formed once. The yield was somewhat low, but the conversion (based on NMR) was high (roughly 90%). Chromatography gave pure **1f**: mp 78–80 °C (MeOH–H_2O); ^1H NMR and mass spectral data agreed with literature values.[2b]

Registry No. **1a**, 22317-35-7; **1c**, 7107-93-9; **1e**, 83248-99-1; **1f**, 22317-34-6.

A Spectroscopic Method for the Determination of Optical Purities of Chiral, Chelating Diphosphines

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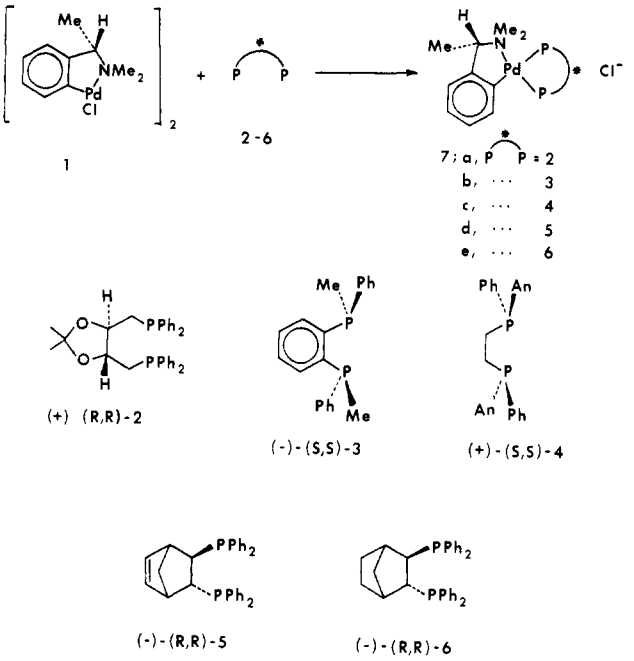
In the past decade there has been a rapid expansion of activity in the area of asymmetric catalytic hydrogenation of prochiral olefins mediated by Rh(I) complexes of chiral, chelating diphosphines.[1] This effort has involved mechanistic work,[2] as well as the design and synthesis of new chiral diphosphines to be tested for their efficacy in asymmetric induction during catalytic hydrogenation.[3]

The synthesis of optically active diphosphines can involve the elaboration of an optically active purcursor[3a-e,g] or the preparation of racemic diphosphines or their dioxides, followed by resolution of the dioxides[3f] or resolution of the diphosphines.[3h,4] Although it would be very useful to have a general spectroscopic method for the evaluation of the optical purity of any chiral disphosphine, to our knowledge such a technique has not been reported. In this note we describe and illustrate such a method.

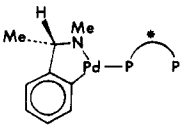
The diphosphine complexes (**7**, Scheme I) were formed in situ from (−)-bis(μ-chloro)bis[(*R*)-dimethyl(α-methylbenzyl)aminato-C^2,*N*]dipalladium(II) (**1**)[3h,4,5] and the corresponding diphosphines **2–6** by dissolving the two reagents in $CDCl_3$ in a molar ratio of 0.50:1.0, respectively, to give ca. 0.1 M homogeneous, straw-yellow solutions. Both ^{31}P and ^1H NMR spectra were recorded on these solutions. Either one optically pure ligand was used, followed by the addition of the antipode, along with a concomitant increase in the amount of **1** (with **2**, **3**, **5**, and **6**), or one enantiomer was run, followed by another run on a racemic mixture (with **4**[6]). Pertinent NMR spectroscopic data are presented in Table I.

Scheme I



It is apparent that in each of the five cases studied, this spectroscopic method can be used to determine optical purity. In principle, one would expect at least a pair of doublets in the ^{31}P NMR spectrum for each optically pure ligand, since the phosphorus atoms trans to nitrogen should be chemically different from those trans to carbon, and coupled. This was found to be true for ligands **3** and **4**, but since the two phosphino sites in **5** and **6** are chemically different (exo and endo) two complexes of each enantiomer are formed (85:15 with **5** and 97:3 with **6**). The chemical shifts of these species are sufficiently different that no difficulty was experienced in determining diastereomeric ratios, and thus optical purities.

In contrast to the ^{31}P NMR spectra of **7b–e**, which all feature pairs of doublets, **7a** exhibits only a singlet for each diasteriomeric complex. A priori, this could be due to fortuitous ^{31}P chemical shift equivalence of the phosphorus atoms in each diastereomeric complex (**7a**) or to rapid site–site exchange of the two phosphino ligands. The ^{31}P NMR signal remained sharp for **7a** down to −90 °C, indicating that if the latter case obtains, the mechanism for achieving equivalence has a low activation barrier. Presumably, such a mechanism would involve decoordination of one of the chelating phosphines to form a tricoordinate species such as **8** followed by recoordination trans to either



8

the nitrogen or carbon ligand. Evidence for the facility of the deligation/religation sequence with six-membered chelates of Rh(I) has been presented by Collman.[7] Consistent with this notion is our observation that the reaction of (−)-**3** with **7a** to give **7b** and (+)-**2** is rapid and quan-

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(4) Roberts, N. K.; Wild, S. B. *J. Am. Chem. Soc.* **1979**, *101*, 6254.

(5) Roberts, N. K.; Wild, S. B. *J. Chem. Soc., Dalton Trans.* **1979**, 2015.

(6) We are most grateful to Dr. Karl Koenig of Monsanto for a generous gift of optically active and racemic **4**.

