distances can be compared to the C41⋯H51 distance (>5 Å) found in the **6a** twisted-chair ring wherein the H51 proton has a different orientation. In all cases, the equatorial cyclohexyl group has the

same staggered conformation relative to the six-membered heterocycle; the cyclohexyl tertiary proton H31/H61 is ca. 180° from the methylene C3/C6 (see Figure 2). The axial cyclohexyl group also has a staggered conformation relative to the six-membered heterocycle as shown in the Pt1–P2–C21–H21/Pt2–P4–C51–H51 torsion angles (Table IV) of the chair ring of **7a** (Figure 2a), the chair ring of **6a** (Figure 2b), and the **6a** twisted-chair ring (Figure 2c).

The phenyl group at the phosphido junction for the four- and six-membered rings is oriented toward the core interior in the case of **6a** and **7a**, whereas the orientation in **6f** is toward the interior of the six-membered heterocycle. This situation is seen in the Pt1–P1–C11–C12/Pt2–P3–C41–C42 torsion angles (Table IV) of the chair ring of **7a**, the chair ring of **6a**, the twisted-chair ring of **6a**, and the twisted-chair rings of **6f** (see Figure 1).

In the **6a** crystal and the **7a** crystal, no intermolecular contacts are closer than the normal van der Waals radii. In addition, no significant variations were found in the internal angles and bond lengths of the cyclohexyl rings to indicate packing distortions (see supplementary material, Tables I–IV).

NMR Studies. Both the chiral and *meso*-[PtCl(μ-CyPP)]$_2$ diastereomers **6a** and **7a** exhibited markedly different ^{31}P{^{1}H} NMR chemical shift values for the bridging (phosphido) phosphorus atoms relative to the chemical shift differences between the terminal phosphorus atoms. The chiral **6a** isomer gave two phosphorus signals at δ_P −4.5 and −144.4 ppm, whereas the **7a** diastereomer showed two resonances at δ_P −4.1 and −171.1 ppm. The ^{31}P{^{1}H} NMR spectra displayed relatively intense patterns for AA′XX′ and AA′XX′M spin systems plus a relatively weak AA′XX′MM′ pattern. The three patterns reflect the natural abundance of ^{195}Pt (ca. 33.8% $I = ^1/_2$) which yields 43.8%, 44.8%, and 11.4% of the isotopomeric diplatinum complexes containing zero, one, or two ^{195}Pt atoms, respectively. Since palladium does not contain a natural abundance magnetic nucleus with $I = ^1/_2$, the analogous palladium(II) complexes (**6c**, **6d**, **7c**, and **7d**) give only the AA′XX′ pattern.

In the solid state structure of **6a**, the pair of phosphido phosphorus atoms and the pair of phosphino P atoms are each heterotopic since in the crystal the molecule does not occupy a special position of C_2 symmetry. However, the phosphorus-31 spectrum of a CH$_2$Cl$_2$ solution of **6a** at ambient temperature shows higher symmetry than in the crystal, since both phosphido P atoms, as well as both phosphino P atoms, are isochronous.

For each diplatinum complex, the phosphorus signal appearing at relatively high field (e.g., δ −144.4 and −171.1 ppm for **6a** and **7a**, respectively) is assigned to the bridging phosphido phosphorus atoms, while the signal at relatively low field (e.g., δ −4.5 and −4.1 ppm for **6a** and **7a**, respectively) is assigned to the −P(C$_6$H$_{11}$)$_2$ phosphorus atoms. This assignment is consistent with the similar chemical shift values of δ +7.54, +4.64, and −1.81 ppm observed for the −P(C$_6$H$_{11}$)$_2$ phosphorus signals, which can be assigned unequivocally, in [PtCl$_2$(CyPPH)] (**2**), [Pt(CH$_3$)$_2$(CyPPH)] (**19**),[22] and *trans*-[Pt(CyPPH)$_2$]Cl$_2$ (**20**),[22] respectively. Moreover, this assignment is supported by the observations that the higher field (phosphido) resonances exhibit two unequal $^1J_{Pt-P}$ coupling constants of approximately the same magnitude [due to magnetic nonequivalence], whereas the lower field (phosphino) resonances show markedly different $^1J_{Pt-P}$ and $^3J_{Pt-P}$ values. The ^{31}P{^{1}H} NMR spectral parameters for the dimetallic complexes **6a**, **6b**, **7a**, and **7b** are given in Table V. The chemical shift and coupling constant values are consistent with those observed previously for the complexes [PtCl(PHPh$_2$)(μ-PPh$_2$)]$_2$ (**17**) and [Pt(dppe)(μ-PPh$_2$)]$_2$Cl$_2$ (**18**).[23] In addition, the high-field positions of the phosphido resonances are consistent with the absence of a metal–metal bond.[2e,24]

The diastereomeric [PtCl(μ-PP)]$_2$ complexes were synthesized in a similar fashion to the corresponding [PtCl(μ-CyPP)]$_2$ com-

(22) Waid, R. D. Ph.D. Dissertation, The Ohio State University, Columbus, Ohio, 1982.

(23) Brandon, J. B.; Dixon, K. R. *Can. J. Chem.* **1981**, *59*, 1188–1200.

(24) Kreter, P. E.; Meek, D. W. *Inorg. Chem.* **1983**, *22*, 319–325.

Table V. ^{31}P{^{1}H} and ^{195}Pt{^{1}H} NMR Spectral Parameters of Phosphido-Bridged Pd(II) and Pt(II) Complexes

