Table I. Energies and Geometries of $C_4H_4Li_2$ Isomers

	total energies, hartrees		relative energies, kcal/mol		bond lengths, Å (STO-3G)[a]				
structure	STO-3G//STO-3G	4-31G//STO-3G	STO-3G//STO-3G	4-31G//STO-3G	$r(C_1-C_4)$	$r(C_1-C_2)$	$r(C_2-C_3)$	$r(C_1-M)$	$r(C_2-M)$
IV-Li	-166.58116	-168.40602	0.0	0.0	2.966	1.369	1.517	1.968	2.188
		-168.41671[b]		(0.0)[b]	2.505[b]	1.336[b]	1.502[b]	2.074[b]	2.413[b]
X	-166.42868	-168.32652	95.7	49.9	3.324	1.333	1.498	1.908	3.008
XI	-166.46491	-168.35050	73.0	34.8	3.758	1.329	1.494	1.863	2.412
XII	-166.47343	-168.33613	67.6	43.9	3.805	1.342	1.494	1.776	2.026
XIII-Li	-166.57482[c]	-168.36612	4.0	25.0	1.478	1.478	1.478	1.952	1.952
		-168.37482[b]		(26.3)[b]	1.473[b]	1.473[b]	1.473[b]	2.069[b]	2.069[b]

[a] The usual butadiene numbering was used. [b] 4-31G//4-31G. [c] Reference 12.

C_2 distortions of IV (in which the atoms were shifted out of the σ_v symmetry plane) and relatives of XI and XII twisted around the C-C single bond. The energies did not improve.

A number of additional structural possibilities were probed, but these were not competitive in energy with the global minimum, IV-Li. In particular, a structure in which a five-membered ring, comprised of four carbons and a lithium atom, was capped by lithium (as in the ferroles)[11] proved not to be an energy minimum.

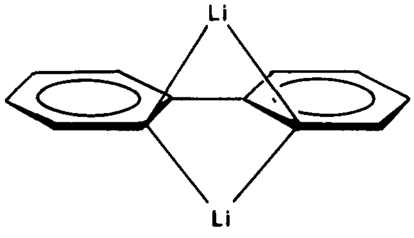
Our combined Möbius-Hückel aromatic candidate (IV-Li) is indicated to be remarkably stable relative to all other forms examined, especially X, suggested by the traditional cis-planar representations of VII-IX.[4] X is unfavorable, both sterically and electronically. XI, the *s*-trans rotamer of X, and the all-trans isomer, XII, are more favorable energetically, but neither can compete with IV-Li. The energy gained on cyclization, XI → IV-Li, 35 kcal/mol (4-31G//STO-3G), provides a good estimate of the resonance energy of our newly proposed Hückel-Möbius aromatic system, IV-Li.

Alternating C-C bond lengths are indicated in the structure of IV-Li, whereas more nearly equal bond lengths are generally associated with Hückel aromatics. The different C_1-C_2 (1.37 Å) and C_2-C_3 (1.52 Å) distances are a natural consequence of the occupation of the two non-degenerate orbitals, V and VI. Despite the short Li⋯Li distance in IV-Li (2.4 Å), the overlap population indicates an antibonding interaction.

IV-Li also competes successfully energetically against the Hückel aromatic alternative, XIII-Li.[12] XIII can be considered to be a derivative of the 6π cyclobutadiene dianion, $C_4H_4^{2-}$,[13] interacting on top and bottom faces with two M^+ cations. Alternatively, XIII-Li can be regarded as one of the simplest "inverse sandwiches"[14] obeying a six interstitial electron rule[15] in which three stablized orbitals are utilized to bind a four-membered ring (C_4H_4 in XIII) and two caps (M in XIII) together.[12] This rule also applies to the BeH capped analogue (XIII-BeH) and to its isoelectronic relatives, the carborane, $C_2B_4H_6$, and the borane, $B_6H_6^{2-}$.[12]

Despite its favorable electronic structure, XIII-Li is indicated (4-31G//4-31G) to be 26 kcal/mol less stable than IV-Li. Both IV and XIII represent energy minima on the $C_4H_4Li_2$ potential-energy surface; their interconversion is orbital symmetry forbidden. In this context, the analysis by Thorn and Hoffmann[11] of transition-metal complexes closely related in geometry to IV and XIII is quite illuminating. However, the ligands examined were not isolobal with Li.

