Mechanism and Stereochemistry of the Reaction of Dichloroplatinum(II) Complexes with Diazo Compounds. X-ray Structures of Four Key Products: [(2*R*,3*R*)-Bis(diphenylphosphino)butane]chloro-[(*S*)-chloro(methoxycarbonyl)methyl]platinum(II), (η^4-1,5-Cyclooctadiene)[3-chloro-5-(dimethoxyphosphonyl)-2-methoxy-4,1,2-platinaoxaphospholane *P*-oxide], (*R,R*)-[Chloro(dimethoxyphosphonyl)methyl][chloro-(trimethylsilyl)methyl](1,5-cyclooctadiene)platinum(II), and Chloro[chloro(dimethoxyphosphonyl)methyl]-(η^4-1,5-cyclooctadiene)platinum(II)

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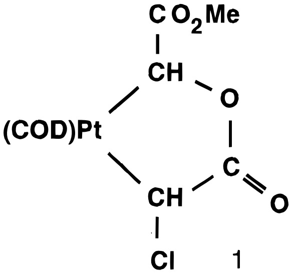
The structures of four key products formed by reaction of diazo compounds of the type $RCHN_2$ (R = CO_2Me, $P(O)(OMe)_2$, $SiMe_3$) with chloroplatinum(II) derivatives have been elucidated by X-ray crystallographic methods. The results confirm our earlier conclusions, based on NMR evidence and mechanistic considerations, concerning the stereochemistries of these products.

Introduction

We have shown[1] that $[(COD)PtCl_2]$ (COD = 1,5-cyclooctadiene) reacts with diazo compounds of the type $RCHN_2$ to give both mono- and bisinsertion products, $[(COD)Pt(CHClR)Cl]$ and $[(COD)Pt(CHClR)_2]$. For R = CO_2Me and $P(O)(OMe)_2$, the major bisinsertion product was shown to be the *R,R*/*S,S* enantiomeric pair, which was accompanied by the *R,S* diastereomer and a mixture of isomeric cyclic products, *viz*. platinalactones (**1**) and platinaoxaphospholanes (**2**). Mixed bisinsertion products, including cyclic ones in some cases, were obtained by reacting the mono-insertion products with a different diazo compound. $[\{(R,R)\text{-}Ph_2PCHMeCHMePPh_2\}PtCl_2]$ reacts more slowly with $RCHN_2$ than does the COD complex and gives both possible monoinsertion products. We suggested that the major diastereomer has the *R* stereochemistry at the newly-created chiral center. With R = CO_2Me, a very slow second insertion was observed, but only minor amounts of simple bisinsertion products were formed, the major products being platinalactones (**3**).



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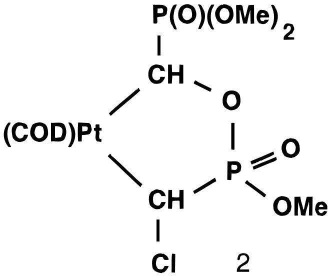

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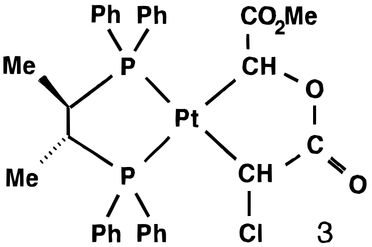

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The stereochemistries assigned to many of the above products were deduced on the basis of mechanistic arguments and/or NMR data. We now report X-ray crystallographic studies on four key compounds, **4**, **5**, **6**, and **7**. These structures establish that the stereochemistries originally proposed are indeed correct and support our mechanistic conclusions.

Results and Discussion

[(2*R*,3*R*)-Bis(diphenylphosphino)butane]chloro[(*S*)-chloro(methoxycarbonyl)methyl]platinum(II) (**4**) was prepared[1] by reaction of $[(COD)Pt(CHClCO_2Me)Cl]$ with (2*R*,3*R*)-bis(diphenylphosphino)butane [(*R*,*R*)-chiraphos] and separation of the resulting diastereomers by TLC. The crystals used for the X-ray study were obtained from the more polar isomer, which corresponds to the minor mono-insertion product upon reaction of $[\{(R,R)\text{-}Ph_2PCHMeCHMePPh_2\}PtCl_2]$ with N_2CHCO_2Me.

