The Rh-Rh distance, 2.410 (1) Å, is the shortest found in dirhodium(II) compounds containing acetates and ortho-metalated phosphines acting as bridging ligands.[3-8] The Rh-O_{eq} distances are in the normal range found in bridging acetates. The Rh-O_{eq} distance for oxygens trans to the P atom (2.185 (6) Å) and trans to the C(2) atom (2.241 (4) Å) are significantly longer than the other Rh-O_{eq} distances, which are in the range 2.009 (5)-2.051 (4) Å. This trans influence can be observed in $Rh_2(O_2CCH_3)_2[(C_6H_4)P(C_6H_5)_2]_2(HO_2CCH_3)_2$,[3] as well as in other reported ortho-metalated compounds[4a] but the longest Rh-O_{eq} distances are found in $(\mathbf{1})(HO_2CCH_3)_2$. The Rh-$O_{eq}$ distance trans to C atom is longer than trans to P atom in agreement with the relative trans influence of P and C observed in other mononuclear metalated compounds.[17] The Rh-O_{ax} distances in compound $(\mathbf{1})(HO_2CCH_3)_2$ are different: Rh(1)-O(19) = 2.378 (6) Å, and Rh(2)-O(23) = 2.255 (11) Å. This can be attributed to two factors: (i) steric effects in axial positions of Rh(1) (presence of the chlorine atom and the aromatic rings), and (ii) different acidities of the metal centers, because of the existence of an unsymmetrical P,C ortho-metalated ligand.

Unlike those in most simple adducts of the tetracarboxylates, the angle Rh-Rh-axial ligands deviate significantly from linearity. In $(\mathbf{1})(HO_2CCH_3)_2$, the angle O(19)-Rh(1)-Rh(2) is 166.3 (1)° and O(23)-Rh(2)-Rh(1) is 172.3 (2)°. Similar deviations from linearity were observed for the ortho-metalated rhodium compounds[3a] and osmium compounds.[3b] The axial acetic acid molecules are hydrogen bonded to oxygen atoms of the bridging acetates (O(21)-O(27) = 2.57 (1) Å; O(25)-O(29) = 2.60 (1) Å). This fact also appears[3] in $Rh_2(O_2CCH_3)_2[(C_6H_4)P(C_6H_5)_2]_2(HO_2CCH_3)_2$ ($d(O\cdots O)$ = 2.527 Å), but in that case each acetic acid interacts with a different carboxylate group.

The distortions from octahedral geometry may be due to significant torsion angles around the metal-metal bond. The four torsion angles are large: P-Rh(1)-Rh(2)-C(2) = 20.3 (3)°, O(27)-Rh(1)-Rh(2)-O(29) = 12.9 (4)°, O(31)-Rh(1)-Rh(2)-O(33) = 10.5 (3)° and O(35)-Rh(1)-Rh(2)-O(37) = 12.0 (3)°. Similar deviations were observed for all the doubly metalated compounds already reported.[3,6b,7]

Acknowledgment. We thank the DGICYT for financial support.

Registry No. $(\mathbf{1})(HO_2CCH_3)_2$, 138093-51-3; (**1**)PCCl, 112841-24-4; **2**, 138093-52-4; **3**, 112841-26-6; **4**, 138093-53-5; **5**, 138093-54-6; **6**, 112841-29-9; **7**, 138093-55-7; **8**, 138093-56-8; **9**, 112841-25-5; **10**, 138093-57-9; **11**, 138093-58-0; **11'**, 138128-60-6; **12**, 138093-59-1; **12'**, 138093-62-6; **13**, 138093-60-4; **13'**, 138093-63-7; **14**, 138093-61-5; **14'**, 138093-64-8; **15**, 138128-59-3; $P(p\text{-}CH_3C_6H_4)_3$, 1038-95-5; $P(p\text{-}ClC_6H_4)_3$, 1159-54-2.

Supplementary Material Available: Complete tables of bond distances and angles and anisotropic displacement parameters (3 pages); a table of structure factors (12 pages). Ordering information is given on any current masthead page.

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Mono- and Dinuclear Complexes of Platinum(II) with Chiral Diphosphines: Pt(P-P')Cl_2 and [Pt(P-P')(μ-OH)]$_2$[BF_4]$_2$ (P-P' = prolophos, *N*-(Diphenylphosphino)-2-((diphenylphosphinoxy)methyl)pyrrolidine, and butaphos, 1-(Diphenylphosphinoxy)-2-(*N*-ethyl-*N*-(diphenylphosphino)amino)butane). Crystal and Molecular Structure of Pt{*S*-prolophos-*P*,*P'*}Cl_2

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Received February 26, 1991

The mononuclear complexes Pt(P-P')Cl_2, **1** and **2**, where P-P' are the chiral ligands (*S*)-*N*-(diphenylphoshino)-2-((diphenylphosphinoxy)methyl)pyrrolidine, *S*-prolophos, and (*R*)-1-(diphenylphosphinoxy)-2-(*N*-ethyl-*N*-(diphenylphosphino)amino)butane, *R*-butaphos, respectively, were prepared and characterized in solution by ^1H, ^{13}C, ^{31}P, ^{195}Pt, and two-dimensional correlation spectra. Only one conformer is observed in solution at room temperature. The structure of complex **1**, Pt{*S*-prolophos}Cl_2, was solved by X-ray diffraction: $C_{29}H_{29}Cl_2NOP_2Pt$, orthorhombic, space group $P2_12_12_1$, a = 16.557 (6) Å, b = 15.697 (6) Å, c = 10.948 (5) Å, Z = 4, and V = 2845 (2) Å^3. The structure was refined to a conventional R factor of 0.040 (R_w = 0.049) for 2700 observed reflections with $I > 3\sigma(I)$. The ligand P-P' is coordinated in an endobidentate fashion to the platinum atom, which exhibits a slightly distorted square-planar geometry. The seven-membered ring adopts a twist-boat conformation. Treatment of complexes **1** and **2** with silver tetrafluoroborate in methanol solution afforded the dinuclear species [(P-P')Pt(μ-OH)$_2$Pt(P-P')][BF_4]$_2$ (**3**, P-P' = prolophos, and **4**, P-P' = butaphos). The dinuclear unit is maintained even in the gas phase, as shown by the MS-FAB spectrum of complex **4**. Complex **1**, in the presence of tin(II) chloride, was found to catalyze the hydroformylation of styrene to (*R*)-(−)-2-phenylpropanal with 37% optical purity.

Introduction

Among the many chiral diphosphines which have been prepared and tested as ligands in asymmetric catalytic processes,[1] two aminophosphine-phosphinite ligands (P-P'), viz. *N*-(diphenylphosphino)-2-((diphenylphosphinoxy)methyl)pyrrolidine, prolophos, and 1-(diphenylphosphinoxy)-2-(*N*-ethyl-*N*-(diphenylphosphino)amino)butane, butaphos, were described several years ago by some members of our group.[2] The cationic rhodium(I) complexes, [Rh(COD)(P-P')]$^+$, were shown to be efficient homogeneous hydrogenation catalysts toward several prochiral substrates under mild conditions.[2] In ruthenium chemistry, the use of the *S*-prolophos ligand has allowed the high-yield isolation

