New Chiral Complexes of Palladium(0) Containing P,S- and P,P-Bidentate Ligands

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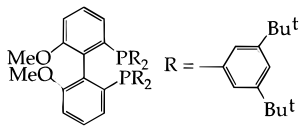
New chiral complexes of Pd(0) containing either the bis(phosphine) (6,6′-dimethoxybiphenyl-2,2′-diyl)bis(3,5-di-*tert*-butylphenylphosphine) (MeO-BIPHEP, **1)** or the phosphine−sulfur chelate (2,3,4,6-tetra-*O*-acetyl-1-{(2-diphenylphosphino)benzyl)thio}-β-D-glucopyranose ((2-$Ph_2PC_6H_4CH_2$)−S−CHCH(OAc)CH(OAc)CH(OAc)CH(CH_2OAc)O, **2**) have been prepared, and the solid-state structure of one of these, Pd(benzoquinone)(**2**), has been determined. These Pd(0) complexes reveal interesting solution dynamics, as shown by 2-dimensional exchange spectroscopy. For the MeO-BIPHEP derivatives, one can obtain useful structural insights based on the observed restricted rotation around the aryl(3,5-di-*tert*-butylphenyl) P−C bonds.

Introduction

Complexes of Pd(0) are often invoked and occasionally directly employed as catalyst precursors in homogeneous Heck,[1] cross-coupling,[2] carbonylation,[3] and allylic alkylation[4] reactions. Monodentate tertiary phosphines, especially PPh_3, together with an olefin or acetylene compound are the most common accompanying ligands for this oxidation state.[5] However, the literature also contains examples of stable compounds containing chelating bis(phosphines)[6] and diimine[7] Pd(0) ligands. Recently, a bidentate P,N-chelate[8] has been shown to afford a stable Pd(0) complex.

A variety of auxiliaries have proven very successful in enantioselective allylic alkylation[9,10] chemistry. In our research on this reaction, we have studied several new palladium complexes containing the ligands **1** and **2**. The 3,5-di-*tert*-butylphenyl compound **1** is a member



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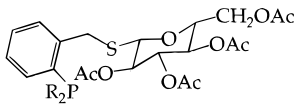
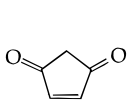


2

of the MeO-BIPHEP class, reported by Schmid and coworkers,[11] whereas we have prepared the sugar−phosphine, **2**, previously.[12] Ligand **2** is interesting in that the chirality does not reside in the P,S-backbone.

Compound **1** is a promising auxiliary in Pd reactions as well as in catalytic hydrogenation chemistry using Ru(II).[11,13] Regrettably, when coordinated, **2** suffers from conformational flexibility in that the six-membered P,S-chelate ring can exist in two forms. Moreover, the sulfur atom, which becomes a stereogenic center upon coordination, can invert readily in solution at ambient temperature.[14] These two factors reduce the effectiveness of **2** in enantioselective catalysis.

We report here on the preparation and characterization of several new Pd(0) complexes based on compounds **1** and **2**. The new chiral complexes, **5**−**9**, (Chart 1), have been prepared using the 1,3-pentenedione, **3**, and benzoquinone, **4**, and/or the classical dibenzylidene acetone (dba) as additional stabilizing ligands. The P,S com-



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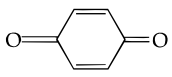

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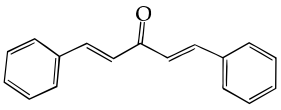

dba

plexes **5** and **6** represent the first examples of isolable well-characterized Pd(0) compounds containing a sulfur donor.

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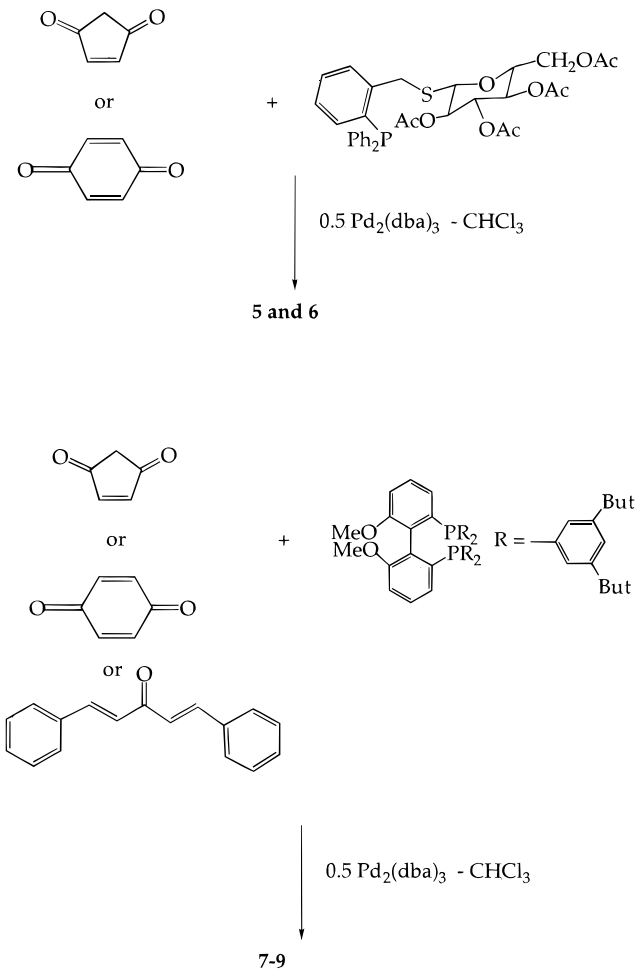
Chart 1. Synthesis of 5−9