compound	core geometry	$\delta_{1,2}{}^a$	$\delta_{3,4}{}^a$	$\delta_{5,6}{}^b$	$^2J_{12}$	$^2J_{13}$	$^2J_{14}$	$^4J_{34}$	$^1J_{15}$	$^1J_{25}$	$^1J_{35}$	$^3J_{45}$	$^2J_{56}$
dl-[PtCl(μ-CyPP)]$_2$ (**6a**)	bent	-144.4	-4.5	-467.0	-158.1^c	-2.3^c	+362.3^c	+6.2^c	+2291.5^c	+1725.4^c	+2122.4^c	+5.0^c	+259^c
dl-[PtCl(μ-PP)]$_2$ (**6b**)	bent	-146.5	-8.3	-499.2	-155.9	-4.4	+383.0	+6.0	+2228.4	+1820.2	+2115.2	+6.0	+342
dl-[PdCl(μ-CyPP)]$_2{}^d$ (**6c**)	bent	-126.6	-0.3		-235.2	+16.4	+396.7	0.0					
dl-[PdCl(μ-PP)]$_2{}^{d,e}$ (**6d**)	bent	-144.4	-11.9		-246.0	+12.5	+417.8	0.0					
dl-[Pt(CH$_3$)(μ-CyPP)]$_2{}^{d,g}$ (**6e**)	bent	-154.7	+1.1	f	-138.3	-19.1	+324.4	+6.3	+1213.7	+1768.4	+2165.3	+3.9	f
dl-[Pt(CH$_3$)(μ-PP)]$_2$ (**6f**)	bent	-152.8	+0.4	-534.2	-131.1	-23.3	+336.6	+7.6	+1150.6	+1873.4	+2181.2	+12.7	+667
$meso$-[PtCl(μ-CyPP)]$_2$ (**7a**)	planar	-171.1	-4.1	-417.6	-176.6	+3.1	+374.2	-4.2	+2287.6	+1768.4	+2135.1	+32.6	+639
$meso$-[PtCl(μ-PP)]$_2{}^{d,h}$ (**7b**)	planar	-168.3	-4.3	f	-173.3	+0.7	+395.6	-6.2	+2242.5	+1875.4	+2139.5	+39.2	f
$meso$-[PdCl(μ-CyPP)]$_2{}^d$ (**7c**)	planar	-167.3	-3.2		-303.6	+33.3	+416.2	0.0					
$meso$-[PdCl(μ-PP)]$_2{}^{d,e}$ (**7d**)	planar	-171.5	-10.8		-299.8	+26.7	+435.0	+0.1					
[Pt(μ-PPh$_2$)(dppe)]$_2$Cl$_2$ (**18**)	planar^j	-181.6	+49.3	f	-207.5	0.0	+291.9	+7.1	+1774.7	+1774.7	+2112.6	+63.1	f
$trans$-[PtCl(μ-PPh$_2$)(PHPh$_2$)]$_2{}^i$ (**17**)	planar^j	-139.2	-2.4	f	-162.0	-1.0	+395.4	+7.6	+2364.2	+1991.1	+2184.0	+29.2	f
$trans$-[PtCl(μ-PPh$_2$)(PEt$_3$)]$_2{}^i$ (**24**)	f	-136.2	+14.4	f	-177.7	+4.5	+374.3	+9.5	+2634.7	+1609.5	+2171.8	+31.3	f
[Pd(μ-PPh$_2$)(dppe)]$_2$Cl$_2{}^i$ (**26**)	f	-181.6	+47.4		-349.4	+28.2	+311.0	0.0					
$trans$-[PdCl(μ-PPh$_2$)(PHPh$_2$)]$_2{}^i$ (**23**)	f	-132.9	-3.1		-261.1	+20.9	+423.1	+0.2					
$trans$-[PdCl(μ-PPh$_2$)(PEt$_3$)]$_2{}^i$ (**25**)	f	-127.9	+14.5		-289.5	+31.9	+405.9	+2.9					

^{a} ppm from 85% H$_3$PO$_4$. ^{b} ppm from cis-PtCl$_2$[S(CH$_3$)$_2$]$_2$ reference. ^{c} Hz. ^{d} 36.43-MHz spectrum. ^{e} In dimethylformamide. ^{f} Not determined. ^{g} In benzene. ^{h} In chloroform. ^{i} Data from ref 23. ^{j} Data from ref 2e.

plexes. One diastereomer (α isomer) gives phosphorus resonances at δ -8.4 and -146.5 ppm, whereas the β isomer has resonances at δ -5.2 and -169.2 ppm. By analogous reasoning to that used for the [PtCl(μ-CyPP)]$_2$ complexes, the higher field signal in each diastereomer may be assigned to the bridging phosphorus atoms. Thus, it is concluded that the configurations of the α- and β-isomers are **6b** and **7b**, respectively, based upon the close similarity of their ^{31}P{^{1}H} NMR spectral parameters to those of **6a** and **7a** (see Table V).

On the basis of the above reasoning, the [PdCl(μ-CyPP)]$_2$ and [PdCl(μ-PP)]$_2$ complexes, which give phosphorus-31 NMR resonances at δ -0.3, -126.6 ppm and δ -11.9, -144.4 ppm, respectively, are each assigned the dl configuration [**6c** and **6d**, respectively]. Similarly, the diastereomeric palladium(II) complexes which have phosphorus-31 NMR resonances at δ -3.2, -167.3 ppm and δ -10.8, -171.5, respectively, are each assigned the meso configuration [**7c** and **7d**, respectively].

In the four comparisons that are possible, the bridging phosphido chemical shifts appear to be very sensitive to the nature of the core geometry, whereas the terminal phosphino signal is relatively insensitive to the bending of the Pt–P–Pt–P core. This sensitivity to the stereochemistry of the core is reflected by the higher chemical shifts of the phosphido P atoms in the planar core of the meso complexes compared to the corresponding values of the dl isomers, which have bent cores. On the other hand, in the one comparison that is possible, the ^{195}Pt resonance is deshielded 49.4 ppm in the planar-core complex (i.e., meso-**7a**) compared with that in the bent-core diastereomer (**6a**).

An additional comparison can be made from the ^{195}Pt NMR chemical shifts. Substitution of a dicyclohexylphosphino group by a diphenylphosphino moiety in the diplatinum complexes resulted in a δ_{Pt} shift of 32.2 ppm to higher field (-467 ppm vs. -499.2 ppm, Table V). This effect is opposite to the situation found with the [PtCl$_2$(CyPPH)] (**12**), and [PtCl$_2$(PPH)] (**15**) precursors which have δ_{Pt} = -993 and -955 ppm, respectively. However, in complexes with chelating triphosphine ligands, e.g., [PtCl(R$_2$P(CH$_2$)$_3$P(Ph)(CH$_2$)$_3$PR$'_2$)]Cl (**21**), replacement of cyclohexyl groups by phenyl groups also increases the δ_{Pt} values, e.g., δ_{Pt} = -1185 ppm (when R = R$'$ = Cy), -1234 ppm (when R = Cy, R$'$ = Ph), and -1240 ppm (when R = R$'$ = Ph).[22,25] A final ^{195}Pt NMR comparison can be made between the [PtCl(μ-
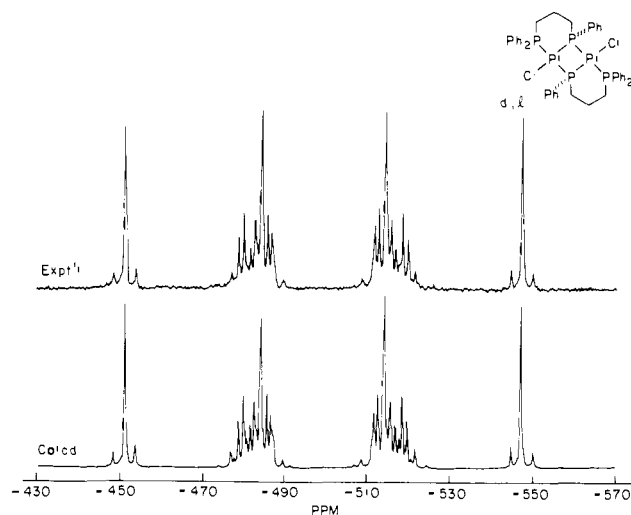

