Chiral Phosphito−Thioether Complexes of Palladium(0). Comments on the Pd, Rh, and Ir Regio- and Enantioselective Allylic Alkylations of PhCH=CHCH(OAc)R, R = H, Me, Et

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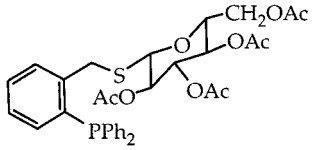
The new chiral auxiliary (*R*)-2-ethylthio-1-(phenylethyl)-(*R*)-binaphthyl phosphite, **1**, and three stable Pd(0) olefin complexes containing this chelate, **2**−**4**, have been synthesized. The structure of the maleic anhydride complex **3** has been determined by X-ray diffraction methods. Solution details for **2**−**4** and aspects of their dynamics have been elucidated via 2-D NMR spectroscopy. The fumaronitrile complex **2** exchanges intramolecularly, whereas the maleic anhydride and pentenedione derivatives, **3** and **4**, respectively, exchange intermolecularly. Ligand **1** has been used as auxiliary in the Pd, Rh, and Ir regio- and enantioselective allylic alkylation reactions of PhCH=CHCH(OAc)R, R = H, Me, Et, with the anion of dimethyl malonate. Modest to good selectivities are reported.

Introduction

Zerovalent complexes of palladium are often postulated in catalytic C−C bond-making reactions.[1−3] Although the tris and tetrakis PPh_3 complexes of Pd(0), together with $Pd_2(dba)_3$, are now commercially available, there is still not much known with respect to chiral complexes of Pd(0) and specifically very little on compounds containing auxiliaries with different donor atoms. Two groups have recently isolated Pd(0) complexes with P,N donor combinations,[4,5] and a third has reported on the in situ identification of a catalytic Pd(0) intermediate with a P,N ligand.[6] We have characterized the first chiral P,S complexes of Pd(0)[7] using the thiosugar−phosphine shown.



There are several structural studies involving chiral bis-phosphine complexes.[8,9]

Pd(0) derivatives are intermediates in the increasingly popular enantioselective allylic alkylation reaction. For both the alkylation and amination reactions of 1,3-diphenyl allyl precursors, observed enantiomeric excesses (ee's) of >90% and occasionally >98% are almost routine.[10−18] Somewhat more challenging is the regioselective allylic alkylation of less symmetric allylic precursors, e.g., PhCH(X)CH=CHR or PhCH=CHCH(X)R, where X is a good leaving group and R = Me or some other relatively small substituent. Recent studies report very good regioselectivity by using Rh[19a,b] and Ir[19c] mixed phosphine/phosphite catalyst precursors,

(1) Consiglio, G.; Waymouth, R. M. *Chem. Rev.* **1989**, *89*, 257.
(2) de Meijere, A.; Meyer, F. E. *Angew. Chem.* **1994**, *106*, 2473−2506.
(3) *Metal-Catalyzed Cross-Coupling Reactions*; Diederich, F.; Stang, P. J., Eds.; Wiley-VCH: Weinheim, 1998.
(4) Fernandez-Galan, R.; Jalon, F. A.; Manzano, B. R.; Rodriguez de la Fuente, J.; Vreahami, M.; Jedlicka, B.; Weissensteiner, W.; Jogl, G. *Organometallics* **1997**, *16*, 3758−3768. Gomez-de la Torre, F.; Jalon, F. A.; Lopez-Angeno, A.; Manzano, B. R.; Rodriguez, A.; Sturm, T.; Wassensteiner, W.; Martinez-Ripoll, M. *Organometallics* **1998**, *17*, 4634−4644.
(5) Selvakumar, K.; Valentini, M.; Wörle, M.; Pregosin, P. S.; Albinati, A. *Organometallics* **1999**, *18*, 1207−1215.
(6) Steinhagen, H.; Reggelin, M.; Helmchen, G. *Angew. Chem.* **1997**, *109*, 2199−2202.
(7) Tschoerner, M.; Trabesinger, G.; Albinati, A.; Pregosin, P. S. *Organometallics* **1997**, *16*, 3447.
(8) Bolm, C.; Kaufmann, D.; Gessler, S.; Harms, K. *J. Organomet. Chem.* **1995**, *502*, 47.
(9) Herrmann, W. A.; Brossmer, C.; Priermeier, T.; Oefele, K. *J. Organomet. Chem.* **1994**, *481*, 97−108.
(10) Boog-Wick, K.; Pregosin, P. S.; Trabesinger, G. *Organometallics* **1998**, *17*, 3254−3264.
(11) Brown, J. M.; Hulmes, D. I.; Guiry, P. J. *Tetrahedron* **1994**, *50*, 4493−4506.
(12) Hayashi, T. *Catalytic Asymmetic Synthesis*; VCH Publishers: Weinheim, 1993. Johannsen, M.; Jorgensen, K. A. *Chem. Rev.* **1998**, *98*, 1689−1708.
(13) Hayashi, T.; Kawatsura, M.; Uozumi, Y. *J. Am. Chem. Soc.* **1998**, *120*, 1681−1687.
(14) Pfaltz, A.; Prètôt, R. *Angew. Chem.* **1998**, *110*, 337−339. von Matt, P.; Pfaltz, A. *Angew. Chem.* **1993**, *105*, 614−615. von Matt, P.; Lloyd-Jones, G. C.; Minidis, A. B. E.; Pfaltz, A.; Macko, L.; Neuburger, M.; Zehnder, M.; Rüegger, H.; Pregosin, P. S. *Helv. Chim. Acta* **1995**, *78*, 265. Schaffner, S.; Kueller, J. F. K.; Neuburger, M.; Zehnder, M. *Helv. Chim. Acta* **1998**, *81*, 1223−1232.
(15) Rieck, H.; Helmchen, G. *Angew. Chem.* **1995**, *107*, 2881−2883.
(16) Koning, B.; Meetsma, A.; Kellogg, R. M. *J. Org. Chem.* **1998**, *63*, 5533−5540.
(17) Togni, A.; Burckhardt, U.; Gramlich, V.; Pregosin, P. S.; Salzmann, R. *J. Am. Chem. Soc.* **1996**, *118*, 1031−1037.
(18) Trost, B. M.; van Vranken, D. L. *Chem. Rev.* **1996**, *96*, 395. Trost, B. M.; Rasdinov, R.; Grenzer, E. M. *J. Am. Chem. Soc.* **1997**, *119*, 7879−7880. Trost, B. M.; Ariza, X. *Angew. Chem.* **1997**, *109*, 2749−2751. Trost, B. M. *J. Am. Chem. Soc.* **1998**, *120*, 70−79.