Our X-ray analysis of **4** establishes that the Pt coordination is square planar (Figure 1. The principal dimensions for this complex and for complexes **5**, **6**, and

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(1) McCrindle, R; McAlees, A. J. *Organometallics* **1993**, *12*, 2445−2461.

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Table 1. Summary of Principal Dimensions (Å, deg) in 4−7

4	Pt−C1	2.120(14)	C1−Pt−Cl1	93.4(4)	P1−C4−C5−P2	−55.8(12)	Pt−P2−C31−C36	−10.0(15)
	Pt−Cl1	2.349(4)	C1−Pt−P1	176.9(4)	Pt−P1−C11−C12	−102.5(14)	Pt−P2−C41−C42	−121.7(14)
	Pt−P1	2.277(4)	C1−Pt−P2	90.6(4)	Pt−P1−C11−C16	73.3(15)	Pt−P2−C41−C46	54.1(15)
	Pt−P2	2.208(4)	Cl1−Pt−P1	89.58(13)	Pt−P1−C21−C22	−2.1(17)	Cl1−Pt−C1−Cl2	82.9(6)
	C1−Cl2	1.88(2)	Cl1−Pt−P2	175.13(15)	Pt−P1−C21−C26	−17.5(13)	Cl1−Pt−C1−C2	−38.6(11)
	C1−C2	1.46(2)	P1−Pt−P2	86.48(13)	Pt−P2−C31−C32	171.3(13)		
5	Pt−C1	2.260(7)	C11−Pt−C13	82.2(3)	C11−P1−O3−C13	37.8(7)	O1−P1−C11−Cl	−55.7(6)
	Pt−C2	2.253(8)	C11−P1−O3	98.8(3)	C11−Pt−C13−O3	−20.7(6)	O3−C13−P2−O4	−171.4(6)
	Pt−C5	2.250(7)	C13−O3−P1	115.3(5)	C13−Pt−C11−P1	39.8(4)		
	Pt−C6	2.247(8)	O3−C13−Pt	113.9(5)	O3−P1−C11−Pt	−51.1(4)		
	Pt−C11	2.054(8)	P1−C11−Pt	104.6(4)	P1−O3−C13−Pt	−8.8(8)		
	Pt−C13	2.074(8)						
	C11−Cl	1.796(8)						
6	Pt−C11	2.066(5)	C11−Pt−C31	83.8(2)	Cl2−C31−Pt	116.4(3)	C31−Pt−C11−Cl1	−150.1(3)
	Pt−C31	2.061(5)	Cl1−C11−Pt	115.9(3)			C31−Pt−C11−Si	88.5(3)
	C11−Cl	1.846(5)	Cl1−C11−Si	104.8(3)			C11−Pt−C31−Cl2	−141.1(3)
	C31−Cl	1.824(6)	Cl2−C31−P	106.7(3)			C11−Pt−C31−P	96.6(3)
7[a]	Pt1−C1A	2.260(6)	C1A−Pt1−C5A	96.0(2)	C2A−Pt1−C11	159.9(2)	Cl1A−Pt1−C11−Cl2A	−142.5(3)
	Pt1−C2A	2.263(6)	C1A−Pt1−C6A	80.4(3)	C2A−Pt1−Cl1A	93.7(2)	Cl1A−Pt1−C32−P1	94.4(3)
	Pt1−C5A	2.166(5)	C2A−Pt1−C5A	81.2(2)	C5A−Pt1−C11	92.1(2)		
	Pt1−C6A	2.157(6)	C2A−Pt1−C6A	87.7(3)	C5A−Pt1−Cl1A	161.8(2)		
	Pt1−C11	2.058(5)	C1A−Pt1−C11	164.8(2)	C6A−Pt1−C11	98.6(2)		
	Pt1−Cl1A	2.3160(15)	C1A−Pt1−Cl1A	89.4(2)	C6A−Pt1−Cl1A	160.3(2)		
	C11−Cl2A	1.811(6)						

[a] Dimensions for molecule 1 only: those of molecule 2 are very similar (see text).