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Table I. ^{31}P and Selected ^{1}H NMR Chemical Shifts of the Palladium Complexes Presented in Scheme I[a]

	^{31}P, δ (J)[b]		^{1}H, δ			
			R,R[c]		S,S[c]	
complex	R,R[c]	S,S[c]	NMe	CMe[d]	NMe	CMe[d]
7a	33.6 (s)[e]	33.7 (s)[e]	2.70[f]	1.80	2.73	1.75
7b	44.7 (25)	47.6 (26)	2.63, 2.88[g]	1.53	2.70	1.48
	29.3 (25)	31.0 (26)				
7c	48.4 (27)	45.3 (25)	2.83	1.63	2.71	1.70
	32.1 (27)	32.8 (25)				
7d	48.4[e,h]	46.7 (5)[e]		1.85		1.89
		44.6 (5)				
7e	42.6 (7)[e]	45.5 (8)[e]		1.93		1.96
	42.0 (7)	44.2 (8)				

[a] Spectra determined on ca. 0.1 M solutions in $CDCl_3$. The ^{31}P chemical shifts are defined as positive when downfield from external 85% H_3PO_4. [b] The absorptions for **7b-e** are pairs of doublets with coupling constants in hertz in parentheses. [c] Configurations of the chiral centers in the *free* diphosphine ligand. [d] All signals are doublets, J = 6 Hz. [e] It is important to use a 1:1 ratio of 1 to diphosphine to obtain this spectrum. [f] The most pronounced chemical shift differences are due to the acetonide methyl resonances: *R,R*, 1.20; *S,S*, 1.10. [g] The two NMe groups are magnetically different in this complex. [h] Narrow, unresolved multiplet.

titative as observed by ^{31}P NMR spectroscopy. On the other hand, reaction of (−)-**3** with **7c** (five-membered chelate) is much slower (at least a factor of 30), and the conversion to **7b** and (+)-**4** proceeds to an equilibrium mixture slightly favoring **7b** + (+)-**4** (ratio **7b**/**7c** = 70:30). Apparently the religation process to form a five-membered chelate is so much more favored entropically than for a seven-membered chelate, that a species such as **8** is not formed in the former case, thus making site–site exchange slow or even nonexistent for the two phosphines.

In spite of the very small ^{31}P NMR chemical shift difference between the diastereomeric complexes of **7a**, we were able to optimize the conditions for determining the spectrum so that we were able to detect the presence of less than 3% of the minor isomer in a synthetic mixture. We also quantitated two synthetic mixtures of **2**: (a) (+)-**2**/(−)-**2**, 88.1:11.9 (prepared), 88.3:11.7 (measured); (b) 59.6:40.4 (prepared), 59.0:41.0 (measured). We observed similar accuracy in determining the composition of synthetic mixtures of (+)- and (−)-**3** by the above-described method. We have noted also that in most of the ^{1}H NMR spectra there are absorptions in each diastereomeric pair of **7** that may be used to quantitate enantiomeric ratios, although generally not with the accuracy of the ^{31}P NMR method.

Finally, this technique has the advantage that the diphosphine can be recovered essentially quantitatively from **7**, using a method described previously.[4] Thus, valuable ligands need not be lost in the evaluation of optical purity, as is the case with a technique for determining optical purities of chiral monophosphines.[8]

Experimental Section

General Procedures. Proton-decoupled ^{31}P NMR spectra were determined on either a Varian FT-80[9] or Bruker WH-90 instrument at 32.4 and 36.4 MHz, respectively. ^{1}H NMR spectra were taken on either a Varian EM-390 or FT-80 instrument.

The following compounds were prepared by procedures described in the literature: (+)-bis(μ-chloro)bis[(*S*)-dimethyl(α-methylbenzyl)aminato-C^2,*N*]dipalladium(II) (**1**),[5,10] (−)-(*S,S*)-1,2-bis(methylphenylphosphino)benzene,[4] (−)-(*R,R*)-5-*exo*-6-*endo*-bis(diphenylphosphino)bicyclo[2.2.1]heptane (**6**).[3i] The ligands (+)-(*R,R*)-2,2-dimethyl-4,5-bis(diphenylphosphinomethyl)dioxolane (diop, **2**) and its enantiomer are commercially available (Alfa); (+)-(*S,S*)-1,2-bis(2-anisylphenylphosphino)ethane (dipamp, **4**) and its racemate were obtained as a gift.[6]

Preparation of [(*S*,*S*)-1,2-Bis(2-anisylphenylphosphino)ethane]-[(*S*)-dimethyl(α-methylbenzyl)aminato-C^2,*N*]palladium(II) Chloride (7c). The diphosphine **4** (185 mg, 0.404 mmol) was added in one portion to the palladium dimer **1** (119 mg, 0.202 mmol) in $CDCl_3$ (4 mL) to give a clear straw-yellow solution, upon which the spectra reported in Table I were determined.

All solutions of other complexes were prepared as above, although generally only on half the scale, since only ca. 2 mL of solution is necessary for the ^{31}P NMR spectral determination.

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(9) We are grateful for an NSF matching grant to E.P.K. and A. H. Cowley of this department, which enabled the purchase of this instrument.

(10) In our hands this preparation gave the complex **1** contaminated with a small amount of black solid that we suspect to be Pd(0). Dissolution of the complex in dichloromethane (ca. 1:10, w/v) followed by filtration and evaporation of the solvent gave **1** as a yellow powder.

A Facile Stereoselective Route to the Sex Pheromone of the Codling Moth via Thermolysis of an Allylic Sulfoxide

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In recent years considerable attention has been focused on the possibility of minimizing use of pesticides in insect control programs. One particular development in this area has been the examination of the use of insect sex pheromones[1] as a means of controlling insect behavior. Among the insect pests for which a sex pheromone has been identified is the codling moth, *Laspeyresia Pomonella* L., a major worldwide pest of apple orchards. The sex pheromone produced by the virgin female of this species was first isolated in 1969,[2] but the structure remained

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