Isolobal transition-metal analogues may be realizable if IV exhibits "aromaticity". It is also possible that crystalline derivatives of IV, e.g., VII-IX, amenable to X-ray analysis, might be prepared.[4b] The symmetrical double bridging exemplified by IV-Li, which may be present in VII-IX as well (e.g., XIV),[16] is a general feature of polylithium compounds, at least as is indicated by our published[17] and unpublished[1] calculations on numerous systems.



XIV(C_{2v})

Acknowledgment. This work was supported by the Fonds der Chemischen Industrie. We thank Dr. E. D. Jemmis for calculations on XIII,[12] Professor W. Heilbronner for perceptive comments, Dr. J. Chandrasekhar for much help, the Regionales Rechenzentrum for assistance, and Professor R. Hoffmann for his interest.

Supplementary Material Available: STO-3G//STO-3G and 4-31G//4-31G geometries (coordinates and Z matrices) for IV-Li and X-XIII (5 pages). Ordering information is given on any current masthead page.

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Received August 11, 1980

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(12) Jemmis, E. D. Ph.D. thesis, Princeton University, 1978. Jemmis, E. D.; Schleyer, P. v. R., to be published. The possibility of a benzocyclobutadienyl dianion structure for VIII was specifically considered in ref 8b, but ruled out. A metallacycle-ion-pair alternative was suggested.

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(17) Apeloig, Y.; Schleyer, P. v. R.; Binkley, J. S.; Pople, J. A.; Jorgensen, W. L. *Tetrahedron Lett.* **1976**, 3923. Jemmis, E. D.; Chandrasekhar, J.; Schleyer, P. v. R. **1979**, *101*, 2848. Kos, A. J.; Poppinger, D.; Schleyer, P. v. R.; Thiel, W. *Tetrahedron Lett.* **1980**, *21*, 2151. Apeloig, Y.; Clark, T.; Kos, A. J.; Jemmis, E. D.; Schleyer, P. v. R. *Isr. J. Chem.* **1980**, *20*, 43.

Thionium Ions as Carbonyl Substitutes. Synthesis of Cyclic Imino Thioethers and Lactams

Sir:

The unparalleled role of the carbonyl group in organic synthesis suggested consideration of functional equivalents. Foremost among the possibilities stands the thionium ion whose higher polarity and low π bond strength led us to refer to it as "super carbonyl".[1] Its

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(1) Trost, B. M.; Reiffen, M.; Crimmin, M. T. *J. Am. Chem. Soc.* **1979**, *101*, 257 and references therein. Reetz, M. T.; Huttenhain, S.; Walz, P.; Lowe, U. *Tetrahedron Lett.* **1979**, 4971. Brinkmeyer, R. S. *Ibid.* **1979**, 207. Mizyuk, V. L.; Semenovsky, A. V. *Ibid.* **1978**, 3603. Kozikowski, A. P.; Ames, A. *J. Am. Chem. Soc.* **1980**, *102*, 860.

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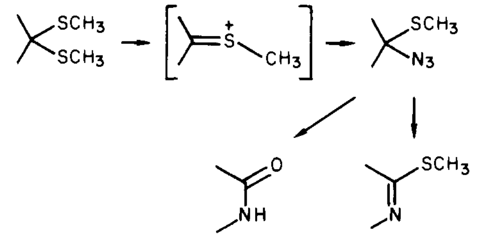
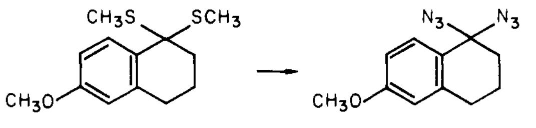
special role stems from the possibility of generating it from a thioketal—a typical carbonyl protecting group which normally had to be hydrolyzed before reacting further and a type of system available through use of lithiated thioacetals as acyl anion equivalents.[2] We wish to report that thioketals, previously used as relatively inert protecting groups, can be chemoselectively activated to generate thionium ions and used in a thionium ion version of the Beckmann[3] or Schmidt[4] rearrangement and to report the advantages accrued thereto.