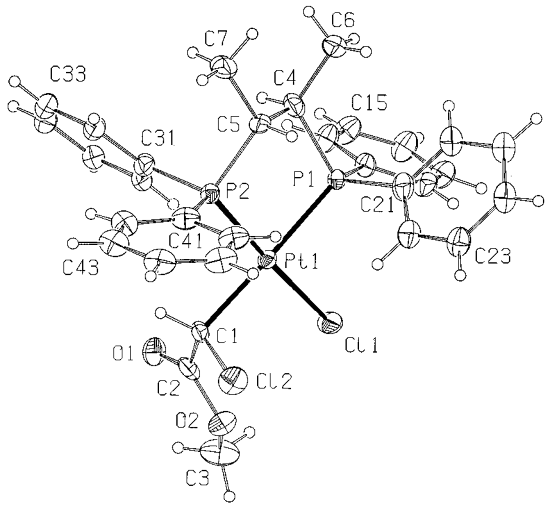
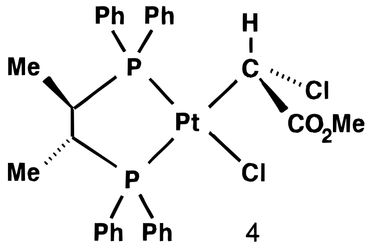


Figure 1. A view of **4** with an indication of the numbering scheme; phenyl ring C atoms are labeled C*i*1−C*i*6, (*i* = 1−4). Anisotropic displacement ellipsoids are drawn at the 30% probability level.



4

7, discussed below, are listed in Table 1, and full details for all four structures are in the Supporting Information). The difference found for the Pt−P bond lengths is consistent with the expected relative trans-influences of the −Cl and $-CHClCO_2Me$ ligands, with Pt−P2 (trans to Cl) = 2.208(4) Å and Pt−P1 = 2.277(4) Å. These bond lengths are shorter than the corresponding ones reported[2] for the similar complex [(*R*,*R*-diop)Pt(*R*-$CHClCO_2Et$)Cl], reflecting the lower steric demand of the chiraphos ligand *versus* diop. The Pt−C and Pt−Cl bond lengths found for **4** are comparable with those reported[2] for the diop complex. The absolute configuration of the chiraphos moiety, as revealed by the analysis, is that anticipated, while the stereochemistry at the carbon directly attached to Pt is *S*, as suggested[1] previously on the basis of mechanistic arguments. The five-membered ring, as found[3] for other chiraphos complexes, adopts a half-chair conformation with the methyl groups equatorial, while the phenyl groups adopt pseudoaxial (torsion angles: Pt−P1−C21−C22 = −2.1(17)° and Pt−P2−C31−C36 = −10.0(15)°) and pseudoequatorial dispositions (torsion angles: Pt−P1−C11−C16 = 73.3(15)° and Pt−P2−C41−C46 = 54.1(15)°), although the latter shows a notable deviation from an idealized pseudoequatorial orientation (torsion angle *ca* 70°). There appear to be no unusually short contacts between this phenyl group (or its pseudoaxial partner) and the $-CHClCO_2Me$ ligand, which adopts a conformation about the Pt−C bond in which the α-CH bond lies close to the coordination plane and is directed toward the space between the P2−C31 and P2−C41 bonds, while the Cl and CO_2Me substituents occupy sterically less encumbered positions above and below the coordination plane. Similar conformations have been reported[2,4] for −CHXR ligands in related complexes. In our previous publication,[1] we suggested that the $-CHClCO_2Me$ ligand in **4** might adopt a conformation in which the Cl atom rather than the H atom lies close to the coordination plane and between the phenyl groups. We reasoned that in this conformation a potential steric interaction between the bulky ester function and the pseudoaxial phenyl would be avoided. However, one might imagine the structure shown in Figure 1 to be derived from an idealized one, in which the C1−H bond lies right in the coordination plane, by a small rotation about the C1−Pt bond, which brings

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(2) Bergamini, P.; Costa, E.; Sostero, S.; Orpen, A. G.; Pringle, P. G. *Organometallics* **1992**, *11*, 3879−3885.