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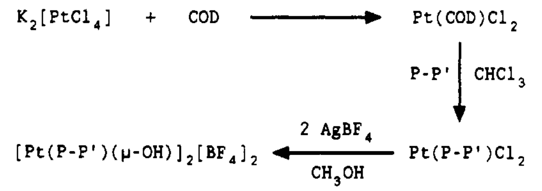
Table I. ^{1}H NMR Spectral Data[a]

compd	Ar	2-CH	1-CH_2	5-CH_2	3-CH_2	4-CH_2	6-CH_3	7-CH_3	OH
prolophos[b]		3.81 [7]	3.96 [8, 2.5]	2.94 [2]	1.89 [2.5, 1.5]	1.76			
			3.74 [2]	2.66 [3.5]		1.60			
butaphos	7.9–7.2	3.2 [23]	4.03 [10.2, 6.4) [7]	3.05	1.80[d]		0.94 t (7.4)	0.69 t (7.0)	
			3.87 (10.2, 6.3) [8]						
Pt{*S*-prolophos}Cl_2 (**1**)	8.1–7.0	4.91	3.69	3.08	2.10	1.89			
			3.38	2.69	1.42				
Pt{*R*-butaphos}Cl_2 (**2**)	8.0–7.1	5.1 [13]	3.96 (11.7, 11.7) [23]	3.06 (7.0)	1.71[d]		0.74 t (7.4)	0.79 t (7.0)	
			3.48 (11.7, 3.5) [3.5]		1.35[d]				
[Pt{*S*-prolophos}(μ-OH)]$_2$[BF_4]$_2$ (**3**)	7.8–6.9	5.1	3.80	3.1	2.4	1.95			0.56[c]
	6.6–6.4		3.45	2.8	1.5				
[Pt{*R*-butaphos}(μ-OH)]$_2$[BF_4]$_2$ (**4**)	8.0–6.9	5.3	4.0	3.1	2.00		0.70 t (6.6)	1.0 t (7.0)	–0.4[c]
			3.5		1.57				

[a] Chemical shifts are in ppm (δ) downfield from Me_4Si; coupling constants (J) are in Hz; spectra are in $CDCl_3$ at room temperature; all signals are multiplets unless otherwise stated; J_{H-H} and J_{P-H} are given after the δ values in parentheses and in square brackets, respectively. [b] From ref 4. [c] Pseudotriplet (J_{app} = 2.5 (**3**), 2.8 (**4**)). [d] From ^{1}H-2D JRES.

Scheme I



(COD = *cis,cis*-1,5-cyclooctadiene. P-P′: **1**, **3**, *S*-prolophos; **2**, **4**, *R*-butaphos)

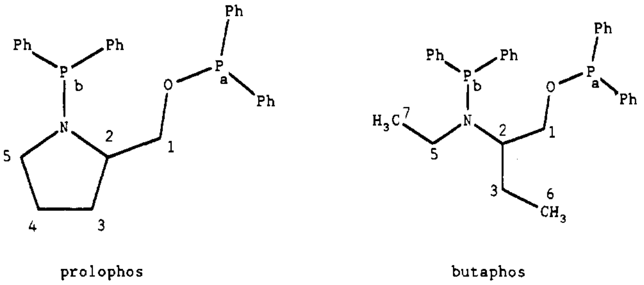


Figure 1. Numbering scheme for the ligands prolophos and butaphos.

of the optically pure species *S*-Ru{*S*-prolophos}(η^5-C_5H_5)H.[3] More recently, a palladium complex, [Pd{*S*-prolophos}(η^3-CH_2CMeCH_2)]$^+$, was synthesized: in a detailed NMR investigation, the absolute configuration in solution of two diastereoisomers was assigned and information was gained on the regiochemistry of nucleophilic addition to an allyl moiety.[4a] The resolution of the [Rh(COD){*S*-prolophos}][ClO_4],[2] *S*-Ru{*S*-prolophos}(η^5-C_5H_5)Cl,[3] and [Pd{*S*-prolophos}(η^3-CH_2CMeCH_2)][PF_6] (two independent molecules)[4b] structures has shown that this diphosphine acts as an endobidentate ligand and that the seven-membered ring adopts a boat conformation. On the whole, as for the coordination of the chelating ligand, the structures of these species display several analogous features.

Here, because of our interest in platinum chemistry with chelating diphosphines,[5] we report the syntheses of the mononuclear complexes Pt(P-P′)Cl_2, P-P′ = *S*-prolophos, **1**, and P-P′ = *R*-butaphos, **2**, as well as of the dinuclear species [Pt(P-P′)(μ-OH)]$_2$[BF_4]$_2$, P-P′ = *S*-prolophos, **3**, and P-P′ = *R*-butaphos, **4**. The latter type of complexes were shown previously to be useful intermediates in the synthesis of polynuclear hydrides;[5] the hydrido derivatives which were obtained from **3** and **4** will be described elsewhere.[6] A preliminary report of this work was provided.[7]

Results

The syntheses of the compounds **1–4** are summarized in Scheme I. Complex **1** was characterized by a X-ray structural study whose results are presented in Figures 3–5 and Tables IV–VIII. The behavior of the new species in solution was investigated by ^{1}H, ^{13}C, ^{31}P, ^{195}Pt, and two-dimensional correlation spectra. The chemical shifts and coupling constants are reported in Tables I and II. Complex **1**, in the presence of tin(II) chloride, was tested as a catalyst in the hydroformylation of styrene; the results are reported in Table III. These findings will be introduced at appropriate places in the sections which follow.

Discussion

The synthesis of mononuclear complexes **1** and **2**, Pt{*S*-prolophos}Cl_2 and Pt{*R*-butaphos}Cl_2, respectively, is presented in Scheme I. The white complexes, obtained in good yields, are stable to air both in the solid state and in solution. The observation in the IR spectra of two absorptions assignable to the Pt–Cl stretches (320 m, 287 m (**1**), and 307 m, 283 m cm^{-1} (**2**); Nujol mull), taken together with the ^{31}P NMR spectra (one set of satellites, intensity ratio central peak:satellites = 1:4:1), suggests that species **1** and **2** are mononuclear, as confirmed by the X-ray structure of complex **1**.

Dinuclear derivatives [Pt(P-P′)(μ-OH)]$_2$[BF_4]$_2$ (**3** (P-P′ = *S*-prolophos) and **4** (P-P′ = *R*-butaphos)) were obtained by the reaction of dichlorides **1** and **2** with 2 equiv of $AgBF_4$ in methanol solution, according to a procedure previously reported for other related hydroxo-bridged platinum(II) derivatives.[5] Besides the IR spectra, which showed evidence of OH stretches (Nujol mull, 3540–3440 cm^{-1}), the presence of a hydroxo group was also supported by the ^{1}H NMR spectra. Indeed, although the synthesis was carried out in methanol, no resonance assignable to OCH_3 protons was observed, whereas a signal at high field (δ 0.56 and –0.4 for **3** and **4**, respectively), which disappeared by treatment with D_2O was assignable to a bridging hydroxo group. At variance with what has been observed in related species,[5,8] the OH resonances do not appear as broad singlets but are resolved into pseudotriplets by coupling to two ^{31}P nuclei, as shown by selective ^{31}P-decoupled experiments ($J(P_a$–H) ~ $J(P_b$–H) ~ 2 Hz). The low values of P–H coupling constants and the absence of satellites due to coupling to ^{195}Pt rule out the alternative assignment of these signals to a bridging hydride.

Hydroxo species of this type raise questions as to their nuclearity and should be better described as oligomers [Pt(L-L)(OH)]$_n$[BF_4]$_n$. Although the ^{31}P{^{1}H} NMR spectra of **3** and **4** provide no evidence about the nuclearity of the species (see below), we nevertheless feel it appropriate to describe **3** and **4** as dinuclear complexes on the basis of the FAB mass spectrum of complex **4**.

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The spectrum shows not only a quasi-molecular ion $[M - H]^+$ at *m/z* 1393 but also a more intense peak at *m/z* 1481, corresponding to the $[Pt_2(P\text{-}P')_2(OH)_2BF_4]^+$ unit. The occurrence of this species in the gas phase, apparently resulting from ion pairing, suggests a strong interaction between the cation and one of the BF_4 anions. In the solid state such an interaction through a hydrogen bond ($O-H\cdots FBF_3$) was observed in a related hydroxo-bridged platinum derivative.[9] The peculiar feature shown by the mass spectrum, albeit not unprecedented,[10] is certainly worth further investigation.

NMR Spectra. The ^1H, ^{13}C, ^{31}P, and ^{195}Pt NMR data (chemical shifts and coupling constants) of the complexes **1–4**, as well as of the free ligands, are reported in Table I and II.

In the discussion, the ^1H, ^{13}C, and ^{31}P resonances are numbered as in Figure 1.