Generation of thionium ions in a synthetically useful fashion from thioketals is critically dependent on the electrophilic activating reagent. Attempts to convert the thioketal to the α-azido sulfide[5] with iodine, *N*-chlorosuccinimide, a carboxylic or sulfinic acid, or a mercury salt in the presence of azide ion only led to vinyl sulfide or starting material. On the other hand, treatment with iodine azide[6] led to the α-azido sulfides in high yields (see eq 1 and Table I). A limitation exists with respect to benzylic systems such as **1** in which only the diazide was isolated.

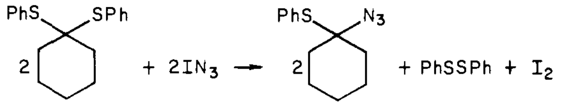


(1)



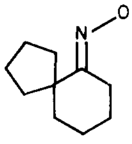
1

Aryl thioketals also react; in this case, isolation of diphenyl disulfide and detection of iodine suggest the formulation of the reaction as in eq 2. The azido sulfides are characterized by an IR band at 2100 ± 10 cm^{-1} and ^{13}C peaks for the carbon bearing azide and the S–CH$_3$ carbon at δ 71.7–80.8 and 10.2–12.6, respectively. While the azides appeared to be reasonably stable and were purified by normal chromatographic procedures, the pure azides were normally not stored for long times.



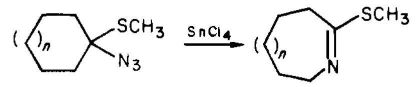
(2)

Addition of 4 equiv of trifluoroacetic acid to a chloroform solution of the α-azido sulfide led to a rapid and virtually quantitative rearrangement directly to the amides and lactams, from which the usually crystalline products were isolated in yields of 65–85% (see Table I). Rearrangements of normal and medium-ring systems proceeded equally well. The more highly substituted carbon preferentially to exclusively migrated (Table I, entries 5–9), consistent with migration to an electron-deficient species in analogy to the Schmidt reaction. The examples chosen illustrate decided advantages over the Beckmann rearrangement and Schmidt reaction. For example, rearrangement of **2** led to the lactam **4** (see Table I) in only 6% yield under Beckmann conditions[11] but in 66% yield from the azido sulfide **3**. Schmidt reaction of pinacolone led exclusively to fragmentation products,[14] but the corresponding rearrangement of **5**, R = *tert*-butyl (Table I, entry 7), proceeded in 82% yield. Tetrazole formation which frequently plagues the Schmidt reaction does not become a problem here. The mildness of the rearrangement conditions is also a decided advantage.



2

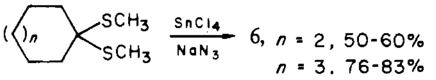
Rearrangement of the α-azido sulfides with 1.1 equiv of commercial stannic chloride in acetonitrile at 25 °C led to intermediate imino thioethers (eq 3) which are characterized by an IR band at 1630 cm^{-1} and a ^{13}C absorption at δ 167.8–169.5. Imino thioethers represent an amide whose carbonyl group is activated toward nucleophilic attack.[15] Thus, this rearrangement constitutes a direct method for formation of the activated form of an amide.



(3)