Figure 3. The ^{195}Pt{^{1}H} FT-NMR spectra (64.3 MHz, CH$_2$Cl$_2$): **6b** experimental (top) vs. calculated spectrum (bottom) for a mixture of 5-spin (AA$'$XX$'$M) and 6-spin (AA$'$XX$'$MM$'$) isotopomers in a 4:1 ratio.

PP)]$_2$ (**6b**) and [PtMe(μ-PP)]$_2$ (**6f**) complexes. Substitution of a chloro ligand by a methyl ligand shifts the ^{195}Pt resonance to higher field; this increased shielding perhaps indicates an increase of electron density around the metal when a methyl ligand replaces a chloride. The inductive character of the methyl ligand is reflected in the chemical shift of the trans phosphorus atom: δ -154.7 and -153.2 ppm for the methyl complexes **6e** and **6f**, respectively, whereas δ -144.4 and -146.5 ppm for the analogous chloro complexes **6a** and **6b**, respectively.

All coupling constants (with the exception of the two-bond platinum–platinum coupling constant) were calculated by iterative techniques by use of ^{31}P{^{1}H} resonances arising from the AA$'$XX$'$ and AA$'$XX$'$M spin systems, as well as the AA$'$XX$'$MM$'$ spin system when the ^{195}Pt{^{1}H} NMR spectra were available. The platinum–platinum coupling constants, $^2J_{Pt-Pt}$, were calculated from the ^{195}Pt{^{1}H} NMR spectra only, since the resonances for the six-spin system usually were either hidden or too weak in intensity in ^{31}P{^{1}H} NMR spectra. In those diplatinum complexes that were examined by ^{195}Pt{^{1}H} NMR, computer simulations of the 64.30-MHz spectra showed that one could measure the $^2J_{Pt-Pt}$ coupling constant directly from the AA$'$XX$'$MM$'$ satellite peaks
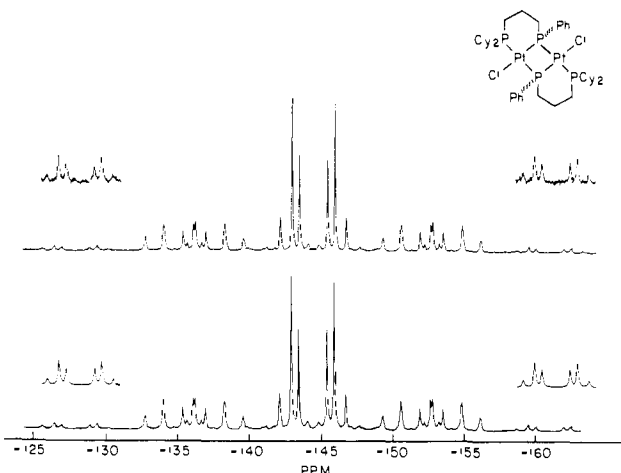
(25) Waid, R. D.; Meek, D. W. *Inorg. Chem.*, **1984**, *23*, 778–782.

Figure 4. The $^{31}P\{^1H\}$ FT-NMR spectra (121.5 MHz, CH_2Cl_2): **6a** phosphido region experimental (top) vs. calculated (bottom) for a mixture of 4-spin (AA'XX'), 5-spin (AA'XX'M), 6-spin (AA'XX'MM') isotopomers in a 4:4:1 ratio.

surrounding the intense outside peaks of the AA'XX'M spin system (see Figure 3). Figure 4 is typical of the computer simulations of the combined patterns for the four-, five-, and six-spin systems in the $^{31}P\{^1H\}$ NMR spectra. The coupling constants are labeled according to diagram **22**. We have assumed that the one-bond, platinum–phosphorus coupling constants are positive.[26]

22
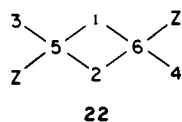
In a comparison of the four diplatinum complexes with planar P_2Pt_2 cores (**7a, 7b, 17, 18**) with four complexes that have bent Pt_2P_2 cores (**6a, 6b, 6e, 6f**), the magnitude of the three-bond coupling constant $^3J_{45}$ appears to be sensitive to the stereochemistry of the core. In this comparison of eight structures, the four complexes with bent cores show considerably smaller $^3J_{45}$ values (+3.9 to +12.7 Hz) compared to the four complexes with planar cores (+32.6 to +63.1 Hz). The best comparisons are probably those between diastereomeric complexes that differ only in core geometry: $^3J_{45} = +32.6$ Hz for **7a** vs. +5.0 Hz for **6a** and +39.2 Hz for **7b** vs. +6.0 Hz for **6b**. The two-bond coupling constant $^2J_{56}$ is larger (+639 Hz) for the diastereomer with the planar core (**7a**), compared to the isomer with the bent core (**6a**, $^2J_{56} = +259$ Hz). While the difference in the $^2J_{56}$ values can be rationalized on the basis of a better orbital overlap in the case of a planar core, other examples are needed to determine the generality of this observation. In both the platinum and palladium complexes, the coupling between *trans*-phosphorus atoms is considerably larger than coupling between *cis*-phosphorus atoms, i.e., $^2J_{14} > ^2J_{12}$ or $^2J_{13}$.[27] In a comparison of four diastereomeric pairs, complexes with planar cores (**7a-7d**) give slightly larger $^2J_{12}$ and $^2J_{14}$ values than the corresponding isomers with bent cores (**6a-6d**).