^{1}H and ^{13}C Spectra. In the ^1H NMR spectra, the assignment of the resonances is complex, owing to the presence of coupled spin systems and overlapping multiplets. The spectra were interpreted by means of several one- and two-dimensional experiments and are described in detail for complex **2**.

In the range δ 0–5.5 (aliphatic protons), the ^1H spectrum of complex **2** shows one broad resonance (a, ca. δ 5.1), five complex multiplets (b–f, δ 4.1–1.2), and two triplets (g,g′, δ 0.9–0.7) with an a/b/c/d/e/f/g, g′ intensity ratio of 1/1/1/2/1/1/6. The two triplets at high field were readily assigned to the CH_3 protons; the other resonances were assigned by means of a 2D H-H COSY experiment (Figure 2a). Thus resonances e and f, which, in addition to a geminal interaction, are coupled to g′ (CH_3) and to a, were assigned to the 3-CH_2 protons, resonance d, coupled only to methyl g, was assigned to the 5-CH_2 group, and resonances b and c, coupled to each other and to a, were assigned to the 1-CH_2 group. The resonance at the lowest field, a, was associated to the proton on the chiral atom (2-CH). The assignment of resonances b–d to the CH_2 protons directly bonded to the P_a and P_b atoms, respectively, was confirmed by an H–P chemical shift correlated 2D spectrum.

Because of the complexity of the CH_2 resonances, it is not easy to obtain the full set of the *J*(H–H) and *J*(P–H) values directly. Thus, in particular, it is difficult to establish whether the 1-CH_2 protons have a cis or trans arrangement relative to the hydrogen on chiral carbon 2. The ^{31}P-decoupled ^1H spectrum (Figure 2b) helps assign resonance d, which looks like a quartet due to coupling to the vicinal CH_3 group (^3J(H–H) = 7.0 Hz), to the 5-CH_2 protons. Moreover, the 1-CH_2 resonance now proves to be a doublet of doublets, centered at δ 3.48, c, with spacings of 11.7 and 3.5 Hz, and a pseudotriplet, at δ 3.96, b, with a spacing of 11.7 Hz.

The 1-CH_2–CH complex pattern was simulated as an AXY system, assuming ^3J(H–H) $\sim$ ^2J(H–H) $\sim$ 11.7 Hz for resonance b and ^2J(H–H) = 11.7 Hz and ^3J(H–H) = 3.5 Hz for resonance c. Taking the relationship between vicinal coupling constants and dihedral angles into account, resonance b (^3J(H–H) = 11.7 Hz) was assigned to a hydrogen syn- or transperiplanar (with an angle very close to 180 or 0°) with respect to the hydrogen on the chiral carbon, and resonance c (^3J(H–H) = 3.5 Hz) to a hydrogen syn- or anticlinal, i.e. with an angle close to 60 or 120°. This simulation fits the observed spectrum also taking ^3J(P–H) values into account. These values, at first estimated by comparing the $^1H\{^{31}P\}$ and the ^1H spectra, were determined, for resonances a and b, by means of a NMR ^1H-2D JRES homonuclear experiment. Resonances a, e, and f, which retained a complex pattern even in the $^1H\{^{31}P\}$ spectra, were not fully resolved.

The ^1H spectra of the other complexes (**1**, **3**, **4**) and of the free ligand butaphos were analyzed with the same experiments described in detail for complex **2**. The spectra of the free ligands, apart from the CH_3 resonances, are more complex than the spectra of the complexes owing to less separation of the signals and to a large upfield shift of the CH resonances, which are hidden under other signals (e.g. 5-CH_2, butaphos).

Table II. ^{13}C, $^{31}P\{^1H\}$, and $^{195}Pt\{^1H\}$ NMR Spectral Data[a]

compd	^{13}C (aliphatic groups)							$^{31}P\{^1H\}$			$^{195}Pt\{^1H\}$
	2-CH	1-CH_2	5-CH_2	3-CH_2	4-CH_2	6-CH_3	7-CH_3	P_a	P_b	J_{P-P}	
S-prolophos[b]	63.6 [29.1]	73.1 [16.1]	47.2 [8.1]	29.7 [6.0]	25.4 [4.5]			113.7 s	46.7 s		
R-butaphos	62.6 dd [25.2] [8.1]	73.4 dd [16.6] [10.3]	45.4 d [9.0]	25.5 d [13.5]		11.8 s	15.2 s	113.2 s	43.9		
1	59.65[c]	70.19 d [5.0]	49.7 s	28.03 d [6.9]	26.34 d [4.9]			80.3 d [3944]	50.9 d [4029]	14.0	−4326 dd
2	60.3 dd [8.7] [6.8]	68.98 d [5.4]	40.5 s	22.6 d [5.9]		12.1 s	16.6 d [2]	78.5 d [3999]	67.8 d [4114]	10.5	−4271 dd
3								70.0 d [4027]	44.3 d [3970]	29.0	−3945 dd
4	62.2[c]	69.88 d [5.0]	39.76 s	22.65 d [7.0]		11.85 s	16.94 s	67.3 d [4069]	58.3 d [4077]	26.7	−3819[d]

[a] $CDCl_3$ solution at room temperature; coupling constants (*J*) are in Hz; chemical shifts are in ppm referred to Me_4Si (^{13}C), external H_3PO_4 (^{31}P), and Na_2PtCl_6 (^{195}Pt); J_{P-C} and J_{Pt-P} are given after the δ values in brackets. [b] From ref 4. [c] Pseudotriplet ($J_{app} \sim 6$ (**1**), 6.9 (**4**)). [d] Pseudotriplet ($J_{app} \sim 4080$).

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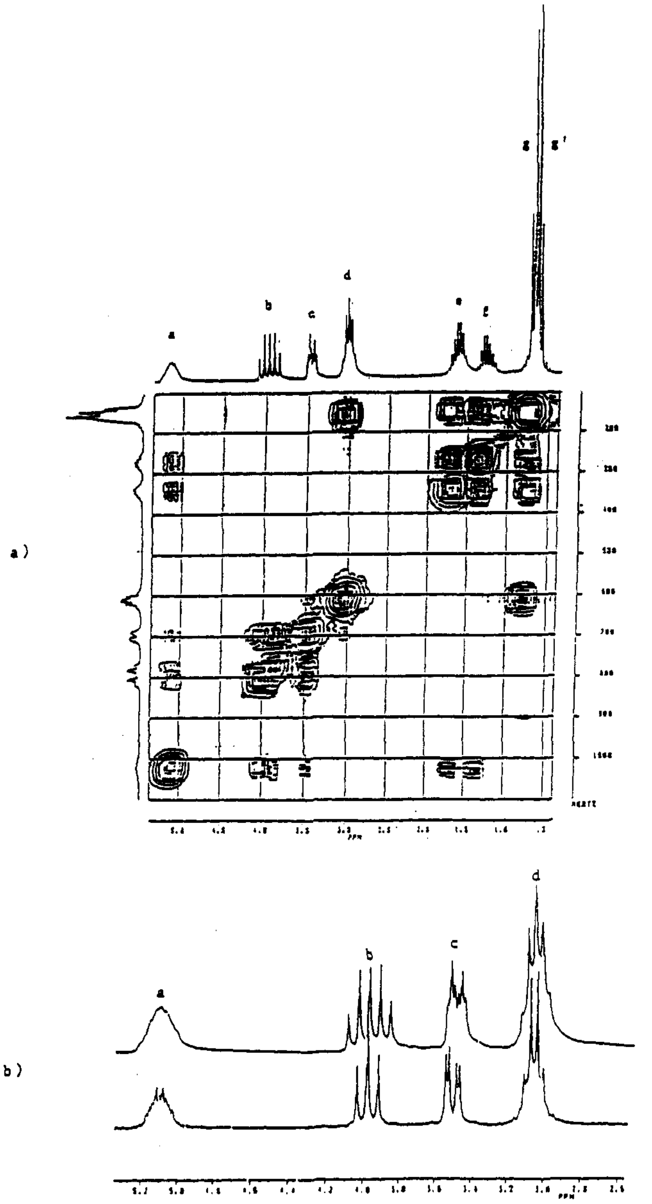


Figure 2. ^1H NMR spectra of compound **2** (aliphatic region): (a) 2D COSY-90; (b) ^1H (top) and $^1H\{^{31}P\}$ (bottom) of multiplets a–d.