6, n = 1, 80%
n = 2, 81%

The importance of these activated systems for structural elaboration led us to search for a one-step synthesis of the imino thioether from the thioketal. Addition of 1.1 equiv of sodium azide to 1.1 equiv of freshly distilled stannic chloride in methylene chloride at room temperature followed by 1.0 equiv of 1,1-bis(methylthio)cycloheptane or -cyclooctane led to vigorous nitrogen evolution and, after quenching with aqueous sodium hydroxide, to the imino thioether (eq 4) contaminated by minor amounts of vinyl sulfide and tetrazole. Distillation or chromatography gave pure imino thioethers. Difficulties in extending this reaction to large scale (>10 mmol) were attributed to the heterogeneous nature of the reaction and led to replacement of sodium azide by trimethylsilyl azide. To a solution of the thioketal in methylene chloride at −78 °C was added a mixture of 1 equiv of trimethylsilyl azide, 1 equiv of stannic chloride, and 10 mol % of iodine in methylene chloride.[16] After the solution was stirred at −78 °C for 15 min, 0 °C for 1 h, and room temperature for 1 h (in one case, the reaction was run only at −78 °C for 3.5 h), the reaction was quenched by pouring into an ice-cold solution of sodium hydroxide and sodium thiosulfate. For small-scale reactions, an appreciably better yield was obtained by using 0.5 equiv of preformed diazidotin dichloride and 1.0 equiv of stannic chloride in methylene chloride at −78 °C and warming to room temperature (see Table II, entry 1). As summarized in Table II, this method allowed direct production of the imino thioethers with the same selectivities as previously noted. Most important is the chemo-



(4)

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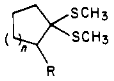
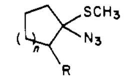
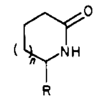
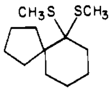
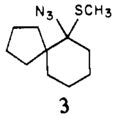
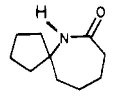
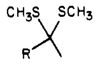
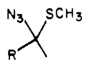
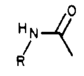
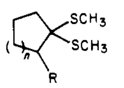
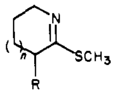
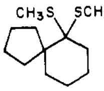
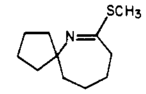
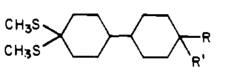
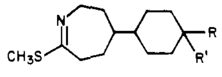
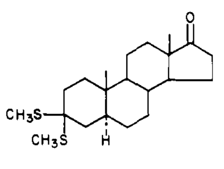
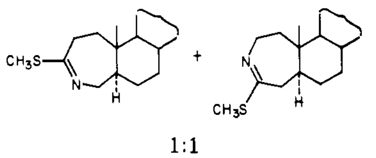
Table I. Preparation of α-Azido Sulfides and Their Rearrangements

entry	thioketal[a]	azide[b]	isolated yield, %	lactam[d]	mp, °C	isolated yield, %
						
1	$n = 1$, R = H	$n = 1$, R = H	83	$n = 1$, R = H	33-37[e]	88
2	$n = 2$, R = H	$n = 2$, R = H	96	$n = 2$, R = H	68-70[e]	79
3	$n = 3$, R = H	$n = 3$, R = H	92	$n = 3$, R = H	oil[f]	64
4	$n = 4$, R = H	$n = 4$, R = H	86	$n = 4$, R = H	78-80[g]	75
5	$n = 2$, R = CH_3	$n = 2$, R = CH_3[c]	81	$n = 2$, R = CH_3	85-86[h]	74
6		 3	71	 4	108-110[i]	66
		 5				
7	R = t-C_4H_9	R = t-C_4H_9	75	R = t-C_4H_9	95-96[j]	82
8	R = cyclohexyl	R = cyclohexyl	79	R = cyclohexyl[k]	102-103[l]	75
9	R = n-C_5H_{11}	R = n-C_5H_{11}	91	R = n-C_5H_{11}[m]	oil	85

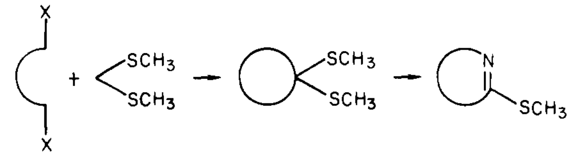
[a] The reactions were run on a 5-mmol scale of starting material. [b] The azides were formed by adding the thioketal in CH_2Cl_2 to 7.5 mmol of IN_3 (generated in the CH_3CN in situ from ICl and NaN_3) in 6 mL of CH_3CN and 5 mL of CH_2Cl_2 at -78 °C for 2 h (caution: exothermic) and then allowing the solution to warm to -10 °C. [c] This compound was a 4:1 mixture of two isomers as determined by NMR spectroscopy. [d] The rearrangement was performed by adding 4 equiv of CF_3CO_2H to a chloroform solution of the α-azido sulfide at 25 °C and stirring for 2 h. [e] Reference 7. [f] Reference 8. [g] Reference 9. [h] Reference 10. [i] Reference 11. [j] Reference 12. [k] A 90:10 crystalline mixture (mp 94-96 °C) of *N*-cyclohexylacetamide and *N*-methylcyclohexanecarboxamide was obtained in quantitative yield from which pure *N*-cyclohexylacetamide was isolated in 75% yield by recrystallization. [l] Reference 13. [m] An 80:20 mixture of *N*-pentylacetamide and *N*-methylcaproamide.