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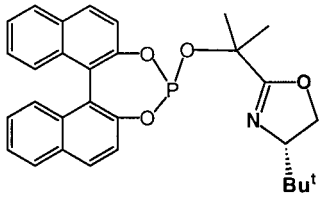
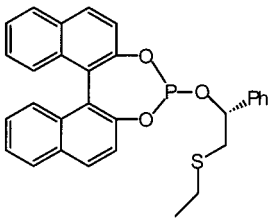
although these latter papers do not address the question of enantioselectivity. With Ir, Bartels and Helmchen[19d] have managed both regioselectivity and enantioselectivity via a P,N chelate combination. Trost and Hachiya[19e] and Lloyd-Jones and Pfaltz[19f] have also managed excellent regioselectivity and enantioselectivity using Mo and W catalysts, respectively. Returning to Pd-based catalysts, Pfaltz and Prétôt,[20a] using the phosphito−oxazoline chelate shown, have, again, achieved good regioselective and enantioselective results in the alkylation of $PhCH{=}CHCH_2OAc$. They find linear/branched ratios of ca. 24:76 with an ee of 90% for the branched isomer. Hayashi[20b] has also reported good regioselective and enantioselective results using monophosphine ligands for the reduction of allylic esters with formic acid.



We report here on our preparative Pd(0) and catalytic allylic alkylation results using the phosphito−thioether **1**. Ligand **1** contains two donor types that are not necessarily electronically very different; however, the ethyl−thioether moiety is relatively small and the binaphthol−phosphite, fairly large.



Results and Discussion

The preparation of the stable olefin Pd(0) complexes **2**−**4** is shown in Scheme 1 and involves displacement of dibenzylideneacetone (dba) from Pd(0) as previously described.[5,7] The complexes are obtained as stable yellow crystalline materials in 64−72% yield and were characterized by NMR and mass spectroscopic methods, together with microanalytical data. Their ease of preparation and relative stability, taken together with our earlier work,[7] suggest that thioethers may be broadly suitable as ligands for Pd(0).

Solid-State Structure of 3. It proved possible to obtain suitable crystals of the maleic anhydride derivative, **3**, from methylene chloride/hexane, and an ORTEP view of this Pd(0) complex is shown in Figure 1. This is only the second structure of a Pd(0) thioether complex.[7]

The local coordination geometry has the atoms Pd, P, S, C2L, and C3L almost coplanar, with the two carbons ca. 0.19 and 0.15 Å out of the plane defined by the Pd, P, and S atoms. The S-methylene carbon, C14, is ca −1.38 Å below this plane, and the remaining atoms of the maleic anhydride are above this plane. The Pd−S, 2.3726(8) Å, Pd−P, 2.2328(7) Å, and Pd−C(olefin), 2.114(3) Å, 2.143(3) Å separations are as expected. The length of the complexed double bond, C2L−C3L, 1.402(4) Å, is consistent both with π-back-bonding from Pd(0) and the reported Pd(0)−maleic anhydride−diimine structure of van Asselt et al.[21] These authors find an olefin C−C bond length of 1.408(11) Å, which is not

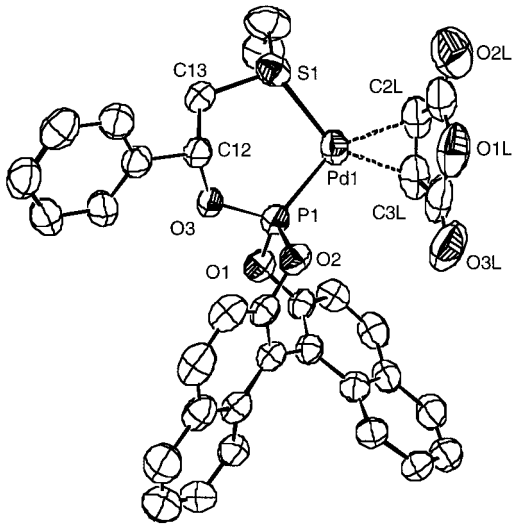
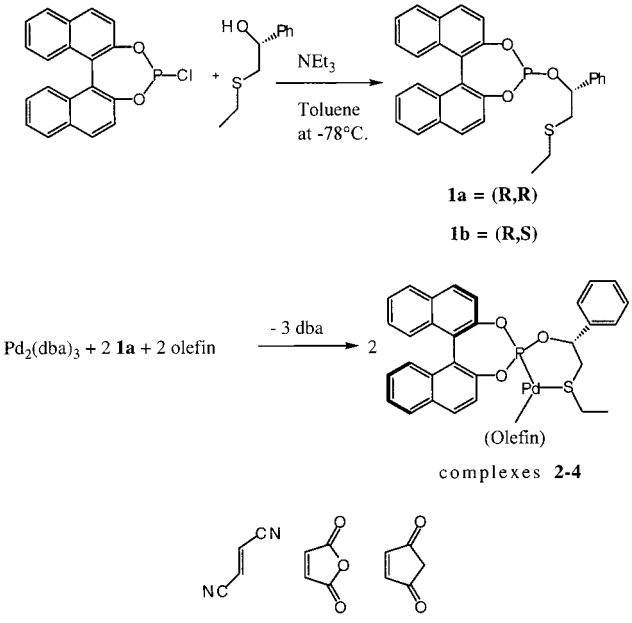


Figure 1. ORTEP view of the Pd(0) complex **3**. Selected bond distances (Å) and angles (deg): Pd(1)−C(3L), 2.114(3); Pd(1)−C(2L), 2.143(3); Pd(1)−P(1), 2.2328(7); Pd(1)−S(1), 2.3726(8); P(1)−O(3), 1.597(2); P(1)−O(1), 1.618(2); P(1)−O(2), 1.618(2); S(1)−C(14), 1.802(3); S(1)−C(13), 1.824(3); O(1L)−C(1L), 1.404(4); O(1L)−C(4L), 1.430(5); O(2L)−C(1L), 1.178(4); O(3L)−C(4L), 1.175(4); C(1L)−C(2L),1.455(5); C(2L)−C(3L), 1.402(4); C(3L)−C(4L), 1.452(5); C(3L)−Pd(1)−C(2L), 38.4(1); C(3L)−Pd(1)−P(1), 112.2(1); C(2L)−Pd(1)−P(1), 150.4(1); C(3L)−Pd(1)−S(1), 149.3(1); C(2L)−Pd(1)−S(1), 110.9(1); P(1)−Pd(1)−S(1), 98.13(3).