No remarkable difference was observed between the spectra of the mono- and dinuclear species, suggesting that the latter are highly symmetrical systems.

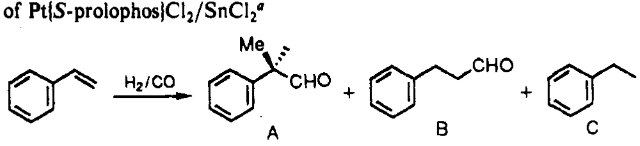
The ^{13}C resonances were assigned by 2D C–H correlation spectra. The carbon–phosphorus coupling constants were obtained by JMOD ^{13}C experiments.

^{31}P and ^{195}Pt Spectra. The $^{31}P\{^1H\}$ NMR spectra of the free ligands showed two signals, namely at δ 113.7 and 46.7 (prolophos)[4a] and at δ 113.2 and 43.9 (butaphos),[2] assigned to P_a and P_b, respectively.

In the spectra of mononuclear complexes **1** and **2**, two distinct doublets were observed (P_a and P_b), each coupled to a platinum atom. The ^1J(Pt–P) values are rather large when compared with those observed for other seven-membered systems having the phosphorus atoms trans to ligands with low trans influence, e.g. $Pt(DIOP)Cl_2$.[11] Similarly, large values were also observed for dinuclear complexes **3** and **4** and therefore seem typical of these ligands, which have electronegative atoms bonded to the coordinated phosphorus atoms.

A remarkable feature of the spectra is the upfield shift of the P_a resonance. In contrast, in the rhodium and palladium complexes,[2,4a] deshielding of both the phosphorus atoms upon coordination was observed. We cannot, at the moment, offer any simple explanation of this effect: however, it is worth mentioning that, between the two phosphorus atoms, a stronger π-acceptor behavior was previously ascribed to the P_a atom, at least for the prolophos ligand.[4a]

Table III. Asymmetric Hydroformylation of Styrene in the Presence of Pt{*S*-prolophos}$Cl_2/SnCl_2$[a]



Sn/Pt	conv	% (A + B)	% C	*b*/*n*[b]	O.P., %	conf
5[c]	94	93	6	1.2	24	*R*
2.5[c]	96	95	5	1.2	29	*R*
2.5[d]	9	74	26	1	37	*R*

[a] H_2/CO = 2 (130 atm), 40 °C, 40 h. [b] Branched/normal ratio. [c] Styrene/Pt = 126, benzene as solvent. [d] Carried out in neat styrene, styrene/Pt = 1260.

No evidence of the dinuclear nature of complexes **3** and **4** is given by the ^{31}P spectra, which are very simple, showing one set of resonances (doublets) for each of the two different phosphorus atoms, with one set of satellites. An analogous spectrum was observed for dinuclear hydroxo-bridged species with other chelating diphosphines, e.g., $[Pt(dPp)(\mu\text{-}OH)]_2[BF_4]_2$ (dPp = 1,3-bis(diphenylphosphino)propane). The latter complex was shown to be dinuclear by X-ray analysis.[12]

In agreement with the ^{31}P spectra, the ^{195}Pt spectra of complexes **1**–**3** consist of a doublet of doublets, whereas for **4** the resonance appeared as pseudotriplet, owing to the small difference between the two platinum–phosphorus coupling constants, as obtained from the ^{31}P spectrum. The ^{195}Pt resonances of mononuclear species **1** and **2** are significantly displaced at high field with respect to those of dinuclear complexes **3** and **4**. The opposite is true for the ^{31}P resonances.

On the whole, the NMR data, in particular those relative to complex **2**, Pt{*R*-butaphos}Cl_2, for which an exhaustive NMR analysis was carried out, indicated that only one conformer exists in solution in a wide range of temperatures. Indeed the ^1H and $^{31}P\{^1H\}$ spectra exhibited no significant differences from room temperature down to −80 °C. Most of the conformations possible for a seven-membered ring can be ruled out if one considers (a) that the hydrogens of the CH_2 group inside the O–CH_2–CH–N< backbone of the ligand have a clinal and periplanar disposition, respectively, and (b) that complex $[Rh(COD)\{S\text{-butaphos}\}]^+$ was shown to display good enantioselectivity in the catalytic hydrogenation of α-*N*-acetylcynammic acid to give (*S*)-*N*-acetylphenylalanine. According to Kagan's rule,[13] the stereoselectivity should be dictated by a diastereotopic array of the phenyl substituents generated by a λ conformation of the *S* ligand, and hence, a δ conformation should be true for *R*-butaphos. Although no discussion on conformations can be persuasive without using molecular modeling computer programs, if we assume, as is sometimes done,[14] that even simple molecular models can give sound indications, we cannot help noting that a conformation similar to that observed for complex **1** in the solid state fits both the aforementioned observations. Unfortunately, no direct comparison can be made, since the structure of complex **2** in the solid state is unavailable. It was recently pointed out that, among the rhodium complexes with diphosphines having a seven-membered ring, in the solid state only few have an idealized C_2 conformation

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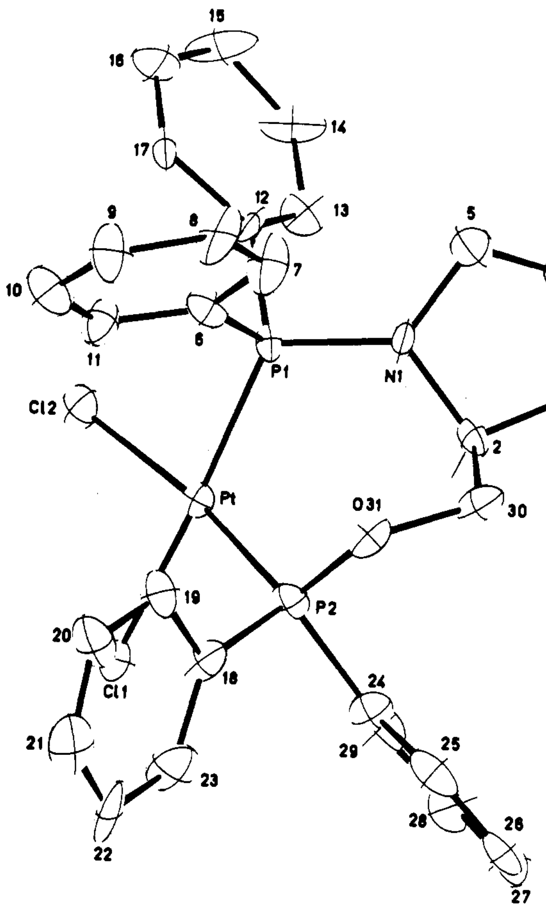

Figure 3. ORTEP plot of **1** along *b* with the atom-numbering scheme. Thermal ellipsoids enclose 25% of the electron density.

of the chelated ring, while many others have alternative low-energy conformations.[15] Of these, several conform rather well to a cycloheptane twist-boat geometry, i.e., the conformation observed for the platinum complex **1** in the solid state.

Hydroformylation Reactions. It is known that platinum complexes in the presence of tin(II) chloride are useful catalysts in stereospecific addition of hydrogen and carbon monoxide to prochiral olefines,[16] though rhodium is more efficient.[17] Nevertheless platinum complexes with chiral chelating phosphines have been shown to have a higher stereoselectivity, though the reaction times are impracticable.[16c]

Table III summarizes the results of adding H_2/CO to styrene, performed with the Pt{*S*-prolophos}Cl_2/$SnCl_2$ system under conventional conditions, with and without solvent.