The stronger trans influence of the phosphine vs. the chloro ligand is demonstrated by the larger $^1J_{15}$ values as compared to the corresponding $^1J_{25}$ values. Similarly, the stronger trans influence of the methyl ligand is clearly seen in the smaller $^1J_{15}$ values as compared to the $^1J_{25}$ values for the corresponding complexes. Strong trans-influence ligands (e.g., CH_3, R_3P) are known to reduce the $^1J_{M-P}$ coupling constants when compared to those of the analogous chloro compounds.[28-30]
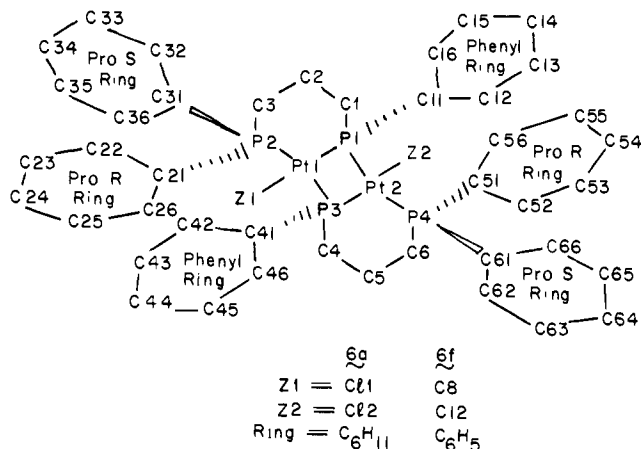

Figure 5. The atomic designations for the structures **6a** and **7a**.

In a limited comparison of **6a** vs. **6e** and **6b** vs. **6f**, substitution of a chloro ligand by a methyl ligand decreased the magnitude of $^1J_{12}$ and $^1J_{14}$, whereas the value of $^2J_{13}$ increased considerably. Replacement of a cyclohexyl group by a phenyl group increases the magnitude of the $^1J_{15}$ and $^1J_{25}$ coupling constants in the three cases studied: **7b** vs. **7a**, **6b** vs. **6a**, and **6f** vs. **6e**. On the other hand, the magnitude of $^1J_{35}$ changed very little. In both the Pd and Pt series, smaller increases are noted for the $^2J_{14}$ values.

A comparison of similar platinum and palladium complexes [**6a** with **6c**, **6b** with **6d**, **7a** with **7c**, and **7b** with **7d**] shows that the phosphorus–phosphorus coupling constants, $^2J_{12}$, $^2J_{13}$, and $^2J_{14}$, are all larger for the corresponding palladium complex. Of the three $^2J_{P-P}$ constants, the $^2J_{12}$ constant seems to be the most sensitive to a change of the metal. The four-bond, P–P coupling constant $^4J_{34}$ is so small (~ 0 Hz) in the four palladium complexes that the $^{31}P\{^1H\}$ spectra show only six of the ten lines expected for each portion of the AA'XX' spin system. Brandon and Dixon[23] have reported similar observations in comparing other phosphido-bridged platinum and palladium complexes having similar structures: [$MCl(\mu-PPh_2)(PHPh_2)]_2$ (**17** [M Pt]; **23** [M = Pd]); [$MCl(\mu-PPh_2)(PEt_3)]$ (**24** [M = Pt]; **25** [M = Pd]), and [$M(\mu-PPh_2)(dppe)]_2Cl_2$ (**18** [M = Pt]; **26** [M = Pd]). While only a relatively limited amount of data is available regarding the magnitude of cis-$^2J_{P-P}$ and $trans$-$^2J_{P-P}$ coupling constants in Ni, Pd, and Pt complexes of comparable structures, the values of $^2J_{P-P}$ (albeit with some exceptions) seem to decrease down the nickel triad.[23,31] However, additional sets of data are needed before more general conclusions can be drawn.

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In conclusion, within the series of compounds studied, certain $^{31}P\{^1H\}$ and $^{195}Pt\{^1H\}$ NMR spectral parameters appear to be sensitive to the stereochemistry of the $M-\mu P-M-\mu P$ core. Further studies are under way to probe the relationships between the core stereochemistry and NMR spectral parameters.

Experimental Section

Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. Infrared spectra were recorded on a Perkin-Elmer 337 spectrophotometer. Except when noted otherwise, phosphorus-31 and platinum-195 NMR spectra (7 T) were recorded in dichloromethane solution at 121.50 and 64.30 MHz, respectively, on a Bruker WM-300 Fourier transform spectrometer (equipped with an Aspect 2000 data system) at The Ohio State University Chemical Instrument Center. Some phosphorus-31 NMR spectra were recorded in other solvents at 36.43 MHz on a Bruker HX-90 Fourier transform spectrometer and are so noted. Protons were decoupled from the phosphorus nuclei by broad-band irradiation. For phosphorus-31 NMR spectra, an acetone-d_6 solution of trimethyl phosphate $[(CH_3O)_3P=O]$ in a coaxial insert tube was used as an external lock and an external secondary reference (δ 1.594 relative to 85% H_3PO_4), respectively. For platinum-195 NMR spectra, unless noted otherwise, dichloromethane-d_2 was used as an internal lock, and a saturated aqueous solution of potassium tetrachloroplatinate was used as an external secondary reference [δ 1927[32] relative to *cis*-PtCl$_2$-(SMe$_2$)$_2$]. For phosphorus-31 and platinum-195 NMR spectra, negative chemical shifts are upfield from the respective reference standards. Proton FT-NMR spectra were recorded in deuterated solvents at 300 or 90 MHz on the Bruker WM-300 or Bruker HX-90 Fourier transform spectrometers, respectively. The deuterated solvents were used as an internal lock, and the residual protio-peaks were used as internal secondary references (relative to tetramethylsilane). Proton CW-NMR spectra were recorded in deuterated solvents at 60 MHz on a Varian EM-360 spectrometer with tetramethylsilane as an internal reference. Iterative calculations and simulated NMR spectra were calculated on the Aspect 2000 computer with use of the PANIC program of the Bruker Instrument Corp. PANIC is a microcomputer version of the LAOCOON[33] program. TLC analyses were performed on Eastman chromatogram silica gel sheets with a fluorescent indicator, and they were developed with use of an eluant of dichloromethane/petroleum ether (38–56 °C), 2:1 v/v.