Scheme 1. Synthesis of the Complexes



(19) (a) Evans, P. A.; Nelson, J. D. *Tetrahedron Lett.* **1998**, *39*, 1725−1728. (b) Evans, P. A.; Nelson, J. D. *J. Am. Chem. Soc.* **1998**, *120*, 5581−5582. (c) Takeuchi, R.; Kashio, M. *Angew. Chem.* **1997**, *109*, 268. (d) Janssen, J. P.; Helmchen, G. *Tetrahedron Lett.* **1997**, *38*, 8025. (e) Trost, B. M.; Hachiya, I. *J. Am. Chem. Soc.* **1998**, *120*, 1104−1105. (f) Lloyd-Jones, G. C.; Pfaltz, A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 462−464.

(20) (a) Pfaltz, A.; Prétôt, R. *Angew. Chem.* **1998**, *110*, 337−339. (b) Hayashi, T. *J. Organomet. Chem.* **1999**, *576*, 195−202.

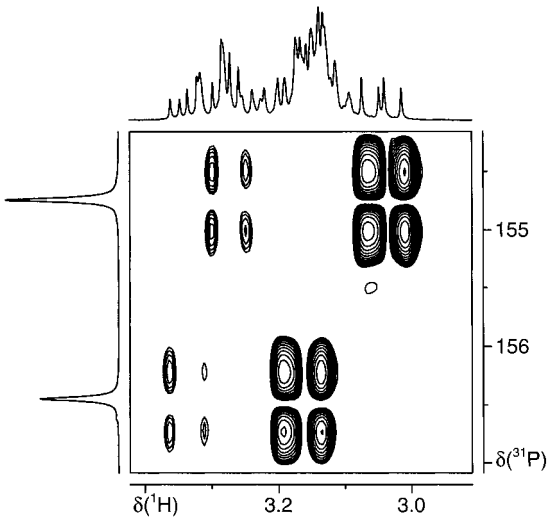


Figure 2. $^{31}P,^{1}H$, correlation for the fumaronitrile compound **2** allowing the indentification of the olefin signals in the two diastereomers. The intense cross-peaks arise from the olefinic protons pseudo-trans to ^{31}P, whereas the weaker cross-peaks stem from the olefinic protons pseudo-cis to ^{31}P (400 MHz, CD_2Cl_2).

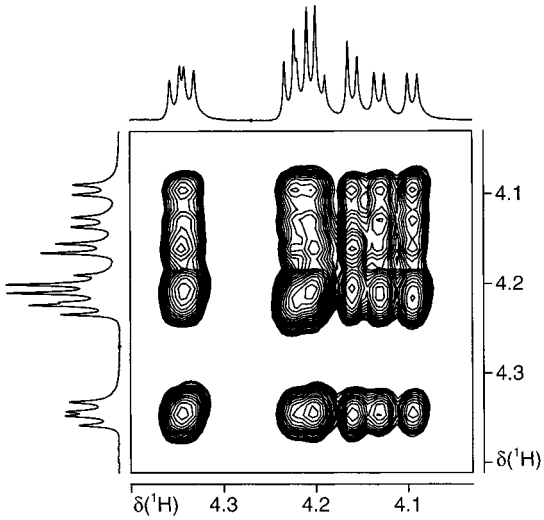
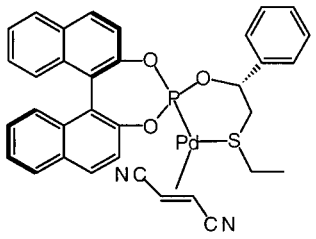


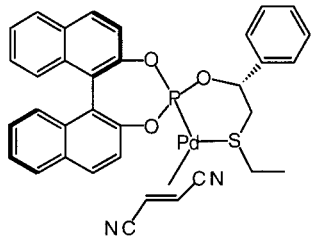
Figure 3. Section of the phase-sensitive NOESY spectrum of the maleic anhydride complex **3**. All four olefinic proton resonances, from the two rotational isomers of **3**, are in exchange, thus (in contrast to **2**) suggesting intermolecular exchange (400 MHz, CD_2Cl_2).

significantly different from ours. Interestingly, the P−Pd−S chelate bite angle, 98.13(3)°, is relatively large. Possibly the special constraints of both the phosphite and the sulfur lone pair combine to afford this unexpected result. Dierkes and van Leeuwen have emphasized the importance of chelate bite angle in connection with homogeneous catalysis.[22] The chelate ring has a boat conformation with the C-phenyl group in a pseudoequatorial position.

NMR Spectroscopy. The Pd(0)−olefin derivatives **2**−**4** exist as a mixture of two isomers in solution in almost, but not quite, equal proportions. For the fumaronitrile compound **2**, the mixture contains diastereomers that arise due to the *Re* and *Si* faces of the olefin. The fumaronitrile protons have very similar chemical shifts but can be assigned to the individual isomers using a $^{31}P,^{1}H$ correlation[23] (see Figure 2). There is a substantial difference in the three-bond spin−spin interactions ^{3}J(P,H{olefin}) as a function of geometry, with the pseudo-trans P,H coupling much larger. This explains the differing cross-peak intensities; that is, the olefin pseudo-trans to the ^{31}P-spin affords relatively intense cross-peaks. 2-D exchange spectroscopy[23] reveals intramolecular exchange between the fumaronitrile protons within **2a** or **2b**, confirming that the olefins rotate freely; however, there is no evidence for intermolecular exchange on the NMR time scale.