The change in the $SnCl_2$/platinum complex ratio does not affect the selectivity of the catalyst: the main products are branched 2-phenylpropanal and linear 3-phenylpropanal, in a 1.2/1 ratio, while the hydrogenation product ethylbenzene remains close to 5%. The stereoselectivity of the reaction is moderately affected, as (*R*)-(−)-2-phenylpropanal was formed with 24% (Sn/Pt = 5) and 29% O.P. (Sn/Pt = 2.5), respectively. When the reaction was performed in neat styrene, an increased substrate/catalyst ratio was accompanied, in the same reaction time, by an obvious decrease in conversion together with a lower selectivity to aldehydes; the stereoselectivity increased, however, as (*R*)-(−)-2-phenyl-propanal was formed in 37% O.P.

Table IV. Crystallographic Data for [Pt{*S*-prolophos}Cl_2]

formula	$C_{29}H_{29}Cl_2NOP_2Pt$
fw	735.5
space group	$P2_12_12_1$
a, Å	16.557 (6)
b, Å	15.697 (6)
c, Å	10.948 (5)
V_c, Å^3	2845.3 (2)
Z	4
D(calcd), g cm^{-3}	1.72
μ(Mo Kα), cm^{-1}	55.10
no. of unique reflcns measd	2828 ($-h,k,l$)
no. of data with $F_o^2 \geq 3\sigma(F_o^2)$	2700
no. of params refined	325
R^a and R_w^b	0.040, 0.049

[a] $R = (\sum|F_o| - K|F_c|)/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - K|F_c|)^2/\sum w|F_o|^2]^{1/2}$.

Table V. Bond Lengths (Å) and Angles (deg) (with Esd's in Parentheses)

	In the Coordination Sphere		
Pt–Cl(1)	2.345 (4)	Cl(1)–Pt–Cl(2)	88.4 (1)
Pt–Cl(2)	2.362 (4)	Cl(1)–Pt–P(1)	176.6 (1)
Pt–P(1)	2.239 (4)	Cl(1)–Pt–P(2)	86.2 (1)
Pt–P(2)	2.228 (4)	Cl(2)–Pt–P(1)	90.0 (1)
		Cl(2)–Pt–P(2)	172.3 (1)
		P(1)–Pt–P(2)	95.1 (1)
	In the Bidentate Phosphine Ligand		
P(1)–N(1)	1.654 (9)	Pt–P(1)–N(1)	115.8 (4)
P(1)–C(6)	1.84 (1)	Pt–P(1)–C(6)	108.3 (4)
P(1)–C(12)	1.82 (1)	Pt–P(1)–C(12)	118.6 (5)
P(2)–O(31)	1.594 (9)	N(1)–P(1)–C(6)	109.6 (6)
P(2)–C(18)	1.80 (1)	N(1)–P(1)–C(12)	98.6 (5)
P(2)–C(24)	1.79 (2)	C(6)–P(1)–C(12)	105.2 (6)
N(1)–C(2)	1.48 (1)	Pt–P(2)–O(31)	115.9 (4)
C(2)–C(3)	1.57 (2)	Pt–P(2)–C(18)	112.8 (5)
C(2)–H(2)	0.91	Pt–P(2)–C(24)	117.6 (5)
C(2)–C(30)	1.56 (2)	O(31)–P(2)–C(18)	98.5 (5)
C(3)–C(4)	1.51 (2)	O(31)–P(2)–C(24)	104.9 (6)
C(4)–C(5)	1.52 (2)	C(18)–P(2)–C(24)	104.9 (7)
C(5)–N(1)	1.46 (2)	P(1)–N(1)–C(2)	123.2 (8)
C(30)–O(31)	1.49 (1)	P(1)–N(1)–C(5)	127.5 (9)
		C(2)–N(1)–C(5)	109.2 (9)
		N(1)–C(2)–C(3)	104.9 (9)
		N(1)–C(2)–C(30)	112.1 (9)
		C(3)–C(2)–C(30)	110.2 (9)
		C(2)–C(3)–C(4)	105 (1)
		C(3)–C(4)–C(5)	106 (1)
		C(4)–C(5)–N(1)	103 (1)
		N(1)–C(2)–H(2)	110
		C(3)–C(2)–H(2)	108
		C(30)–C(2)–H(2)	112
		C(2)–C(30)–O(31)	109.6 (9)
		C(30)–O(31)–P(2)	121.8 (8)
	In the Phenyl Rings[a]		
C(P)–C(ortho)	1.397 (10)	C(ipso)	118.1 (9)
C(ortho)–C(meta)	1.397 (8)	C(ortho)	121.4 (5)
C(meta)–C(para)	1.384 (9)	C(meta)	119.0 (6)
		C(para)	120.9 (1.0)

[a] Weighted average values.

Structure of Complex 1, Pt{*S*-prolophos}Cl_2, in the Solid State. The crystal structure of complex **1** consists of discrete monomeric molecules. An ORTEP view of **1** is shown in Figure 3, along with its numbering scheme. The packing of the molecules in the crystal is represented in Figure 4. Crystallographic data, selected bond distances and angles, and final atomic coordinates are reported in Tables IV–VI, respectively. The least-squares planes of the moieties in compound **1**, the displacements of atoms from them, and the χ^2 values, with the corresponding probability *P* that the moieties are nonplanar, are shown in Table VII.

The environment of the platinum atom can be described as approximately square planar. With respect to the least-squares plane of the coordination sphere, the following out-of-plane displacements (Å) were observed: Pt, 0.0056 (5); Cl(1), −0.055 (4); Cl(2), −0.102 (4); P(1), −0.055 (4), P(2), −0.109 (4). An unusually short Cl(2)···C(12) intramolecular contact of 3.28 (1) Å

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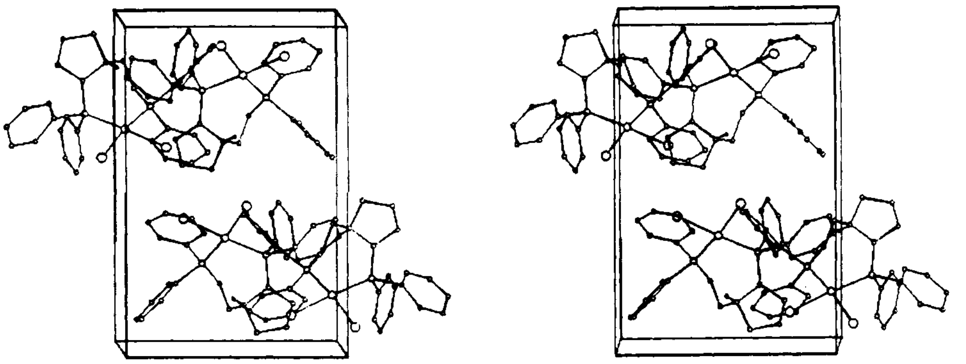

Figure 4. Stereoscopic view of the unit cell of **1**. The +*a* direction points upward, the +*b* direction to the observer, and the +*c* direction to the right.

Table VI. Final Coordinates and Equivalent Isotropic Thermal Parameters (with Esd's in Parentheses) for Non-Hydrogen Atoms