All reactions were carried out under an atmosphere of high-purity nitrogen by using standard Schlenk techniques. Solutions of air-sensitive reagents were transferred between reaction vessels with syringes flushed with nitrogen, stainless steel needles, or a glass transfer tube equipped with a Teflon stopcock. Solvents were purged with nitrogen for 30 min prior to use. Dicyclohexylphosphine, diphenylphosphine, and phenylphosphine were purchased from Strem Chemical Co. and distilled under nitrogen prior to use. ($\pm$)-1-(Diphenylphosphino)-3-(phenylphosphino)propane (*dl*-(PPH); 11),[34] dimethyl(1,5-cyclooctadiene)platinum(II),[35] and dichloro(1,5-cyclooctadiene)platinum(II)[35] were prepared by literature methods.

($\pm$)-1-(Dicyclohexylphosphino)-3-(phenylphosphino)propane (*dl*-(CyPPH); 10). To a Pyrex Schlenk flask containing dicyclohexylphosphine (25.0 g, 126 mmol) dissolved in dry tetrahydrofuran (300 mL) and cooled to 0 °C was added a 1.2 M methyllithium/diethyl ether solution (155 mL, 186 mmol). The clear solution became dark red immediately and evolved a large quantity of methane gas. A finely divided yellow suspension of lithium dicyclohexylphosphide appeared in the reaction vessel as it was allowed to warm to room temperature. This suspension was slowly transferred via a stopcock-equipped glass tube to a second flask containing a solution of 1,3-dichloropropane (100 g, 890 mmol) in diethyl ether (200 mL) under vigorous stirring. The first reaction vessel was washed with diethyl ether (100 mL) which was then added to the contents of the second flask. After the mixture was stirred overnight, the solvents were removed at reduced pressure and the cloudy oily residue was treated with ethanol (60 mL) and water (150 mL) and then extracted with diethyl ether (3 × 150 mL). The ether extracts were dried overnight over anhydrous MgSO$_4$ and filtered. Distillation of the solvents at reduced pressure yielded ca. 85% of the crude intermediate 1-chloro-3-(dicyclohexylphosphino)propane as a yellow oil.

A solution of crude 1-chloro-3-(dicyclohexylphosphino)propane (22.6 g, ca. 82 mmol) in toluene (100 mL) was added dropwise from a pres-

sure-equalizing funnel to a mechanically stirred solution of liquid ammonia at −78 °C containing sodium metal (2.0 g, 87 mmol), phenylphosphine, $C_6H_5PH_2$ (9.5 g, 86 mmol), and diethyl ether (100 mL). The ammonia was then allowed to evaporate overnight, and the residue was treated with a saturated aqueous solution of NH$_4$Cl (200 mL). The separated organic layer was added to diethyl ether extracts of the aqueous layer, dried over anhydrous MgSO$_4$, and filtered. The solvent was distilled at reduced pressure at 50 °C (0.1 torr). Distillation of the residue in vacuo in a Kugelrohr apparatus yielded 18.54 g (65%) of 10 as an oily liquid: bp 130–160 °C (0.1 torr); ^{1}H NMR (60 MHz, C$_6$D$_6$) δ 7.4 and 7.0 (m, 5 H, aromatic H), 4.1 (broad d, 1 H, PH, $^1J_{P-H}$ = ~204 Hz), 0.7–2.1 (m, 28 H, aliphatic H); $^{31}P\{^1H\}$ NMR (36.43 MHz, C$_6$H$_6$) δ −7.72 (s, 1 P, Cy$_2$P), −54.0 (broad d, 1 P, P(H)Ph, J_{P-H} = 204.5 Hz); IR ν_{max} (neat) 3060 (aromatic C–H), 2850 (aliphatic C–H), 2280 cm^{-1} (P–H).

($\pm$)-Dichloro(1-(dicyclohexylphosphino)-3-(phenylphosphino)-propane)platinum(II) (*dl*-[PtCl$_2$(CyPPH)]; 13). To a slurry of dichloro(1,5-cyclooctadiene)platinum(II) (230 mg, 0.62 mmol) in benzene (20 mL) was added a 0.41 M toluene solution of 10 (1.5 mL, 0.62 mmol). Addition of the diphosphine caused the disappearance of the solid starting material and rapid precipitation of a finely divided white solid. Reduction of the solvent volume to 1–2 mL in a stream of nitrogen followed by addition of diethyl ether (40 mL) yielded more solid. After the solid was filtered and washed with diethyl ether (2 × 40 mL), it was recrystallized from nitromethane to yield 327 mg (86%) of 13 as white crystals: $^{31}P\{^1H\}$ NMR (36.43 MHz, CH$_2$Cl$_2$) δ 7.54 (Cy$_2$P, $^1J_{Pt-P}$ = 3303 Hz, $^2J_{P-P}$ = 19.7 Hz), −28.83 (P(H)Ph, $^1J_{Pt-P'}$ = 3390 Hz, $^2J_{P-P}$ = 19.7 Hz), ^{31}P NMR (36.43 MHz, CH$_2$Cl$_2$) δ 7.54 (Cy$_2$P, $^1J_{Pt-P}$ = 3300 ± 10 Hz), −28.8 (P(H)Ph, $^1J_{Pt-P'}$ = 3390 ± 10 Hz, $^1J_{P-H}$ = 430 ± 10 Hz); $^{195}Pt\{^1H\}$ (Me$_2$SO) δ −993 (dd, $^1J_{Pt-P}$ = 3303 Hz, $^1J_{Pt-P'}$ = 3390 Hz).

Anal. Calcd for C$_{21}$H$_{34}$Cl$_2$P$_2$Pt: C, 41.05; H, 5.58; Cl, 11.54. Found: C, 41.36; H, 5.71; Cl, 11.29.

($\pm$)-Dichloro(1-(diphenylphosphino)-3-(phenylphosphino)propane)-platinum(II) (*dl*-[PtCl$_2$(PPH)]; 14). Starting with 9, the same method as for 13 yielded 83% of the title complex (14) as white crystals: mp 220 °C dec; $^{31}P\{^1H\}$ NMR (36.43 MHz, CH$_2$Cl$_2$) δ −5.74 (Ph$_2$P, $^1J_{Pt-P}$ = 3403 Hz, $^2J_{P-P}$ = 24.42 Hz), −28.85 (P(H)Ph, $^1J_{Pt-P'}$ = 3256 Hz, $^2J_{P-P}$ = 24.42 Hz), ^{31}P NMR (36.43 MHz, CH$_2$Cl$_2$) δ −5.74 (Ph$_2$P, $^1J_{Pt-P}$ = 3400 ± 10 Hz), −28.85 (Ph(H)P, $^1J_{Pt-P'}$ = 3255 ± 10 Hz, $^1J_{P-H}$ = 460 ± 10 Hz); $^{195}Pt\{^1H\}$ NMR (Me$_2$SO) δ −955 (dd, $^1J_{Pt-P}$ = 3403 Hz, $^1J_{Pt-P'}$ = 3256 Hz).