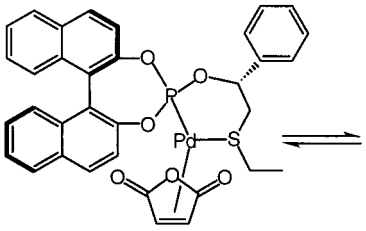


2a

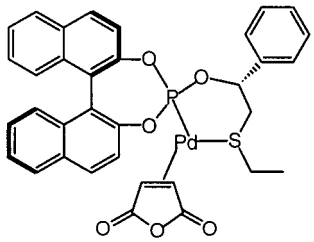


2b

For the maleic anhydride derivatives **3a** and **3b** (as well as for the pentenedione analogues **4a** and **4b**), the two observed isomers stem from rotation of the olefin. In contrast to **2**, NMR exchange spectroscopy (see Figure 3) reveals that all four of the olefin protons from **3a**,**b** exchange with one another, presumably via olefin



3a



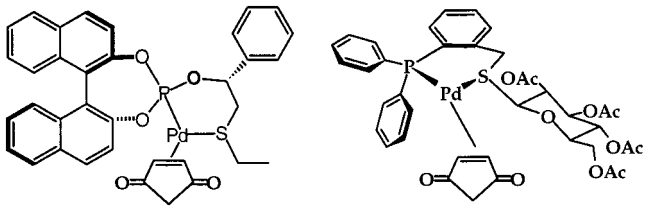
3b

(21) Asselt, V.; Elsevier, C. J.; Smeets, W. J. J.; Spek, A. *Inorg. Chem.* **1994**, *33*, 1521−1531.
(22) Dierkes, P.; van Leeuwen, P. W. N. M. *J. Chem. Soc., Dalton Trans.* **1999**, 1519.
(23) Pregosin, P. S.; Salzmann, R. *Coord. Chem. Rev.* **1996**, *155*, 35. Pregosin, P. S.; Trabesinger, G. *J. Chem. Soc., Dalton Trans.* **1998**, 727−734.

Table 1. ^{1}H and ^{13}C NMR Data for the Complexed Olefins Plus ^{31}P for 2−4

compound	isomer	δ^1H	δ^{13}C	δ^{31}P
2	major	3.05, 3.28	28.4, 31.2	154.7
	minor	3.16, 3.34	29.7, 31.6	156.4
3	major	4.20, 4.25	51.8, 53.5	156.4
	minor	4.11, 4.34	52.8, 53.4	156.6
4	major	4.64, 4.69	72.9, 73.1	156.8
	minor	4.55, 4.79	72.6, 73.5	157.0

Scheme 2. δ ^{13}C for the Olefinic Carbons of the Complexed Pentenedione, 4

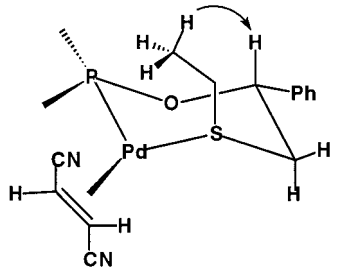


4 72.9, 73.1 72.2, 80.6

72.6, 73.5

dissociation and recombination. This difference in the dynamics of Pd(0) olefin complexes has been observed previously.[5]

NOE spectroscopy did not allow an immediate distinction between the diastereomeric structures **2a** and **2b**; however, a rather weak NOE between one binaphthol proton and an olefinic resonance has allowed a tentative assignment, and this is given in Table 1 and the structure indicated below. With respect to the chelate ring conformation, there is a fairly strong NOE between the methyl group of the S-Et and the CHO-methine protons in **2** (and **3**). Consequently, the S-Et



group is assigned a pseudoaxial, and the C-phenyl a pseudoequatorial position, in agreement with the solid-state data for **3**. The pseudoaxial S-group has been found in a number of Pd and Pt chelate complexes of thioethers.[7,24] The dynamics of the cyclopentenedione compounds **4** are similar to those for **3**.

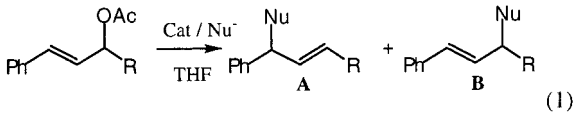
In Table 1 we show selected ^{13}C NMR olefin data for **2**−**4**. These chemical shifts support significant differences in the amount of π-back-bonding from the Pd(0) to the olefin. In addition, the similarity of the olefin chemical shift data *within a complex* suggests that the phosphito and thioether donors are not very different. This is in contrast to previous observations[7] for the Pd-(0) complexes of a phosphino−thiosugar (see Scheme 2) in which the two olefinic carbons had significantly different δ values.

Table 2. Regio- and Stereoselective Allylic Alkylation Results Derived from the Reactions of the Phosphito−Thioether Auxiliary, 1[a]

					ratio, % of isomers (ee)	
entry	R	catalyst	time, h	yield	A	B
1	H	Pd	4	95	32 (25)	68
2[b]	H	Pd	4	95	35 (20)	65
3	Me	Pd	4	90	40 (55)	60 (42)
4	Et	Pd	7	90	61 (68)	39 (74)
5	H	Rh	24	95	49 (14)	51
6[b]	H	Rh	24	95	39 (24)	61
7[c]	H	Rh	20	95	24 (42)	76
8	Me	Rh	48	80	19 (6)	81 (17)
9	Et	Rh	60	70	16 (81)	84 (45)
10	H	Ir	24	90	71 (53)	29
11[b]	H	Ir	24	90	69 (13)	31
12	Me	Ir	30	85	19 (70)	81 (35)
13	Et	Ir	48	80	28 (70)	72 (52)

[a] Ligand **1a** was used in all reactions unless otherwise specified. The ee of the products was determined by NMR methods using Eu(hfc)$_3$ as chiral shift reagent. [b] Using **1b**, the *R,S*-diastereomer. [c] One equivalent of triphenylphosphine was added. The isomers were not separated. [Pd(μ^3-PhCHCHCHPh)]$_2$, Rh$_2$(COD)$_2$Cl$_2$, and Ir$_2$(COD)$_2$Cl$_2$ are the precursors for Pd-, Rh-, and Ir-catalyzed reactions, respectively. 2 mol % Pd, 4 mol % Rh, and 4 mol % Ir were used for catalytic reactions. No attempt was made to optimize the various ratios given above.