atom	*x*	*y*	*z*	*B*, Å^2
Pt	−0.65392 (3)	0.68507 (3)	0.46204 (5)	2.25 (1)
Cl(1)	−0.5959 (2)	0.6438 (3)	0.2758 (4)	4.3 (1)
Cl(2)	−0.5622 (2)	0.5934 (2)	0.5622 (4)	3.7 (1)
P(1)	−0.7022 (2)	0.7275 (2)	0.6431 (3)	2.4 (1)
P(2)	−0.7264 (2)	0.7773 (2)	0.3527 (3)	2.7 (1)
N(1)	−0.8016 (5)	0.7358 (6)	0.6526 (9)	3.2 (4)
C(2)	−0.8560 (6)	0.7264 (8)	0.5461 (10)	3.2 (4)
C(3)	−0.9398 (7)	0.6998 (9)	0.6019 (12)	5.1 (6)
C(4)	−0.9244 (8)	0.6926 (11)	0.7373 (14)	6.0 (7)
C(5)	−0.8501 (10)	0.7472 (10)	0.7630 (13)	4.9 (6)
C(6)	−0.6556 (8)	0.8303 (7)	0.6813 (10)	3.1 (4)
C(7)	−0.7018 (9)	0.8965 (9)	0.7294 (17)	4.9 (6)
C(8)	−0.6652 (12)	0.9729 (10)	0.7620 (18)	6.5 (8)
C(9)	−0.5811 (12)	0.9825 (10)	0.7422 (18)	5.7 (7)
C(10)	−0.5337 (11)	0.9174 (11)	0.6920 (17)	5.0 (6)
C(11)	−0.5716 (8)	0.8407 (9)	0.6627 (15)	4.2 (5)
C(12)	−0.6852 (7)	0.6600 (9)	0.7763 (13)	3.4 (4)
C(13)	−0.7261 (7)	0.5874 (9)	0.7939 (13)	4.2 (6)
C(14)	−0.7128 (10)	0.5357 (11)	0.8946 (14)	5.6 (7)
C(15)	−0.6552 (13)	0.5575 (9)	0.9810 (14)	6.4 (8)
C(16)	−0.6069 (10)	0.6270 (10)	0.9619 (14)	7.5 (6)
C(17)	−0.6220 (7)	0.6784 (11)	0.8579 (13)	4.2 (4)
C(18)	−0.6649 (8)	0.8570 (8)	0.2790 (12)	3.4 (4)
C(19)	−0.6284 (8)	0.9223 (9)	0.3523 (14)	4.5 (6)
C(20)	−0.5800 (9)	0.9842 (10)	0.2984 (15)	7.0 (9)
C(21)	−0.5638 (10)	0.9804 (11)	0.1773 (13)	6.9 (9)
C(22)	−0.5942 (8)	0.9179 (13)	0.1021 (15)	6.5 (8)
C(23)	−0.6434 (11)	0.8540 (10)	0.1562 (15)	5.2 (7)
C(24)	−0.7889 (9)	0.7355 (9)	0.2341 (14)	3.4 (5)
C(25)	−0.8383 (12)	0.7898 (9)	0.1672 (14)	4.9 (6)
C(26)	−0.8951 (10)	0.7606 (10)	0.0803 (15)	6.8 (9)
C(27)	−0.9010 (12)	0.6717 (13)	0.0621 (16)	6.8 (8)
C(28)	−0.8533 (10)	0.6187 (12)	0.1308 (18)	7.7 (8)
C(29)	−0.7964 (10)	0.6483 (12)	0.2093 (17)	4.6 (5)
C(30)	−0.8646 (7)	0.8112 (9)	0.4728 (12)	3.8 (4)
O(31)	−0.7839 (5)	0.8391 (5)	0.4287 (7)	3.4 (3)

should account for the P(2)–Pt–Cl(2) angle (172.3 (1)°) and for the displacement of Cl(2) out of the plane P(1)–Pt–P(2) (0.235 (4) Å).

The P(1)–Pt–P(2) angle is rather large, 95.1 (1)°. The opening of this angle was previously observed in complexes of the same ligand ([Rh(COD){*S*-prolophos}]$^+$, 93.0 (1)°;[2] [Pd(η^3CH$_2$CMeCH$_2$){*S*-prolophos}]$^+$, 97.5 (1) and 94.3 (1)° [4b]) as well as in other complexes having a seven-membered chelating diphosphine, e.g. PdCl$_2$[(−)-DIOP], 97 (1) and 96 (1)° [20] and PtCl$_2$[(−)-DIOP], 97 (2) and 96 (2)°,[18] and thus it seems to be required by the bite of the chelating diphosphine.

The Pt–P distances, 2.228 (4) and 2.239 (4) Å, were found to be in the range of the values reported for similar complexes of chelating diphosphine Pt(P-P)Cl$_2$ (e.g. P-P = 1,2-bis(diphenylphosphino)ethane, 2.215 (2) and 2.221 (2) Å[19] and P-P = 1,5-bis(diphenylphosphino)pentane, 2.237 (3) and 2.256 (3) Å[20]).

Table VII. Planarity of Molecular Regions

plane	eq, χ^2, *P*[a]	atom	displacement,[b] Å
I	$-0.696X - 0.714Y - 0.072Z + 0.522 = 0$	Pt*	0.0056 (5)
	$\chi^2 = 2255.4$ ($n = 2$), $P > 99.00\%$	Cl(1)*	−0.055 (4)
		Cl(2)*	−0.102 (4)
		P(1)*	−0.055 (4)
		P(2)*	−0.109 (4)
II	$0.738X + 0.671Y + 0.072Z + 0.409 = 0$	Pt*	0
		P(1)*	0
		P(2)*	0
		Cl(1)	0.127 (4)
		Cl(2)	0.235 (4)
		N(1)	−1.120 (9)
		O(31)	0.008 (8)
		C(6)	1.682 (13)
		C(12)	−0.398 (13)
		C(18)	1.533 (13)
		C(24)	−1.298 (15)
III	$-0.177X + 0.348Y - 0.921Z + 0.408 = 0$	C(6)*	−0.002 (11)
	$\chi^2 = 0.92$ ($n = 3$), $P = 22.03\%$	C(7)*	0.011 (18)
		C(8)*	−0.008 (20)
		C(9)*	−0.003 (18)
		C(10)*	0.009 (19)
		C(11)*	−0.004 (16)
		P(1)	−0.041 (4)
IV	$0.658X - 0.532Y - 0.532Z + 17.471 = 0$	C(12)*	−0.035 (13)
	$\chi^2 = 19.98$ ($n = 3$), $P > 99.00\%$	C(13)*	0.023 (14)
		C(14)*	0.013 (17)
		C(15)*	−0.044 (18)
		C(16)*	0.012 (16)
		C(17)*	0.024 (14)
		P(1)	−0.009 (4)
V	$-0.798X + 0.572Y - 0.189Z - 15.876 = 0$	C(18)*	0.026 (13)
	$\chi^2 = 9.40$ ($n = 3$), $P = 97.3\%$	C(19)*	−0.021 (14)
		C(20)*	0.005 (16)
		C(21)*	0.009 (17)
		C(22)*	0.004 (16)
		C(23)*	−0.030 (17)
		P(2)	−0.030 (4)
VI	$0.692X + 0.052Y - 0.720Z + 10.278 = 0$	C(24)*	−0.009 (15)
	$\chi^2 = 5.83$ ($n = 3$), $P = 87.4\%$	C(25)*	−0.004 (18)
		C(26)*	0.006 (17)
		C(27)*	0.009 (19)
		C(28)*	−0.029 (19)
		C(29)*	0.029 (18)
		P(2)	−0.194 (4)

[a] *P* = probability that the regions are nonplanar. [b] Starred atoms were included in the calculation of the plane.

At variance with the Pt–P distances, which appear to increase significantly on going from a five- to a seven- and eight-membered ring, the Pt–Cl distances seem to be less sensitive (P-P = 1,2-bis(diphenylphosphino)ethane, 2.350 (2) and 2.364 (2) Å;[19] P-P = *S*-prolophos, 2.345 (4) and 2.362 (4) Å; P-P = 1,5-bis(diphenylphosphino)pentane, 2.344 (4) and 2.358 (4) Å[20]).