(3) Brown, J. M.; Evans, P. L. *Tetrahedron* **1988**, *44*, 4905−4916.

(4) (a) Bergamini, P.; Costa, E.; Sostero, S.; Ganter, C.; Hogg, J.; Orpen, A. G.; Pringle, P. G. *J. Organomet. Chem.* **1993**, *455*, C13−C16. (b) Bergamini, P.; Costa, E.; Sostero, S.; Cramer, P.; Hogg, J.; Orpen, A. G.; Pringle, P. G. *Organometallics* **1994**, *13*, 1058−1060.

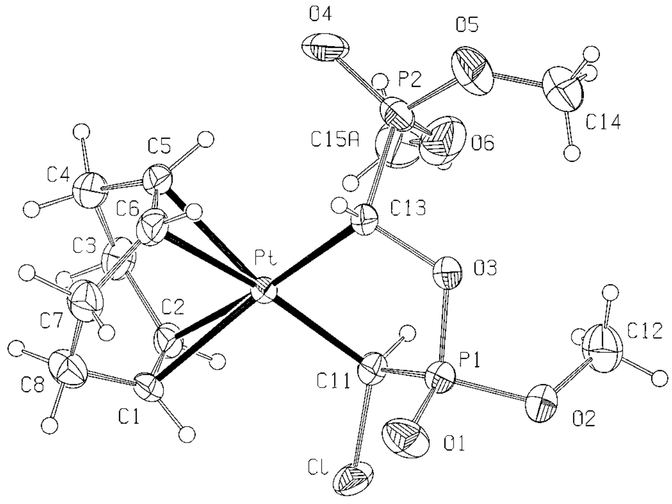
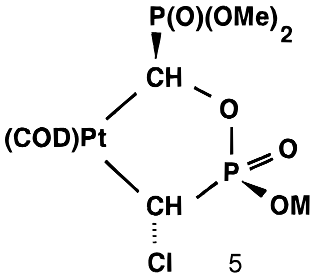


Figure 2. A view of **5** with an indication of the numbering scheme. Anisotropic displacement ellipsoids are drawn at the 30% probability level.

this hydrogen atom closer to the neighboring pseudoaxial phenyl group. This rotation would move the CO_2-Me group away from the same phenyl but drive Cl2 into its pseudoequatorial phenyl partner. The latter interaction is attenuated by this phenyl group twisting away from its idealized position, as noted above, resulting in a Cl2···C46 separation of 3.62(2) Å.

Two isomers of (η^4-1,5-cyclooctadiene)[3-chloro-5-dimethoxyphosphonyl-2-methoxy(4-platina-1,2-oxaphospholane-*P*-oxide)], **2**, were isolated[1] from the reaction of $(COD)PtCl_2$ with excess $N_2CHP(O)(OMe)_2$. Structures for both isomers, including stereochemistry, were advanced on the basis of ^1H and ^{31}P NMR evidence. The present X-ray study confirms the structure and relative stereochemistry originally proposed for the major isomer, **5**.



5

The X-ray analysis of **5**, which had crystallized as a racemic twin, establishes that the Pt coordination is square planar (Figure 2). The platinaoxaphospholane ring adopts an envelope conformation with C11 as the flap and the chloro substituent equatorial. The dimethoxyphosphonyl and methoxy substituents are both trans to the chloro substituent, as proposed earlier[1] on the basis of proton NMR data.