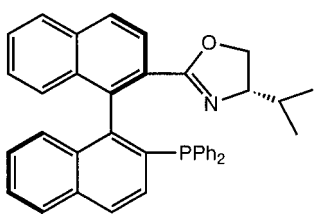
Catalytic Results. Results for the Pd, Rh, and Ir regio- and enantioselective allylic alkylation reactions of eq 1, using the phosphito−thioether, **1**, as auxiliary



R = H, Me, Et (1)

are given in Table 2. Generally speaking, the yields were good and both the regio- and enantioselectivities modest. We chose to study three different allyls, with R = H, Me, and Et, and indeed, the results for R = Et are the most noteworthy. With the Pd catalyst, for R = Et, ligand **1** favors product **A** slightly (61:39) with encouraging, if not satisfactory, ee's (68% and 74%). With the Rh and Ir catalysts, for R = Et (entries 9 and 13), the smaller terminus is attacked preferentially. It is interesting that for R = H with the Ir precursor we obtain the largest amount of branched isomer (see entries 10 and 11).

We have also carried out several experiments with the previously[5,25,26] described P,N ligand **5**, and these are given in Table 3. With the Rh catalyst, the observed regioselectivity strongly favors **B**, although the observed ee for **A** at ca. 80% is acceptable. Where **1a** and **1b** were



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(24) Albinati, A.; Pregosin, P. S.; Wick, K. *Organometallics* **1996**, *15*, 2419−2421. Albinati, A.; Eckert, J.; Pregosin, P. S.; Rüegger, H.; Salzmann, R.; Stössel, C. *Organometallics* **1997**, *16*, 579−590.

(25) Ogasawara, M.; Yoshida, K.; Kamei, H.; Kato, K.; Uozumi, Y.; Hayashi, T. *Tetrahedron Asymmetry* **1998**, *9*, 1779−1787.

(26) Imai, Y.; Zhang, W.; Kida, T.; Nakatsuji, Y.; Ikeda, I. *Tetrahedron Lett.* **1998**, *39*, 4343−4346.

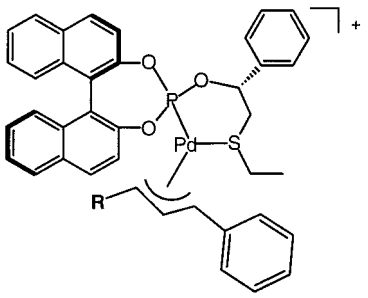
Table 3. Regio- and Stereoselective Allylic Alkylation Results Using the Phosphino−Oxazoline Auxiliary

					ratio (%) of isomers (ee)	
entry	R	metal	time (h)	total yield	A	B
1	H	Rh	24	95	2	98
2	Me	Rh	48	75	10 (80)	90 (13)
3	Et	Rh	72	70	14 (82)	86 (26)
4	H	Ir	12	95	36 (57)	64

[a] ee of the products and their ratio were determined by NMR methods using Eu(hfc)$_3$ as chiral shift reagent. $Rh_2(COD)_2Cl_2$ and $Ir_2(COD)_2Cl_2$ are the precursors for Rh- and Ir-catalyzed reactions, respectively. 4 mol % Rh and 4 mol % Ir were used for catalysis. No attempt was made to optimize the various ratios given above

individually employed (entries 1 and 2, 5 and 6, 10 and 11) we find no change in the preferred enantiomer suggesting that the enantioselectivity arises from the chelate ring backbone.

Comment. We and others[10−18] have emphasized steric effects in rationalizing the observed products of the enantioselective allylic alkylation of 1,3-diphenyl allyl compounds. In the allylation reactions of **1** with the unsymmetrical substrates, reported here, the marked size difference between the phosphito- and thioether moieties was intended to bias a presumed allyl intermediate of type **6**, with the result that the allyl phenyl



6

group would assume a position remote from the binaphthol moiety. Since we anticipated that the phosphito donor would be comparable or better than the thioether (vida supra), we hoped, in analogy with Pfaltz[20a] and Hayashi,[20b] to control the regioselectivity (but not enantioselectivity). We have prepared an analytically pure sample of the Pd−allyl cation **6** with R = Me as its triflate salt (see Experimental Section). The ^{31}P NMR spectrum of this species reveals at least five components (there are cis/trans possibilities, exo/endo structures, and syn/syn vs syn/anti configurations). The four major components, found in the relative ratio 1.0 (A):0.90 (B): 0.23 (C):0.15) (D), undergo selective exchange: A with C, and B with D, as shown by 2-D NMR exchange spectroscopy. On the basis of these results it is clear that, although the catalytic results are promising, there is little structural control and ligand **1** can only be considered as a first step toward simultaneously mastering regioselectivity and enantioselectivity.

Experimental Section

All manipulations were carried out under an argon atmosphere. THF and diethyl ether were distilled from sodium benzophenone ketyl. CH_2Cl_2 was distilled from CaH_2 and hexane from sodium. (*R*)-Styrene oxide was purchased from Fluka. (*R*)-1,1′-Bi-2-naphthol was obtained from E-Merck. (*R*)- and (*S*)-1,1′-bi-2-naphthol were obtained from Gerchem Labs, Hyderabad, India. (*S*,*R*)-2-[4-(Isopropyl)oxazol-2-yl]-2′-(diphenylphosphino)-1,1′-binaphthyl[5] and (*R*)-2-(ethylthio)-1-phenylethanol, and (*R*)-(1,1′-binaphthalene-2,2′-dioxy)chlorophosphine were prepared by literature procedures. The palladium-catalyzed allylic alkylation was carried out as described previously[14] using [Pd(η^3-PhCHCHCHPh)]$_2$ as catalyst precursor.