The seven-membered chelate ring can hardly be compared with the analogous rings described for DIOP complexes,[18] where the five-membered ring is fused at the heptagon side opposite to the

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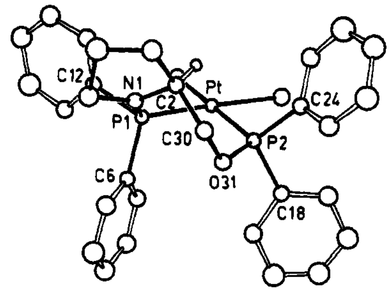

Figure 5. View of the ligand environment about the platinum in **1**.

metal. In *S*-prolophos the proline ring is fused at the heptagon side adjacent to the P(1) atom. Several analogies are observed between complex **1** and the *S*-prolophos complexes of rhodium, [Rh(COD){*S*-prolophos}]$^+$,[2] ruthenium, *S*-Ru{*S*-prolophos}(η^5-C_5H_5)Cl,[3] and palladium, [Pd(η^3-CH_2CMeCH_2){*S*-prolophos}]$^+$.[4b] Thus, in all four species, the N atom of the proline ring has an sp^2 hybridization (complex **1**, sum of the angles at N is 359.9°) and the O atom lies in the P(1)–metal–P(2) plane. In addition, the phenyl rings exhibit a disposition analogous to that found in rhodium and ruthenium complexes, though different from that of the palladium complex. The ligand environment around the platinum atom is pictured in Figure 5: the first carbon atoms of the phenyl rings bound to P(2) deviate 1.53 (1) (C(18)) and –1.30 (1) Å (C(24)) out of the plane P(1)–Pt–P(2), whereas those bound to P(1) deviate 1.68 (1) (C(6)) and –0.40 (1) Å (C(12)). The dihedral angles between the phenyl groups C(6)–C(11) and C(12)–C(17), 79.2 (6)°, and between the phenyl groups C(18)–C(23) and C(24)–C(29), 112.8 (5)°, show that the phenyl groups at each P atom are roughly perpendicular. Pairs of phenyl groups belonging to different P atoms are far from being parallel (dihedral angles: C(6)–C(11) and C(18)–C(23), 59.0 (6)°; C(6)–C(11) and C(24)–C(29), 56.1 (5)°; C(12)–C(17) and C(18)–C(23), 136.8 (5)°; C(12)–C(17) and C(24)–C(29), 35.8 (6)°). The pairs of values for two torsional angles Pt–P–$C_{(phenyl)}$–$C_{(ortho)}$ (Θ) and P–Pt–P–$C_{(phenyl)}$ (Φ) are –44 (1) and –74.7 (5)° for C(6)–C(11), –74 (1) and 165.6 (5)° for C(12)–C(17), –72 (1) and 112.8 (5)° for C(18)–C(23), and 2 (2) and –124.9 (6)° for C(24)–C(29), respectively. The rings C(12)–C(17) and C(18)–C(23) are face-on to the metal, and the ring C(24)–C(29) is edge-on, whereas the fourth ring, C(6)–C(11), is in an intermediate edge-face arrangement.

Significant differences between complex **1** and the other complexes are observed inside the metallacycle. The M–P(1)–N(1) (with the exception of M = Pd), M–P(2)–O(31), and C(2)–C(30)–O(31) angles are narrower in the platinum complex. Thus, the sum of the internal heptagon angles here is 793.5° (versus 807.8 and 805.6° in the rhodium and ruthenium complexes, respectively, and 799.4 and 795.2° in the palladium complex). The C(2)–C(30) and C(30)–O(31) distances (1.56 (2) and 1.49 (1) Å) are comparable to those in the other complexes (M = Rh, 1.50 (2) and 1.44 (1) Å; M = Ru, 1.517 (9) and 1.449 (8) Å; M = Pd, 1.47 (1), 1.50 (1) and 1.44 (1), 1.45 (1) Å, respectively).

In spite of these differences, possibly arising from the different environment around the metals, on the whole the ligand coordination in the four complexes is rather similar, suggesting a preferred spatial arrangement for prolophos, at least in the solid state.

The seven-membered ring adopts a twist-boat conformation, the C(30) atom being the bow and the Pt–P(1) vector the stern of the boat. The puckering parameters[21] (q_2 = 1.289; q_3 = 0.112; Q = 1.294; ϕ_2 = 272.2°; ϕ_3 = 68.0°; ϑ = 85.0°) can be compared with the values for an ideal twist-boat conformation of cycloheptane (q_2 = 0.676; q_3 = 0.069; Q = 0.679; ϕ_2 = 270.0°; ϕ_3 = 90.0°; ϑ = 84.0°). Since the torus mapping the 14 equivalent twist-boat conformations is very thin, ϕ_3 has only a small effect on the twist-boat. The (*S*)-proline ring has an envelope conformation, with puckering parameters Q = 0.336 and ϕ = 4.3° (values for an ideal E conformation are Q = 0.3 and ϕ = 0°). The apex is at C(5).

The effective cone angle ϑ of the phosphine ligand was calculated according to Tolman[22] and found to be 125.7°.

Experimental Section

The solvents were distilled and dried before use according to usual procedures. $SnCl_2 \cdot 2H_2O$ and $AgBF_4$ were purchased from Carlo Erba and Fluka Chemie A.G., respectively. Styrene, from Fluka, was distilled and stored under argon at –18 °C. The platinum complex, Pt(COD)Cl_2, was prepared according to the literature.[23] The phosphine ligands *S*-prolophos and *R*-butaphos were obtained from the appropriate alcohols and purified as previously described.[2] The ligands were stored at low temperature (–5 °C) and handled under an atmosphere of dinitrogen.

The analytical samples were pumped to constant weight (room temperature, ca. 0.1 Torr). Evaporation was always carried out under reduced pressure (water aspirator).

The elemental analyses were performed by the Microanalytical Laboratories of the Milan and Sassari Universities and by Mikroanalytisches Labor Pascher (Remagen, FRG).

Infrared spectra were recorded on Perkin-Elmer 1310 and 457 and Beckman 4210 spectrometers. The mass spectrometric measurements were performed on a VG 7070 instrument, equipped with 11-250J data system and operating in positive ion fast atom bombardment (FAB) conditions with 3-nitrobenzyl alcohol (MNBA). The bombarding Xe atom beam had a translational energy of 8 keV.

^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, and $^{195}Pt\{^1H\}$ NMR spectra were recorded on Bruker WP80 and AC200 and Varian XL-200 spectrometers. The two-dimensional experiments were performed using the Bruker programs COSY, BIRDREV H–C, REVCOR H–P, and JRES; the RECOVER and BIRDREV experiments were performed in reverse detection. The pulsing of frequencies of ^{13}C and ^{31}P was achieved with a BSU3 unit equipping the Bruker AC 200 spectrometer; a 5-mm ^1H-BB reverse probe head was used. Simulated ^1H spectra were obtained using the PANIC program.

GLC measurements were taken on a Carlo Erba gas chromatograph equipped with an automatic integrator, using a Carbowax 20-m column and nitrogen as a carrier. Specific rotations were measured on a Perkin-Elmer 141 polarimeter.

Syntheses. Pt{*S*-prolophos}Cl_2 (1) and Pt{*R*-butaphos}Cl_2 (2). Compounds **1** and **2** were obtained from the appropriate ligand by the same procedure described in detail for **1**:

A solution of the phosphine (353 mg, 0.94 mmol) in chloroform (20 mL) was added under dinitrogen to a stirred suspension of Pt(COD)Cl_2 (448 mg; 0.95 mmol) in the same solvent (30 mL). After 10 min the solution was evaporated to dryness and the residue crystallized from chloroform (15 mL) and diethyl ether, affording the white solid.

1: yield 81%; mp >230 °C. Anal. Calcd for $C_{29}H_{29}Cl_2NOP_2Pt$: C, 47.4; H, 3.9; N, 1.9; Cl, 9.6; O, 2.2; P, 8.4; Pt, 26.5. Found: C, 46.9; H, 4.0; N, 1.9; Cl, 10.3; O, 2.4; P, 8.3; Pt, 26.0. IR (Nujol; cm^{-1}): ν_{Pt-Cl} 320 m, 287 m.

2: yield 75%; mp >200 °C dec. Anal. Calcd for $C_{30}H_{33}Cl_2NOP_2Pt$: C, 47.9; H, 4.4; N, 1.9; Cl, 9.4; O, 2.1; P, 8.2; Pt 26.0. Found: C, 47.4; H, 4.4; N, 1.9; Cl, 9.9; O, 2.4; P, 8.1; Pt, 25.4. IR (Nujol; cm^{-1}): ν_{Pt-Cl} 307 m, 283 m.

Compounds 3 and 4. Compounds **3** and **4** were obtained from **1** and **2**, respectively, by reaction with $AgBF_4$.