Anal. Calcd for C$_{21}$H$_{22}$Cl$_2$P$_2$Pt: C, 41.87; H, 3.68; Cl, 11.77; P, 10.28. Found: C, 41.94; H, 3.73; Cl, 11.84; P, 10.61.

trans-Dichloro-1,2κ^2Cl-μ-[[3-(dicyclohexylphosphino-1κP)propyl]-phenylphosphido-1:2κP]-μ-[[3-(dicyclohexylphosphino-2κP)propyl]-phenylphosphido-1:2κP]diplatinum (*meso*-[PtCl(μ-CyPP)]$_2$; 7a). To a suspension of 13 (600 mg, 0.98 mmol) in tetrahydrofuran (10 mL) was added triethylamine (0.5 mL, 3.6 mmol) with magnetic stirring; the suspended solid dissolved momentarily before a solid separated again. After the mixture was stirred for 12 h, the solid was isolated on a glass filter frit, washed with absolute ethanol (3 × 5 mL), and dried to give 510 mg of the crude complex. The $^{31}P\{^1H\}$ NMR spectrum revealed the presence of two isomers in ca. a 1:1 ratio. TLC analysis showed two new spots (R_f 0.70 in 2:1 CH$_2$Cl$_2$/petroleum ether and 0.53). The crude solid was dissolved in dichloromethane (50 mL), and the solution volume was reduced to ca. 15 mL on a rotary evaporator. A white solid separated from the solution on addition of diethyl ether (40 mL). After filtration with a Schlenk frit, the filtrate was saved for the next step and the sparingly soluble solid was recrystallized from dichloromethane/acetone to yield 250 mg (44%) of the title complex as a white crystalline solid: mp 337 °C; TLC (R_f 0.53); ^{1}H NMR (CD$_2$Cl$_2$) δ 8.14 (broad m, 2 H, aromatic *o*-H), 7.41 (m, 2 H), aromatic *m*-H), 7.34 (m, 1 H, aromatic *p*-H); $^{31}P\{^1H\}$ and $^{195}Pt\{^1H\}$ NMR, see Table V.

Anal. Calcd for C$_{42}$H$_{66}$Cl$_2$P$_4$Pt$_2$: C, 43.64; H, 5.76; Cl, 6.13; P, 10.72. Found: C, 43.47; H, 5.73; Cl, 6.40; P, 10.89.

($\pm$)-*cis*-Dichloro-1,2κ^2Cl-μ-[[3-(dicyclohexylphosphino-1κP)propyl]-phenylphosphido-1:2κP]-μ-[[3-(dicyclohexylphosphino-2κP)propyl]-phenylphosphido-1:2κP]diplatinum (*dl*-[PtCl(μ-CyPP)]$_2$; 6a|6a). Method A. Concentration of the filtrate from the above synthesis to a volume of ca. 3 mL followed by addition of diethyl ether (60 mL) caused a solid to separate. After filtration, the solid was recrystallized from dichloromethane/acetone to yield 220 mg (39%) of the title complex as a white crystalline solid: mp 297.5 °C, TLC (R_f 0.70 in 2:1 CH$_2$Cl$_2$/petroleum ether); ^{1}H NMR (CD$_2$Cl$_2$) δ 7.73 (broad m, 2 H, aromatic *o*-H), 7.21 (m, 1 H, aromatic *p*-H), 7.11 (m, 2 H, aromatic *m*-H); $^{31}P\{^1H\}$ and $^{195}Pt\{^1H\}$ NMR, see Table V.

Anal. Calcd for C$_{42}$H$_{66}$Cl$_2$P$_4$Pt$_2$: C, 43.64; H, 5.76; Cl, 6.13; P, 10.72. Found: C, 43.46; H, 5.76; Cl, 6.12; P, 10.51.

Method B. To a suspension of dichloro(1,5-cyclooctadiene)platinum-(II) (374 mg, 1.01 mmol) in benzene (10 mL) was added a 0.41 M

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toluene solution (2.5 mL, 1.03 mmol) of (±)-1-(dicyclohexyl-phosphino)-3-(phenylphosphino)propane (**10**), and the mixture was refluxed for 90 min. After cooling the white suspension, diethyl ether (40 mL) was added, and then the solid was collected. Recrystallization of the separated solid from dichloromethane/acetone yielded 485 mg (83%) of a white crystalline solid whose TLC R_f value (0.70) and ^{31}P{^{1}H} NMR spectrum (AA'XX', AA'XX'M, and AA'XX'MM' spin systems) were identical in all respects with those of **6a**.

(±)-*cis*-Dichloro-1,2κ^2*Cl*-μ-[[3-(diphenylphosphino-1κP)propyl]-phenylphosphido-1:2κP]-μ-[[3-(diphenylphosphino-2κP)propyl]phenyl-phosphido-1:2κP]diplatinum (*dl*-[PtCl(μ-PP)]₂; **6b|6b**). Starting with (±)-1-(diphenylphosphino)-3-(phenylphosphino)propane (**11**), the same method B as for **6a** yielded 86% of the title compound as white crystals, mp > 250 °C dec, for ^{31}P{^{1}H} and ^{195}Pt{^{1}H} NMR data, see Table V.

Anal. Calcd for C₄₂H₄₂Cl₂P₄Pt₂: C, 44.57; H, 3.74; Cl, 6.27; P, 10.95. Found: C, 44.67; H, 3.50; Cl, 6.51; P, 10.69.

Mixture of (±)-*cis*- and *trans*-Dichloro-1,2κ^2*Cl*-μ-[[3-(diphenyl-phosphino-1κP)propyl]phenylphosphido-1:2κP]-μ-[[3-(diphenyl-phosphino-2κP)propyl]phenylphosphido-1:2κP]diplatinum (*dl*- and *meso*-[PtCl(μ-PP)]₂; 6b|6b) and 7b). Starting with **14**, the same method B as for the preparation of the *dl*- and *meso*-[PtCl(μ-CyPP)]₂ mixture (**6a** and **7a**, respectively) yielded 96% of a mixture of the title complex as a white solid. The ^{31}P{^{1}H} NMR spectrum revealed the presence of two diastereomers—each with AA'XX', AA'XX'M, and AA'XX'MM' spin-system resonances. The ^{31}P NMR resonances of the α diastereomer were identical in all respects with those of **6b**.