Table 4. Crystal and Structure Refinement Data for 3

formula	$C_{34}H_{27}O_6PPdS$
mol wt	700.99
data coll *T*, K	296
diffractometer	Bruker SMART CCD
cryst syst	orthorombic
space group	$P2_12_12_1$
a, Å	12.7426(4)
b, Å	24.2851(7)
c, Å	9.8681(3)
V, Å^3	3053.7(2)
Z	4
$\rho_{(calcd)}$, g cm^{-3}	1.525
μ, cm^{-1}	7.73
radiation	Mo Kα (graphite monochromated, $\lambda = 0.71079$ Å)
measured reflns	$\pm h, \pm k, \pm l$
θ range, deg	$1.7 < \theta < 33.4$
no. data collected	38643
no. indep data	11036
no. obsd reflns (n_o)	4434 [$\|F_o\| > 4.0\ \sigma(\|F\|)$]
transmission coeff	0.8474−1.0000
no. of params refined (n_v)	388
R_{av}[a]	0.0278
R,[b] R_w^2 (obsd reflns)	0.0332, 0.0527
R, R_w^2 (all data)[c]	0.1491, 0.066
GOF[d]	0.747

[a] $R_{av} = \sum|F_o^2 - F_o^2{}_{av}|/\sum_i|F_o^2|$. [b] $R = \sum(|F_o - (1/k)F_c|)/\sum|F_o|$. [c] $R_w^2 = [\sum w(F_o^2 - (1/k)F_c^2)^2/\sum w|F_o^2|^2]$. [d] GOF $= [\sum_w(F_o^2 - (1/k)F_c^2)^2/(n_o - n_v)]^{1/2}$.

Crystallography. Colorless crystals of **3**, suitable for X-ray diffraction, were obtained by crystallization from methylene chloride/hexane and are air stable. A prismatic single crystal was mounted, for the data collection, on a glass fiber at a random orientation on a Bruker SMART CCD diffractometer at room temperature. The space group was unambiguously determined from the systematic absences, while the cell constants were refined at the end of the data collection, using 7765 reflections up to $\theta_{max} \leq 33°$. Data were collected by using ω scans in steps of 0.3°. For each of the resulting 1868 "frames", counting time was 10 s. The collected intensities[27] were corrected for Lorentz and polarization factors and empirically for absorption.[28]

Selected crystallographic and other relevant data are listed in Table 4 and in Table S1. The standard deviations on intensities were calculated in terms of statistics alone, while those on F_o^2 were calculated as shown in Table S1.

The structure was solved by direct and Fourier methods and refined by full-matrix least-squares,[29] minimizing the function $[\sum w(F_o^2 - (1/k)F_c^2)^2]$. Anisotropic displacement parameters were used for all atoms. The contribution of the hydrogen atoms, in their calculated position, was included in the refinement using a riding model (U(H) = 1.5U(bonded atom) Å^2). The handedness of the structure was tested by refining the Flack parameter.[30]

(27) *SAINT: SAX Area Detector Integration*; Siemens Analytical Instrumentation, 1996.
(28) Sheldrick, G. M. *SADABS*; Universität Göttingen, to be published.
(29) Sheldrick, G. M *SHELX-97. Structure Solution and Refinement Package*; Universität Göttingen, 1997.
(30) Flack, H. D. *Acta Crystallogr. A* **1983**, *39*, 876.

No extinction correction was deemed necessary. Upon convergence, the final Fourier difference map showed no significant peaks. The scattering factors used, corrected for the real and imaginary parts of the anomalous dispersion, were taken from the literature.[31] All calculations were carried out by using the PC version of the SHELX-97 programs.[29]

Synthesis of Phosphito−Thioether Ligand (*R,R*), 1a. (*R*)-(1,1′-Binaphthalene-2,2′-dioxy)chlorophosphine (421 mg, 1.2 equiv) in 3 mL of toluene was added to (*R*)-2-ethylthio-1-phenylethanol (182 mg, 1 equiv) and Et_3N (101 mg, 1 equiv) in 3 mL of toluene at −78 °C. The reaction mixture was slowly warmed to room temperature. The resulting solution was stirred at room temperature for 3 h. Ether was added, and the Et_3N·HCl that formed was removed by filtration. The filtrate was washed with water and brine and then dried over $MgSO_4$. The solvent was evaporated, and the residue was purified by silica gel column chromatography to afford 370 mg (75%) of **1a**. The (*R,S*) analogue, **1b**, was prepared in a similar fashion. Anal. Calcd for $C_{30}H_{25}O_3PS$ (496.57): C, 72.56; H, 5.07. Found: C, 72.48; H, 5.21. MS (EI): 496 (M+, 1), 467 (56), 332 (78), 268 (66), 165 (100). For **1a**: ^{1}H NMR (CD_2Cl_2, 298 K, 400 MHz): 5.36 (dt, $^3J_{PH}$ = 9.6, $^3J_{HH}$ = 6.6, OC*H*), 2.95 (d, $^3J_{HH}$ = 6.6, SCH_2), 2.51 (q, $^3J_{HH}$ = 7.4, CH_2), 1.21 (t, $^3J_{HH}$ = 7.4, Me). ^{13}C NMR (CD_2Cl_2, 298 K, 400 MHz): 77.9 (d, $^2J_{PC}$ = 17.9, O*C*H), 40.1 (d, $^3J_{PC}$ = 3.7, S*C*H$_2$), 27.1 (s, *C*H$_2$), 14.9 (s, Me). ^{31}P NMR (CD_2Cl_2, 298 K, 400 MHz): 152.1 (s). For diastereomer **1b**: ^{1}H NMR (CD_2Cl_2, 298 K, 400 MHz): 5.24 (dt, $^3J_{PH}$ = 9.4, $^3J_{HH}$ = 6.4, OC*H*), 3.05 (q, $^2J_{HH}$ = 13.8, $^3J_{HH}$ = 6.6, SCH_2), 2.86 (q, $^2J_{HH}$ = 13.9, $^3J_{HH}$ = 6.6, SCH_2), 2.27 (dq, $^3J_{HH}$ = 7.5, $^4J_{HH}$ = 1.2, CH_2), 1.06 (t, $^3J_{HH}$ = 7.5, Me). ^{13}C NMR (CD_2Cl_2, 298 K, 400 MHz): 77.6 (d, $^2J_{PC}$ = 8.7, O*C*H), 40.3 (d, $^3J_{PC}$ = 3.1, S*C*H$_2$), 26.7 (s, *C*H$_2$), 14.8 (s, Me). ^{31}P NMR (CD_2Cl_2, 298 K, 400 MHz): 141.4 (s).