Table II. Formation of Imino Thioethers from Thioketals

entry	thioketal[a]	imino thioether[b]	isolated[d] yield, %
			
1	$n = 1$, R = H	$n = 1$, R = H	40, 95[f]
2	$n = 2$, R = H	$n = 2$, R = H	46
3	$n = 3$, R = H	$n = 3$, R = H	51
4	$n = 4$, R = H	$n = 4$, R = H	38
5	$n = 2$, R = CH_3	$n = 2$, R = CH_3	31
6		 [c]	41
			
7	R = OCOPh, R' = H	R = OCOPh, R' = H	58
8	R, R' = O	R, R' = O[e]	90
9		 1:1	48

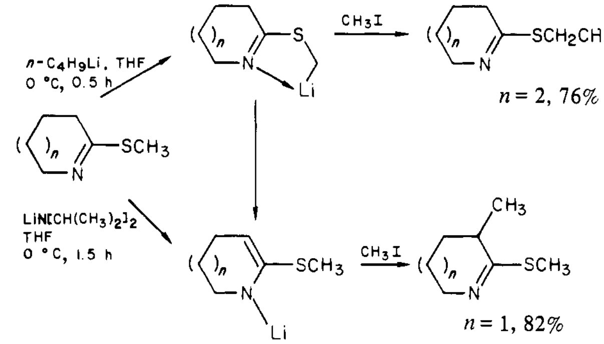
[a] Reactions performed on a 0.5-10-mmol scale. [b] All reactions were normally allowed to warm to 0 °C and then to room temperature (see text). All compounds have been fully characterized by IR, ^1H and ^{13}C NMR, and mass spectroscopy. Satisfactory elemental composition or combustion analyses have been obtained. [c] Reaction performed only at -78 °C. [d] Yields are for isolated pure product. High-performance LC is a very convenient purification procedure. [e] High-performance LC analysis of the initial product (using an RI detector) showed it to be >90% pure. ^1H NMR, IR, and mass spectral data confirm the structure. Attempts to achieve further purification led to substantial loss. Material of this purity had a mp 68-75 °C. [f] For conditions of this higher yield reaction, see text. Satisfactory when performed on small scale (1 mmol).

selectivity (Table II, entries 7–9). As shown in entries 8 and 9, we have reversed the normal reactivity pattern of the thioketal and ketone. Thus, by use of standard methods, reactions can be carried out at the ketone. At the appropriate time, the high reactivity of the "super carbonyl" group, the thionium ion, was unmasked by the thiophilic electrophile. This unprecedented degree of control of reactivity can simplify synthetic design. In addition, the availability of thioketals by direct alkylation methods (see eq 5) enhances the utility of this new rearrangement.



(5)

In addition to imino thioethers serving as activated forms of an amide in terms of susceptibility to nucleophilic attack, we note an interesting behavior toward metalation, as summarized in eq 6, which allows them to be used as nucleophiles. Kinetic metalation occurs at the S–CH_3 group and allows elaboration of the *S*-alkyl group. Alternatively, thermodynamic metalation occurs at the methylene group α to the imine function to give a metalated enamine. Implications of these reactions toward elaboration of alkaloids is an exciting prospect.



(6)

Acknowledgment. We thank the NSF for their generous support of this work. We also express appreciation to NATO and the CNRS for making it possible for M.V. to be a visiting scientist in Madison.

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Received July 21, 1980

Synthesis of 2,2′-Bis(diphenylphosphino)-1,1′-binaphthyl (BINAP), an Atropisomeric Chiral Bis(triaryl)phosphine, and Its Use in the Rhodium(I)-Catalyzed Asymmetric Hydrogenation of α-(Acylamino)acrylic Acids

Sir.