Mixture of (±)-*cis*- and *trans*-Dichloro-1,2κ^2*Cl*-μ-[[3-(dicyclohexyl-phosphino-1κP)propyl]phenylphosphido-1:2κP]-μ-[[3-(dicyclohexyl-phosphino-2κP)propyl]phenylphosphido-1:2κP]dipalladium (*dl*- and *meso*-[PdCl(μ-CyPP)]₂; 6c|6c and 7c). To a suspension of sodium tetrachloropalladate (206 mg, 0.70 mmol) in tetrahydrofuran (7.0 mL) was added a 0.41 M toluene solution (1.7 mL, 0.70 mmol) of **10**; the color changed immediately from rust-red to yellow, and then a yellow solid separated. After collection on a frit, the yellow solid was washed with diethyl ether (2 × 5 mL) and dried in vacuo to yield 232 mg (68%) of the title complex. The ^{31}P{^{1}H} NMR spectrum revealed the presence of *dl* and meso diastereomers, each with an AA'XX' NMR pattern; see Table V.

Mixture of (±)-*cis*- and *trans*-Dichloro-1,2κ^2*Cl*-μ-[[3-(diphenyl-phosphino-1κP)propyl]phenylphosphido-1:2κP]-μ-[[3-(diphenyl-phosphino-2κP)propyl]phenylphosphido-1:2κP]dipalladium (*dl*- and meso-[PdCl(μ-PP)]₂; 6d|6d and 7d). Starting with **11**, the same method as for the preparation of the *dl*- and meso-[PdCl(μ-CyPP)]₂ mixture (**6c** and **7c**, respectively) yielded 82% of a mixture of the complexes **6d|6d** and **7d** as a yellow solid. The ^{31}P{^{1}H} NMR spectrum revealed the presence of *dl*- and meso diastereomers, each with a pattern for an AA'XX' spin system; see Table V.

(±)-Dimethyl(1-(dicyclohexylphosphino)-3-(phenylphosphino)-propane)platinum(II) (*dl*-[Pt(CH₃)₂(CyPPH)]; 19). To a solution of dimethyl(1,5-cyclooctadiene)platinum(II) (396 mg, 1.19 mmol) in tetrahydrofuran (20 mL) was added a 0.41 M toluene solution (2.9 mL, 1.19 mmol) of **10**. After the solution was stirred 3 h, the volume was reduced to ca. 2 mL in a stream of nitrogen. A solid separated upon addition of diethyl ether (20 mL). The solid was collected on a frit and washed with ethanol (2 × 5 mL). After the solid was dried in vacuo, it was recrystallized from tetrahydrofuran/ethanol to yield 444 mg (65%) of **19** as a crystalline solid: ^{31}P{^{1}H} NMR (36.43 MHz) δ 4.64 (Cy₂P, $^1J_{Pt-P}$ = 1773 Hz, $^2J_{P-P}$ = 18.7 Hz), −17.33 (Ph(H)P, $^1J_{Pt-P}$ = 1748 Hz, $^2J_{P-P}$ = 18.7 Hz).

Anal. Calcd for C₂₃H₄₀P₂Pt: C, 48.16; H, 7.03. Found: C, 47.80; H, 6.89.

(±)-Dimethyl(1-(diphenylphosphino)-3-(phenylphosphino)propane)-platinum(II) (*dl*-Pt(CH₃)₂(PPH)]; 27). Starting with **11**, the same method as for the preparation of **19** yielded 60% of **27** as a solid: ^{31}P{^{1}H} NMR (36.43 MHz) δ 3.28 (Ph₂P, $^1J_{Pt-P}$ = 1805 Hz, $^2J_{P-P}$ = 17.7 Hz), −18.05 (Ph(H)P, $^1J_{Pt-P}$ = 1654 Hz, $^2J_{P-P}$ = 17.7 Hz).

(±)-*cis*-μ-[[3-(Dicyclohexylphosphino-1κP)propyl]phenylphosphido-1:2κP]-μ-[[3-(dicyclohexylphosphino-2κP)propyl]phenylphosphido-1:2κP]dimethyl-1,2κ^2*C*-diplatinum (*dl*-[Pt(CH₃)(μ-CyPP)]₂; 6e|6e). To 0.1737 g of Pt(CH₃)₂(COD) dissolved in 2-ethoxyethanol (10 mL) was added 0.86 mL of a 0.606 M CyPPH/C₆H₆ solution. A white precipitate of Pt(CH₃)₂(CyPPH) appeared at room temperature. The temperature of the mixture was raised to 120 °C at which the precipitate redissolved and a yellow color started to develop after 5 min. The solution was maintained at ∼125 °C for 2 h and then cooled to room temperature. A white crystalline compound formed at room temperature; the crystals were isolated, washed with hexane, and dried with a N₂ stream. The ^{31}P{^{1}H} data are in Table V.

Anal. Calcd for C₄₄H₇₂P₄Pt₂: C, 47.39; H, 6.51; P, 11.11%. Found: C, 47.43; H, 6.79; P, 11.45.

Crystallography. Clear, colorless, crystalline rods of (*dl*- or *meso*-dichloro-1,2κ^2*Cl*-μ-[[3-(dicyclohexylphosphino-1κP)propyl]phenyl-phosphido-1:2κP]-μ-[[3-dicyclohexylphosphino-2κP)propyl]phenyl-phosphido-1:2κP]diplatinum (**6a|6a** or **7a**, respectively) were grown by allowing absolute ethanol (layered over a dichloromethane solution of either the racemic or *meso*-dimers) to diffuse slowly into the appropriate solution of the complex. Preliminary room-temperature photographic work indicated that crystals from the racemic mixture belonged to the orthorhombic system D_2^4-$P2_12_12_1$, Z = 4, whereas crystals from the solution of the meso complex belonged to the monoclinic system C_{2h}^5-$P2_1/n$ (alternative setting of $P2_1/c$), Z = 2.