Synthesis of Pd(P-S)(Olefin) [2−4]. A mixture of $Pd_2(dba)_3$·$CHCl_3$ (103 mg, 0.1 mmol), the PS ligand, **1a** (100 mg, 0.2 mmol), and the appropriate olefin (0.2 mmol) in 4 mL of CH_2Cl_2 was stirred at room temperature for 5 h. The yellow solution was filtered and concentrated in vacuo. The solid residue was washed with ether (4 × 1 mL) and recrystallized from CH_2Cl_2/ether to afford yellow crystals of product.

Complex 2. Yield: 85 mg, 64%. Anal. Calcd for $C_{34}H_{27}N_2O_3PSPd$ (681.06): C, 59.96; H, 4.00; N, 4.11. Found: C, 59.92; H, 4.17; N, 4.16. MS (FAB): 680.8 (M^+, 6), 603.8 (M^+ − FN, 16), 496.8 (M^+ − FN − Pd, 10) Major isomer: ^{1}H NMR (CD_2Cl_2, 298 K, 400 MHz): 5.61 (t, $^3J_{PH}$ = 9.7, $^3J_{HH}$ = 9.7, OC*H*), 3.28 (dd, $^3J_{HH}$ = 10.3, $^3J_{PH}$ = 5.3, olefin-H), 3.14 (m, CH_2 and SCH_2), 3.05 (dd, $^3J_{PH}$ = 13.6, $^3J_{HH}$ = 10.3, olefin-H), 1.55 (t, $^3J_{HH}$ = 7.3, $^3J_{HH}$ = 7.3, Me). ^{13}C NMR (CD_2Cl_2, 298 K, 400 MHz): 78.3 (d, $^2J_{PC}$ = 7.2, O*C*H), 40.1 (d, $^2J_{PC}$ = 2.5, S*C*H$_2$), 33.4 (d, $^2J_{PC}$ = 3.5, *C*H$_2$), 31.2 (d, $^2J_{PC}$ = 3.9, *C*-1), 28.4 (d, $^2J_{PC}$ = 56.7, *C*-2), 14.6 (s, Me). ^{31}P NMR (CD_2Cl_2, 298 K, 400 MHz): 154.7 (s). Minor isomer: ^{1}H NMR (CD_2Cl_2, 298 K, 400 MHz): 5.65 (t, $^3J_{PH}$ = 9.5, $^3J_{HH}$ = 9.6, OC*H*), 3.34 (dd, $^3J_{HH}$ = 10.2, $^3J_{PH}$ = 5.7, *H*-1), 3.23 (m, CH_2), 3.18 (m, SCH_2), 3.16 (dd, $^3J_{PH}$ = 13.9, $^3J_{HH}$ = 10.3, *H*-2), 1.56 (t, $^3J_{PH}$ = 7.3, $^3J_{HH}$ = 7.2, Me). ^{13}C NMR (CD_2Cl_2, 298 K, 400 MHz): 79.0 (d, $^2J_{PC}$ = 5.8, O*C*H), 39.5 (s, S*C*H$_2$), 33.3 (d, $^2J_{PC}$ = 3.7, *C*H$_2$), 31.6 (d, $^2J_{PC}$ = 4.3, *C*-1), 29.7 (d, $^2J_{PC}$ = 55.9, *C*-2), 14.8 (s, Me). ^{31}P NMR (CD_2Cl_2, 298 K, 400 MHz): 156.4 (s).

Complex 3. Yield: 94 mg, 68%. Anal. Calcd for $C_{34}H_{27}O_6PSPd$ (701.04): C, 58.25; H, 3.88. Found: C, 58.10; H, 4.09. MS (FAB): 604.0 (M^+ − MA, 20), 497.0 (M^+ − MA − Pd, 13). Major isomer: ^{1}H NMR (CD_2Cl_2, 298 K, 400 MHz): 5.64 (t, $^3J_{HH}$ = 10.3, $^3J_{PH}$ = 9.4, OC*H*), 4.25 (dd, $^3J_{PH}$ = 5.5, $^3J_{HH}$ = 4.2, *H*-1), 4.20 (dd, $^3J_{PH}$ = 14.1, $^3J_{HH}$ = 4.2, *H*-2), 3.15 (m, CH_2), 3.10 (m, SCH_2), 1.51 (d, $^3J_{HH}$ = 7.3, $^3J_{HH}$ = 7.3, Me). ^{13}C NMR (CD_2Cl_2, 298 K, 400 MHz): 79.5 (d, $^2J_{PC}$ = 7.8, O*C*H), 53.5 (s, *C*-1), 51.8 (d, $^2J_{CP}$ = 42.4, *C*-2), 39.7 (d, $^3J_{PC}$ = 2.0, S*C*H$_2$), 33.1 (d, $^3J_{PC}$ = 3.2 *C*H$_2$), 15.0 (s, Me). ^{31}P NMR (CD_2Cl_2, 298 K, 400 MHz): 156.4 (s). Minor isomer: ^{1}H NMR (CD_2Cl_2, 298 K, 400 MHz): 5.56 (dt, $^3J_{HH}$ = 10.2, $^3J_{PH}$ = 8.9, $^3J_{HH}$ = 2.0 OC*H*), 4.34 (dd, $^3J_{PH}$ = 6.1, $^3J_{HH}$ = 4.3, *H*-1), 4.11 (dd, $^3J_{PH}$ = 14.3, $^3J_{HH}$ = 4.2, *H*-2), 3.20 (m, SCH_2), 3.07 (m, CH_2), 1.50 (t, $^3J_{HH}$ = 7.4, $^3J_{HH}$ = 7.3, Me). ^{13}C NMR (CD_2Cl_2, 298 K, 400 MHz): 78.5 (d, $^2J_{PC}$ = 5.1, O*C*H), 53.4 (s, *C*-1), 52.8 (d, $^2J_{CP}$ = 42.5, *C*-2), 40.0 (d, $^3J_{PC}$ = 1.8, S*C*H$_2$), 33.2 (d, $^3J_{PC}$ = 4.1, *C*H$_2$), 14.7 (s, Me). ^{31}P NMR (CD_2Cl_2, 298 K, 400 MHz): 156.6 (s).