The major product formed upon reaction of (COD)-$Pt(CHClSiMe_3)Cl$ with $N_2CHP(O)(OMe)_2$ or of (COD)-$Pt[CHClP(O)(OMe)_2]Cl$ with $N_2CHSiMe_3$ was suggested[1] to be (*R,R*/*S,S*)-[chloro(dimethoxyphosphonyl)-methyl][chloro(trimethylsilyl)methyl](1,5-cyclooctadiene)-platinum(II) on the basis of mechanistic arguments and a proposed NMR correlation with compounds of known stereochemistry. We have now obtained crystals from this material suitable for X-ray studies which confirm the above configurational assignment.

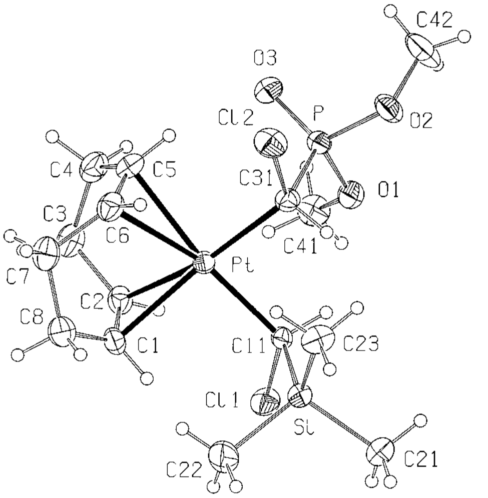
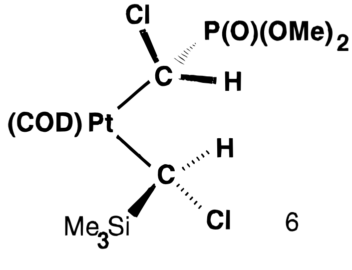


Figure 3. A view of **6** with an indication of the numbering scheme. Anisotropic displacement ellipsoids are drawn at the 30% probability level.

The space group, found for the selected crystal, proved to be polar, indicating that spontaneous resolution had occurred during crystallization. A similar situation was encountered[5] in the case of the bis(phosphonate) complex $(COD)Pt[CHClP(O)(OMe)_2]_2$. The absolute configuration of the enantiomorph (**6**) studied was established unequivocally as *S,S*. Our X-ray analysis of **6** establishes that the Pt coordination is square planar (Figure 3). The bulky $PO(OMe)_2$ and $SiMe_3$ substituents are oriented axially above and below the coordination plane in the least sterically demanding positions available. Consequently, the C−H and C−Cl bonds of the σ-bonded ligands lie close to the coordination plane with the C−H bonds directed toward the more restricted space between the two σ-bonded ligands (H···H = 2.03 Å).



6

In our mechanistic discussions[1] of the formation of **5** and **6** (plus its enantiomer) from the monoinsertion product $(COD)PtCl[CHClPO(OMe)_2]$, (**7**), we suggested that the $CHClPO(OMe)_2$ ligand would prefer to adopt a conformation in which the $PO(OMe)_2$ moiety occupies the position of least steric demand, while the α-CH lies close to the Pt−Cl. The X-ray structure of **7** (see below) confirms that the $CHClPO(OMe)_2$ ligand does indeed adopt this conformation, at least in the solid state. Notably, the greater steric demand of the (*R,R*)-chiraphos ligand *versus* the COD ligand is reflected in the finding that the $CHClCO_2Me$ fragment in **4** adopts a conformation in which the α-CH is adjacent to the phenyl groups of the phosphine ligand rather than to the Pt−Cl.

Our X-ray analysis of **7** showed that the crystals had two independent molecules linked by a water of crystal-

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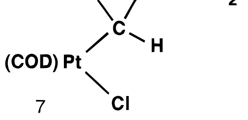
[5] Ferguson, G.; Gallagher, J. F.; McAlees, A. J.; McCrindle, R.; Phillips, J.; Williams, G. J. B. *J. Organomet. Chem.* **1992**, *430*, C23−C26.