[Pt{*S*-prolophos}(μ-OH)]$_2$[BF_4]$_2$ (3). A solution of $AgBF_4$ (547 mg; 2.82 mmol) in methanol (20 mL) was added to a stirred suspension of complex **1** (938 mg; 1.27 mmol) in the same solvent (50 mL). After removal of AgCl, the solution was evaporated to dryness and the residue dissolved in dichloromethane (20 mL). The filtered solution was evaporated to dryness. The crude product was crystallized from methanol (15 mL) and excess diethyl ether to give a white precipitate, which was washed with diethyl ether.

3: yield 70%; mp > 175 °C dec. Anal. Calcd for $C_{58}H_{60}N_2O_4P_4Pt_2B_2F_8$: C, 45.3; H, 3.9; N, 1.8; F, 9.9; P, 8.1; Pt, 25.4; B, 1.4; O, 4.2. Found: C, 45.0; H, 3.8; N, 1.7; F, 9.5; P, 7.7; Pt, 25.2; B, 1.3; O, 4.6. IR (Nujol; cm^{-1}): ν_{OH} 3540 m, br; ν_{BF_4} 1050 vs, br.

[Pt{*R*-butaphos}(μ-OH)]$_2$[BF_4]$_2$ (4). A solution of $AgBF_4$ (540 mg; 2.78 mmol) in methanol (20 mL) was added to a suspension of complex **2** (950 mg; 1.26 mmol) in the same solvent (80 mL). After 10 min, AgCl was filtered off and the resulting pale yellow solution was evaporated to dryness. The residue was extracted with $CHCl_3$ (30 mL). The filtered solution was concentrated to a small volume (ca. 10 mL) and diethyl ether was added. The resulting pale yellow oily product was stirred

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Table VIII. Observed and Calculated Ratios $I(hkl)/I(\bar{h}kl)$ for Reflections with Largest Anomalous Dispersion Effect

hkl	obsd ratio	calcd ratio for the correct enantiomer	*hkl*	obsd ratio	calcd ratio for the correct enantiomer
151	1.508	1.429	673	1.237	1.194
122	1.449	1.214	414	0.687	0.752
132	1.325	1.378	454	0.662	0.690
942	1.282	1.263	215	0.721	0.856
462	1.858	2.028	475	0.733	0.864
14,7,2	0.727	0.813	226	1.199	1.116
282	0.901	0.848	217	1.465	1.515
213	2.017	2.005	327	0.730	0.774
223	1.374	1.194	278	0.519	0.482
233	0.840	0.776	2,4,10	0.810	0.771
143	1.227	1.197			

vigorously under diethyl ether (2 × 60 mL) affording the white analytical sample.

4: yield 83%; mp > 130 °C dec. Anal. Calcd for $C_{60}H_{68}N_2O_4P_4Pt_2B_2F_8$: C, 45.9; H, 4.3; N, 1.8; F, 9.7; P, 7.8; Pt, 24.3. Found: C, 46.3; H, 4.3; N, 1.9; F, 9.5; P, 7.8; Pt, 24.3. IR (Nujol; cm^{-1}): ν_{OH} 3440 m, vbr; ν_{BF_4} 1050 vs, br.

Hydroformylation. The experimental data are reported in Table III. In a typical experiment, a benzene suspension (10 mL) of styrene (1.04 g; 10 mmol), Pt{*S*-prolophos}Cl$_2$ (58.3 mg; 0.079 mmol), and $SnCl_2{\cdot}2H_2O$ in a Schlenk tube, under argon, was stirred for 30 min. The suspension was transferred with a syringe into a 75-mL stainless steel autoclave provided with a glass liner, previously pressurized and vented three times with the gas mixture (2/1H$_2$/CO). The autoclave was pressurized to 130 atm and heated with stirring in an oil bath at 40 °C. After 40 h, the autoclave was quenched in an ice bath and vented, and the reaction mixture was analyzed by GLC. A portion of the solution was diluted with benzene to adjust the concentration of 2-phenylpropanal to 1.5 g/100 mL and analyzed on a polarimeter. Optical purities (O.P.) were calculated on the basis of the value $[\alpha]_D^{21} = -315.8$ (*c* 1.5, C_6H_6) for the optically pure (*R*)-(−)-2-phenylpropanal.[24]

X-ray Data Collection and Structure Determination of Complex 1. Suitable crystals of complex **1** were obtained by crystallization from chloroform/diethyl ether.

A crystal of dimensions 0.35 × 0.35 × 0.45 mm was used for data collection. Accurate unit-cell parameters were determined from a least-squares fit of the 2θ values for 25 reflections measured on the single-crystal Philips PW 1100 computer-controlled diffractometer with graphite-monochromated Mo Kα radiation at the Dipartimento di Chimica Organica, Universitã di Padova (Padova, Italy).

The intensities of 2828 independent reflections in a complete octant of data were collected by the $\theta/2\theta$ scan mode (scan width = 1.2, scan speed = 0.03 s^{-1}) within the angular range $2 < \theta < 25°$. The intensities of two standard reflections, monitored every 180 min, did not alter significantly during the data collection. A total of 2700 reflections having $I > 3\sigma(I)$ were regarded as observed and used in the structure analysis. The data were corrected for Lorentz–polarization effects and for absorption according to North et al.,[25] with minimum and maximum absorption factors of 0.9742 and 1.3830. An approximate absolute scale factor and a mean thermal parameter of 3.98 Å^2 were determined by Wilson's method.[26] Scattering factors for neutral atoms were corrected for anomalous dispersion.

The structure was solved by Patterson and Fourier methods. The positional and isotropic thermal parameters of the platinum atom, derived from the three-dimensional Patterson map, were refined to $R = 0.221$ in three cycles of least-squares refinement. A subsequent three-dimensional difference-Fourier synthesis revealed all the remaining non-hydrogen atoms. The full-matrix least-squares refinement of the positional and first isotropic and later anisotropic thermal parameters reduced *R* to 0.056. The hydrogen atoms were located on a difference-Fourier map and not refined but included in the calculations in fixed positions with the same isotropic thermal parameters of their bonded atoms.

At this stage the absolute configuration of the molecule was determined by the anomalous dispersion method:[27] several selected Bijvoet pairs *hkl* and $\bar{h}kl$, with largest anomalous dispersion effect, were measured and their intensity ratio compared with the calculated ratio for both enantiomers. It is evident from Table VIII that the calculated ratios for enantiomer *S* agree with those observed. The absolute configuration of the molecule corresponds therefore to the postulated *S* form of proline. Consequently the collected reflections of the only octant of data turned out to be $\bar{h}kl$ instead of the *hkl* ones. After this index inversion, both enantiomers were refined: refinement of the correct *S* enantiomer converged on values $R = 0.040$ and $R_w = 0.049$, whereas refinement of the *R* enantiomer converged on greater values, $R = 0.065$ and $R_w = 0.076$. The observed reflections were given unit weight. Weights $w = \sigma^{-2}(|F_o|)$ obtained from counting statistics, introduced in the last cycles, did not lead to better results. The average shift/esd ratio in the final refinement cycle was 0.33, both in the positional and in the thermal parameters of non-hydrogen atoms. The final difference Fourier map showed maximum and minimum, $\Delta\rho$, values 0.303 and −0.389 e Å^{-3}, both of them close to the Pt atom.

Scattering factors for neutral atoms were taken from ref 28, and those for hydrogen atoms, from Stewart et al.[29]

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Registry No. 1, 115999-23-0; **2**, 137918-32-2; **3**, 137918-34-4; **4**, 137918-36-6; prolophos, 83728-79-4; butaphos, 137918-31-1; Pt(COD)Cl$_2$, 12080-32-9; SnCl$_2$, 7772-99-8; styrene, 100-42-5; 2-phenylpropanal, 93-53-8; 3-phenylpropanal, 104-53-0; ethylbenzene, 100-41-4.

Supplementary Material Available: Tables of thermal parameters, positions of hydrogen atoms, other bond distances and angles, selected torsion angles, shortest contact distances, and crystallographic details (10 pages); a listing of structure factors (19 pages). Ordering information is given on any current masthead page.

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