Complex 4. Yield: 90 mg, 72%. Anal. Calcd for $C_{35}H_{29}O_5PSPd$ (699.06): C, 60.13; H, 4.18. Found: C, 60.26; H, 4.35. MS (FAB): 700.0 (M^+, 22), 602.0 (M^+ − dione, 25), 498.2 (M^+ − dione − Pd, 19). Major isomer: ^{1}H NMR (CD_2Cl_2, 298 K, 400 MHz): 5.56 (br, OC*H*), 4.69 (br, olefin-H), 4.64 (br d, $^3J_{PH}$ = 14.4, olefin-H), 3.15 (br, SCH_2), 3.06 (br, CH_2), 2.70 (d, $^2J_{HH}$ = 20.8, CH_2 of the olefin), 2.29 (d, $^2J_{HH}$ = 20.8, CH_2 of the olefin), 1.49 (t, $^3J_{HH}$ = 7.3, $^3J_{HH}$ = 7.2, Me). ^{13}C NMR (CD_2Cl_2, 298 K, 400 MHz): 79.3 (s, O*C*H), 73.1 (br, *C*-1), 72.9 (br d, $^2J_{PC}$ = 45.5, *C*-2), 46.1 (s, *C*H$_2$ of the olefin), 39.8 (s, S*C*H$_2$), 32.3 (s, *C*H$_2$), 15.0 (s, Me). ^{31}P NMR (CD_2Cl_2, 298 K, 400 MHz): 156.8 (s). Minor isomer: ^{1}H NMR (CD_2Cl_2, 298 K, 400 MHz): 5.55 (br, OC*H*), 4.79 (br, *H*-1), 4.55 (br d, $^3J_{PH}$ = 13.1, *H*-2), 3.14 (br, CH_2), 3.08 (br, SCH_2), 2.85 (d, $^2J_{HH}$ = 20.6, CH_2 of the olefin), 2.41 (d, $^2J_{HH}$ = 20.6, CH_2 of the olefin), 1.50 (Me). ^{13}C NMR (CD_2Cl_2, 298 K, 400 MHz): 78.9 (s, O*C*H), 73.5 (br, *C*-1), 72.8 (br, *C*-2), 46.1 (s, *C*H$_2$ of the olefin), 40.3 (s, S*C*H$_2$), 32.7 (s, *C*H$_2$), 15.5 (s, Me). ^{31}P NMR (CD_2Cl_2, 298 K, 400 MHz): 157.0 (s).

Note on ^2J(P,C) for the Complexed Olefins. In the derivatives **2**−**4**, ^2J(P,C) is fairly large in pseudo-trans position to ^{31}P, ca. 40−60 Hz, but <10 Hz in pseudo-cis. In an earlier study on phosphino−oxazoline olefin complexes of Pd(0)[5] these $^2J(P,C)_{trans}$ values were incorrectly given. The correct values for the major isomers, in Hz, are $^2J_{PC}$ = 46.4 and $^2J_{PC}$ = 42.5 for Pd(**5**)(**2**), $^2J_{PC}$ = 30.7 and $^2J_{PC}$ = 31.6 for Pd(**5**)(**3**), and $^2J_{PC}$ = 29.8 and $^2J_{PC}$ = 29.3 for Pd(**5**)(**4**).

Synthesis [Pd(μ^3-PhCHCHCHR)(1a)]CF_3SO_3, R = Me, 6. A solution of [PdCl(η^3-PhCHCHCHMe)]$_2$ (27.3 mg, 0.05 mmol) and $AgCF_3SO_3$ (25.7 mg, 0.1 mmol) in acetone (2 mL) was stirred for 1 h in the dark at room temperature. The AgCl formed was filtered through Celite and then washed with acetone. Ligand **1a** (47 mg, 0.1 mmol) in CH_2Cl_2 (1 mL) was added to the filtrate with stirring. Stirring was continued for 30 min, and then the resulting solution was concentrated in vacuo. The crude product was recrystallized from CH_2Cl_2/hexane to afford 78 mg (89%) of **6**. Anal. Calcd for $C_{41}H_{36}O_6F_3PS_2Pd$ (883.25): C, 55.75; H, 4.11. Found: C, 55.78; H, 4.31. MS (FAB): 733 (M^+ − OTf, 100). Due to the complexity of the mixture (at least five components) the NMR spectra were not analyzed in detail. The allyl complex with R = H was prepared similarly. Yield: 75 mg, 86%. Anal. Calcd for $C_{40}H_{34}O_6F_3PS_2Pd$ (869.29): C, 55.27; H, 3.94. Found: C, 55.37; H, 4.16. MS (FAB): 720 (M^+ − OTf, 100).

General Procedure for Rh- and Ir-Catalyzed Allylic Alkylation A solution of [M_2(COD)Cl]$_2$ (M = Rh or Ir) (0.005 mmol) and ligand (0.01 mmol) in tetrahydrofuran (0.5 mL) was stirred for 15 min. Allyl acetate (0.25 mmol) was added followed by sodium dimethylmalonate (0.5 mmol) in thf (1.5 mL). The reaction mixture was stirred at reflux and periodically monitored by TLC. The reaction solution was cooled, diluted with ether, washed with water and brine, and then dried with $MgSO_4$. The solvent was evaporated in vacuo, and the residue was purified my column chromatography (5% ethyl acetate in hexane). The product was shown to contain a mixture of isomers. Reaction times, yields, and the ratios of isomers are given in Tables 2 and 3.

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(31) *International Tables for X-ray Crystallography*; Wilson, A. J. C., Ed.; Kluwer Academic Publisher: Dordrecht, The Netherlands, 1992; Vol. C.

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Supporting Information Available: Complete numbering scheme for the ORTEP diagram. Tables with experimental parameters (Table S1), anisotropic temperature factors (Table S2), atomic coordinates and equivalent isotropic temperature factors (Table S3), calculated hydrogen coordinates and isotropic displacement parameters (Table S4), extended list of bond lengths and bond angles for **3** (Table S5), and torsion angles (Table S6). This material is available free of charge via the Internet at http://pubs.acs.org.

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