Synthesis of well-designed phosphine ligands is crucial to develop efficient asymmetric catalysis by chiral transition-metal complexes.[1] We have prepared 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (**1**, hereafter abbreviated to BINAP), a new axially dissymmetric *bis(triaryl)phosphine*.[2]

As outlined in Scheme I, racemic BINAP was first synthesized and then the optical resolution was achieved by using the chiral Pd(II) complex **4**[3] through fractional recrystallization of the diastereomers of **5**.[4–6] This method allows the ready preparation of both enantiomers of a new type of diphosphine, BINAP, in an optically pure state.

The molecular structure of [Rh((+)-binap)(norbornadiene)]ClO_4 has been determined by the X-ray crystal structure analysis.[7] The absolute configuration of the dextrorotatory diphosphine ligand was found to be *R*. Perspective drawing of the complex is shown in Figure 1. The rhodium(I) atom has nearly square planar coordination and is surrounded by two phosphorus atoms and two C=C bonds of norbornadiene. The seven-membered chelate ring is fixed to the λ-skew-boat conformation, and this dissymmetry determines the orientation of the four phenyl rings on the phosphorus atoms. These phenyl rings are arrayed in an alternating edge-face manner as was observed for the Rh(I) complex of 1,2-bis[(*o*-methoxyphenyl)phenylphosphino]ethane.[8] The two double bonds of norbornadiene are not perpendicular to the P(1)–Rh–P(2) plane but are tilted 14.6° and 16.1° from the normal to this plane. The angle between the least-squares planes through the two naphthyl groups is 74.3°.

With optically pure BINAP in hand, we have examined the asymmetric hydrogenation of α-(acylamino)acrylic acid derivatives catalyzed by its Rh(I) complexes. When a solution of [Rh((*S*)-binap)(norbornadiene)]ClO_4 [(*S*)-**6**] in methanol was exposed to atmospheric pressure of hydrogen at room temperature, exactly 2.0 mol of hydrogen per Rh atom was taken up to give norbornane and two Rh complexes, (*S*)-**7a** and (*S*)-**8** (~9:1 ratio) (Scheme II).[9] The major, methanol-soluble complex (*S*)-**7a**, isolated as deep red prisms, loses methanol in vacuo at room temperature to produce an air-sensitive complex (*S*)-**7b**,[9] which reverts to (*S*)-**7a** in methanol solution. The minor Rh complex (*S*)-**8** is methanol insoluble and has been isolated as a brown crystalline solid.[10]

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(1) (a) Kagan, H. B.; Dang, T.-P. *J. Am. Chem. Soc.* **1972**, *94*, 6429–6433. (b) Hayashi, T.; Yamamoto, K.; Kumada, M. *Tetrahedron Lett.* **1974**, 4405–4408. (c) Achiwa, K. *J. Am. Chem. Soc.* **1976**, *98*, 8265–8266. (d) Vineyard, B. D.; Knowles, W. S.; Sabacky, M. J.; Bachman, G. L.; Weinkauff, D. J. *Ibid.* **1977**, *99*, 5946–5952. (e) Fryzuk, M. D.; Bosnich, B. *Ibid.* **1977**, *99*, 6262–6267. (f) Ojima, I.; Yoda, N. *Tetrahedron Lett.* **1980**, 1051–1054. Diphosphinites and aminophosphines derived from optically active diamines are also known to be effective ligands for Rh(I)-catalyzed asymmetric hydrogenations: (g) Tanaka, M.; Ogata, I. *J. Chem. Soc., Chem. Commun.* **1975**, 735. (h) Hanaki, K.; Kashiwabara, K.; Fujita, J. *Chem. Lett.* **1978**, 489–490.