Intensity data were collected at 148 K on a Syntex P1̄ diffractometer equipped with an LT-1 low-temperature device. Data collection and data reduction followed the standard practice at The Ohio State University.[37] Table I provides crystallographic and data collection details. Ten reflections measured every 100 reflections indicated small decay rates. Both data sets were corrected for these small decay rates and for absorption. Atomic scattering factors for the non-hydrogen[38] and hydrogen[39] atoms were from the standard sources. Anomalous dispersion corrections for the non-hydrogen atoms were included as $\Delta f'$ and $\Delta f''$ terms.[38] All least-squares refinements were done by using SHELX-76.[40]

The structure of compound **6a** was solved using MULTAN 80[41] for the platinum, chlorine, and phosphorus positions. Locations of the remaining nonhydrogen atoms were found by standard Fourier methods. The determination of the enantiomer was made by refining the nonhydrogen atoms isotropically on F using the reflections having $F_o^2 > 3\sigma(F_o^2)$ and no anomalous dispersion contributions. After convergence of this model, the anomalous dispersion corrections were included in further isotropic refinements of two separate models: the (S_n,S_n)-enantiomer refined to values of R = 0.035 and Rw = 0.039; the (R_n,R_n)-enantiomer, obtained by reversing the signs of all atomic coordinates, refined to values of R = 0.057 and Rw = 0.065. A comparison of these residuals indicates the (S_n,S_n) molecule is the correct enantiomer.

Prior to anisotropic refinement, the phenyl rings were constrained as rigid bodies (D_{6h} symmetry with r_{C-C} = 1.395 Å). Hydrogen positions were located in a difference Fourier map. All hydrogens were added as fixed contributions to the structure factors at idealized positions (C-H = 0.95 Å and B(H) = B_{iso}(C) + 1.0 Å²). In the final cycles of anisotropic refinement, an isotropic extinction parameter was included. The final discrepancy indices on F were R = 0.027 and Rw = 0.027 for the 4667 intensities with $F_o^2 > 3\sigma(F_o^2)$ and 368 variables. The largest peaks (0.9 e/Å³) in the difference electron density map were between the platinum and bridging phosphorus atoms.

Structure **7a** was solved for the platinum position by the Patterson method. All nonhydrogen atoms were located by Fourier methods. Hydrogen positions were again evident in a difference electron density map and were treated as described for structure **6a**; the phenyl rings were refined anisotropically. A secondary extinction parameter was included in the final cycles. At convergence R = 0.026 and Rw = 0.027 for 4365 observed reflections [$F_o^2 > 3\sigma(F_o^2)$] and 227 variables. A peak 1.39 e/Å³ high was found in the final difference Fourier map in a similar location as in structure **6a**.

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Conformations of the Nonbonded and the Coordinated Ligand Nonamethylimidodiphosphoramide (NIPA) in the Solid State and in Solution. X-ray Structure Determinations, NMR Study, and Theoretical Calculations on the NIPA Molecule and the Complex [UO₂(NIPA)₂C₂H₅OH](ClO₄)₂

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Abstract: The structures of crystalline nonamethylimidodiphosphoramide (NIPA) and its uranyl complex [UO₂-(NIPA)₂C₂H₅OH](ClO₄)₂ (B) as determined by X-ray diffraction are compared to results from NMR spectroscopy on solutions. It is shown that in solid NIPA the P=O groups are in a "trans" conformation whereas in polar solvents (CH₂Cl₂, CH₃NO₂) and in the complex they are in a "cis" arrangement. The total energies of the two conformations were calculated theoretically by the CNDO/2 method and a stabilization of ca. 10 kJ mol⁻¹ was found for the "cis" conformation of NIPA when surrounded by a polar solvent. ³¹P–³¹P and ³¹P–¹⁵N coupling constants were equally calculated and agree well with the values of $|^2J_{P-P}^{cis}|$ (15.6 Hz), $|^2J_{P-P}^{trans}|$ (22.0 Hz), and $|^1J_{P-N}^{cis}|$ (33.4 Hz) determined experimentally.

Phosphorylated molecules (i.e., containing the $>P=O$ group) are very good ligands for many metallic ions and are therefore often used as extractants in liquid–liquid extraction processes,[2] especially for the uranyl cation UO₂²⁺.

It has been reported previously[3] that the β-biphosphorylated chelating compound nonamethylimidodiphosphoramide (NIPA, [(Me₂N)₂P(:O)]₂NMe) forms a stable complex with uranyl perchlorate.

Recently we showed that, depending on the method of preparation, complexes of different stoichiometries are formed between NIPA and the UO₂²⁺ ion:[4–6] [UO₂(NIPA)₃]²⁺, 2ClO₄⁻ (A); [UO₂(NIPA)₂S]²⁺,2ClO₄, S = H₂O, CH₃OH, C₂H₅OH (B), and (CH₃)₂CO; [(UO₂)₂(NIPA)₅]⁴⁺,4ClO₄⁻ (C).

The knowledge of the structures of the complexes in the solid state and in solution is particularly important for the better understanding of the exceptional coordinating ability of this class of neutral bidentate ligands.

From the ³¹P NMR spectra of solutions of the complexes in a 2:1 v/v dichloromethane–nitromethane mixture (called C₂N in the following) it was possible to infer the ligand arrangement around the uranyl ion. In all of these complexes the coordination number of uranium is seven, the oxygen atoms of the ligand being located in a plane perpendicular to the linear O=U=O unit.

In complex A two ligand molecules are bidentate whereas the third one is bound to the ion by only one P=O group. Both molecules of NIPA in complex B are bidentate, the fifth coordination site in the equatorial plane being occupied by the oxygen atom of ligand S. Complex C, which has not been isolated in the solid state, exists in equilibrium with complexes A and B in solution. Its peculiar structure may be represented as two [UO₂-(NIPA)₂]²⁺ units containing bidentate NIPA ligands, connected by a bridging NIPA molecule.

All these results suggested that coordinated NIPA can assume different geometries. In the bidentate molecule the two P=O groups are obviously in a "cis" conformation; in the case of the monodentate NIPA in complex A or of the bridging NIPA in complex C they should be in a "trans" conformation for steric reasons.

This assumption is corroborated by the observation of different NMR coupling constants $|^2J_{P-P}|$ for the bidentate (15.6 Hz) and the monodentate molecule (22.0 Hz).

Only crystals of complex B were available for crystallographic studies, A yielding merely oily products in a variety of solvents tried for recrystallization.

If the coordinated ligand can adopt different conformations in its complexes, the same may be true for free NIPA. Therefore,

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