Table 2. Summary of Crystal Data, Data Collection, Structure Solution, and Refinement Details

	4	**5**	**6**	**7**.0.5(H_2O)
		(a) Crystal Data		
mol formula	$C_{31}H_{32}Cl_2O_2P_2Pt$	$C_{13}H_{23}ClO_6P_2Pt$	$C_{15}H_{29}Cl_2O_3PPtSi$	$C_{11}H_{19}Cl_2O_3PPt\cdot0.5(H_2O)$
mol mass	764.50	567.79	582.43	505.23
color, habit	colorless, lath	colorless, plate	colorless, plate	colorless, block
crystal size, mm	0.21 × 0.11 × 0.05	0.45 × 0.40 × 0.25	0.45 × 0.35 × 0.15	0.45 × 0.35 × 0.30
crystal system	orthorhombic	orthorhombic	orthorhombic	triclinic
a, Å	9.7623(6)	9.0299(6)	9.8709(7)	8.0880(7)
b, Å	10.9524(9)	12.0137(8)	11.9516(8)	14.1896(9)
c, Å	27.743(4)	16.4067(10)	17.4082(13)	14.2243(7)
α, deg	90	90	90	107.218(5)
β, deg	90	90	90	95.597(5)
γ, deg	90	90	90	95.083(6)
V, Å^3	2966.3(6)	1779.8(2)	2053.7(3)	1540.0(2)
space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P\bar{1}$
Z	4	4	4	4
$F(000)$	1504	1096	1136	964
D_{calcd}, g cm^{-3}	1.712	2.119	1.884	2.179
μ, mm^{-1}	5.046	8.238	7.238	9.563
		(b) Data Acquisition[a]		
temp, K	294(1)	294(1)	294(1)	294(1)
unit-cell reflcns (θ-range), deg	25 (5.8−13.5)	25 (12.0−19.0)	25 (12.0−19.0)	25 (12.5−20.0)
max. θ for reflcns, deg	24.92	26.91	29.95	26.91
h,k,l range of reflcns	0 to 11, 0 to 12, 0 to 32	−11 to 11, −15 to 15, −20 to 20	−13 to 13, −16 to 16, −24 to 24	−10 to 10, 0 to 18, −18 to 17
decay in 3 standard reflcns	0.9	5.1	9.7	9.2
reflcns measured	2963	4293	6532	6703
unique reflcns	2963	3885	5982	6703
R_{int}		0.028	0.019	
reflcns with $I > 2\sigma(I)$,	2204	3617	5575	5901
absorption correction type	ψ-scans	ψ-scans	ψ-scans	ψ-scans
min, max abs corr	0.7951, 0.9948	0.3219, 0.9995	0.2392, 0.9968	0.6035, 0.9969
		(c) Structure Solution and Refinement[b]		
refinement on	F^2	F^2	F^2	F^2
solution method	Patterson heavy atom	Patterson heavy atom	Patterson heavy atom	Patterson heavy atom
H-atom treatment	riding	riding	riding	riding
Flack parameter	−0.01(2)	0.403(11)	0.014(7)	
no. of variables in L.S.	344	220	209	334
weights:				
k in $w = 1/(\sigma^2F_o^2 + k)$ [$P = (F_o^2 + 2F_c^2)/3$]	$(0.0465P)^2$	$(0.0352P)^2 + 6.6000P$	$(0.0465P)^2 + 2.1144P$	$(0.0657P)^2 + 3.3597P$
R, R_w, gof	0.043, 0.096, 0.96	0.030, 0.070, 1.01	0.030, 0.076, 1.05	0.034, 0.098, 1.08
density range in final Δ-map, e Å^{-3}	−1.367, 0.986	−0.719, 1.384	−1.129, 1.787	−2.563, 2.748
final shift/error ratio	0.000	0.059	0.002	0.002
sec. extnct. type		SHELXL	SHELXL	
sec. extnct. correction		0.0024(2)	0.0083(3)	