(2) Some atropisomeric diphosphines and diphosphinites have been synthesized and used for metal-catalyzed asymmetric hydrogenations, but results are not always satisfactory: 2,2′-bis[(diphenylphosphino)methyl]-1,1′-binaphthyl [Tamao, K.; Yamamoto, H.; Matsumoto, H.; Miyake, N.; Hayashi, T.; Kumada, M. *Tetrahedron Lett.* **1977**, 1389–1392]; 2,2′-bis(diphenylphosphinoxy)-1,1′-binaphthyl [Grubbs, R. H.; DeVries, R. A. *Tetrahedron Lett.* **1977**, 1879–1880]. Quite recently an efficient asymmetric hydrogenation using 2,2′-bis[(diphenylphosphin)amino]-1,1′-binaphthyl as chiral ligand has been reported [Miyano, S.; Nawa, M.; Hashimoto, H. *Chem. Lett.* **1980**, 729–730].

(3) Otsuka, S.; Nakamura, A.; Kano, T.; Tani, K. *J. Am. Chem. Soc.* **1971**, *93*, 4301–4303. Tani, K.; Brown, L. D.; Ahmed, J.; Ibers, J. A.; Yokota, M.; Nakamura, A.; Otsuka, S. *Ibid.* **1977**, *99*, 7876–7886.

(4) Recently resolution of *o*-phenylenebis(methylphenylphosphine) has been attained by the similar procedure: Roberts, N. K.; Wild, S. B. *J. Am. Chem. Soc.* **1979**, *101*, 6254–6260.

(5) The stereospecific synthesis of **1** starting from chiral 2,2′-diamino-1,1′-binaphthyl was difficult.

(6) The Pd(II) complex of (*R*)-**1** [(*R*)-**5**]: mp 157–158 °C dec (from dichloromethane–ethyl acetate–benzene), $[\alpha]^{22}{}_{D}$ +381° (*c* 0.16, acetonitrile); (*S*)-**5**: mp 161 °C dec (from dichloromethane–ether), $[\alpha]^{22}{}_{D}$ −361° (*c* 0.14, acetonitrile); (*R*)-(+)-**1**: mp 240–241 °C, $[\alpha]^{25}{}_{D}$ +229° (*c* 0.32, benzene); (*S*)-(−)-1: mp 241–242 °C, $[\alpha]^{25}{}_{D}$ −229° (*c* 0.31, benzene).

(7) The crystals are dark-red micalike plates. Intensities of the reflections were measured on a diffractometer with Cu Kα radiation up to $2\theta = 120°$. The crystallographic data are $[RhP_2C_{51}H_{40}]ClO_4$, $M_r = 917.179$, orthorhombic, $P2_12_12_1$, $Z = 4$, $a = 11.104$ (1), $b = 35.238$ (2), $c = 10.892$ (1) Å, $U = 4261.6$ (3) Å^3, $D_x = 1.430$ g cm^{-3}, μ(Cu Kα) = 49.81 cm^{-1}. The structure was solved by routine application of the heavy-atom method and refined by block-diagonal least-squares calculations including hydrogen atoms. The final R and R_w values were 0.032 and 0.041, respectively, for all the 3249 observed independent reflections. The absolute configuration of the binaphthyl group in this complex was determined to be *R* by measuring further 1106 $h\bar{k}l$ reflections within the range of $2\theta \leq 70°$ and by comparison of the observed intensity relations between the hkl and $h\bar{k}l$ reflections with the calculated relations. The details of the results will be reported elsewhere.

(8) (a) Knowles, W. S.; Sabacky, M. J.; Vineyard, B. D. *Adv. Chem. Ser.* **1974**, *No. 132*, 274–282. (b) Knowles, W. S.; Vineyard, B. D.; Sabacky, M. J.; Stults, B. R. In "Fundamental Research in Homogeneous Catalysis"; Tsutsui, M., Ed; Plenum Press: New York, 1979; Vol. 3, pp 537–548.

(9) ^{1}H NMR of (*S*)-**7a** (CD_2Cl_2 containing tetramethylsilane): δ 7.50 (m) and 6.82 (m) (BINAP), 3.42 (s, CH_3OH); ^{31}P NMR of (*S*)-**7a** (CD_3OD solution, 5% H_3PO_4 in CD_3OD as external standard): δ 53.1 (d, $J_{Rh-P} = 206$ Hz). The ^{1}H NMR spectrum of (*S*)-**7b** in CD_2Cl_2 resembles closely that of (*S*)-**7a** but lacks the methanol signal.

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