[a] Data collection on an Enraf Nonius CAD4 diffractometer with graphite-monochromatized Mo Kα radiation (λ = 0.710 67 Å). [b] All calculations were done on a Silicon Graphics 4D-35TG computer system initially with the NRCVAX system of programs (Gabe,E. J.,Le Page, Y. , Charland, J-P., Lee, F. L., White, P. S. *J. Appl. Crystallogr.* **1989**, *22*, 384−389) and then with SHELXL-93 (G. M. Sheldrick, 1993) for refinement with all data on F^2.

lization in the asymmetric unit; the analysis establishes that the Pt coordination in each case is square planar (Figure 4), the different trans-influences of the −Cl and $-CHClPO(OMe)_2$ ligands being reflected in the $Pt-C_{COD}$ distances 2.157(6)−2.170(6) and 2.260(6)−2.276(6) Å, respectively). The asymmetric unit contains an enantiomeric pair of molecules linked by a water molecule *via* O−H···O=P hydrogen bonds. While the conformations adopted by the $-CHClPO(OMe)_2$ ligands, with respect to the Pt−C bond, are similar for the two molecules, the $PO(OMe)_2$ moieties adopt different orientations, e.g., compare torsion angles C31−P2−O2B−C42 = 170.6(6)°, and C11−P1−O2A−C22 = −149.7(7)°. As was observed above for **6** and previously for the bis(phosphonate) complex[5] (R,R)-(COD)Pt{CHCl[PO(OMe)$_2$]}$_2$, the σ-bonded carbon ligand has its bulkiest substituent [$PO(OMe)_2$] oriented axially with respect to the coordination plane and the least bulky H substituent



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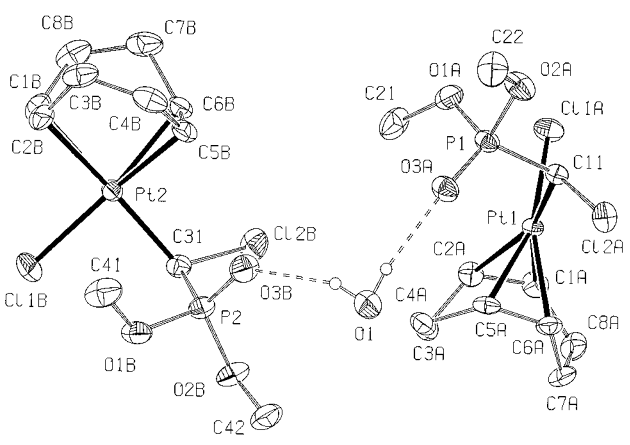

Figure 4. A view of the two independent molecules of **7** linked by hydrogen bonding to the water of crystallization, with an indication of the numbering scheme. Anisotropic displacement ellipsoids are drawn at the 30% probability level.

in the space between the two σ-bonded ligands. The two independent cyclooctadiene rings in this crystal structure and those in the structures of **5** and **6** adopt distorted tub conformations similar to those found[5] in (*R*,*R*)-(COD)Pt{CHCl[PO(OMe)$_2$]}$_2$.

In conclusion, the structures reported here establish the stereochemistries proposed[1] previously and are consistent with the mechanistic arguments used to rationalize the outcome of the reaction of Pt(II) complexes with diazo compounds.

Experimental Section

Crystals of **4** were grown from benzene/ethyl acetate. The small well-formed crystals deposited initially when left under the solvent for over a year, gradually attained a size suitable for X-ray crystallography. Crystals of **5** and **6** were obtained from ether/pentane (a trace of dichloromethane was needed to ensure initial dissolution of **5**), while **7** was crystallized from dichloromethane/pentane; the resulting crystals proved to contain water of crystallization. Crystal data and details of data collection, structure solution, and refinement are summarized in Table 2.

Acknowledgment. We thank NSERC, Canada, for financial support.

Supporting Information Available: Lists of fractional coordinates, calculated hydrogen coordinates, anisotropic thermal parameters and interatomic distances, and angles and a printout of the crystallographic information file for **4**, **5**, **6**, and **7** (68 pages). Ordering information is given on any current masthead page.

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