Results and Discussion

Preparation of the Complexes. The new complexes were prepared by dissolving the Pd(0) source, usually $Pd_2(dba)_3$ $CHCl_3$, together with the chiral bidentate ligand and then adding the appropriate olefin. This reaction is illustrated in Chart 1, and the numbering systems used for the ligands are shown in Chart 2. The sugar−phosphine derivatives **5** and **6** were obtained in pure form after recrystallization. As these complexes are relatively soluble, the isolated yields were modest, ca 40%; however, in situ NMR measurements show that these reactions with **2** are essentially quantitative. The MeO-BIPHEP complexes, **7**−**9**, were obtained in analytically pure form after column chromatography with yields ranging from 75 to 96%.

X-ray Diffraction Studies. There are still relatively few solid-state structures on MeO-BIPHEP complexes.[11,15−17] Consequently, the structure of the P,S-benzoquinone complex **6** was determined by X-ray diffraction methods, and an ORTEP plot of the molecule is shown in Figure 1a. The immediate coordination sphere consists of the Pd atom and one double bond of the quinone, together with the P and S atoms of **2**.

The metal−phosphine bond length, Pd−P1 2.314(1) Å, falls within the literature range for this type of separation in Pd(0) complexes.[17−21] The 2.354(1) Å

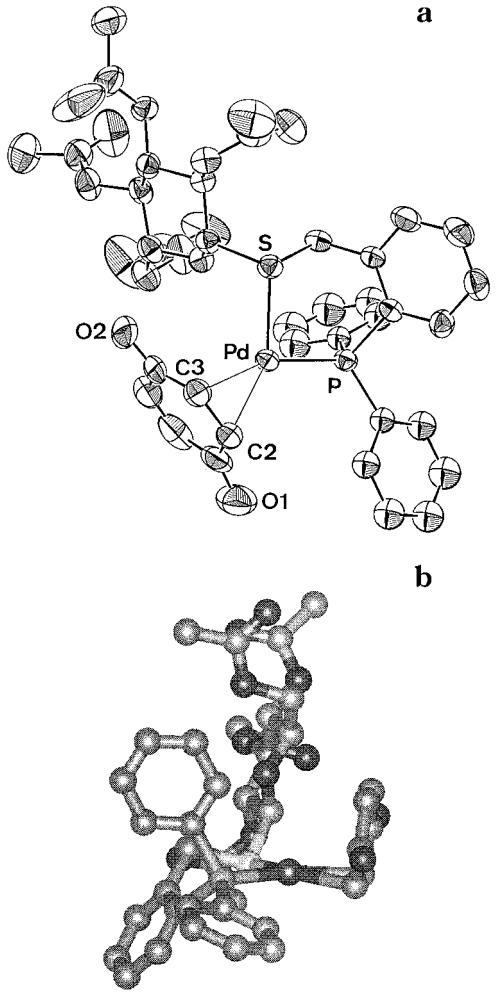


Figure 1. (a) ORTEP plot for **6.** (b) Ball and stick plot showing that one side of the coordination plane is relatively crowded.

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) in 6

Pd1−S1	2.354(1)	P1−C111	1.825(6)
Pd1−P1	2.314(1)	P1−C121	1.820(6)
Pd1−C2	2.138(6)	O1−C1	1.227(9)
Pd1−C3	2.138(5)	O2−C4	1.245(8)
S1−C13	1.828(5)	O3−C14	1.427(7)
S1−C14	1.798(6)	C5−C6	1.33(1)
P1−C7	1.838(5)	C2−C3	1.411(9)
S1−Pd1−P1	93.73(5)	Pd1−S1−C13	106.4(2)
S1−Pd1−C3	107.4(2)	Pd1−S1−C14	106.2(2)
S1−Pd1−C2	145.2(2)	C13−S1−C14	103.4(2)
P1−Pd1−C3	158.4(2)	C4−C3−C2	121.2(7)
P1−Pd1−C2	119.9(2)	C1−C2−C3	120.9(6)
C2−Pd1−C3	38.5(2)		

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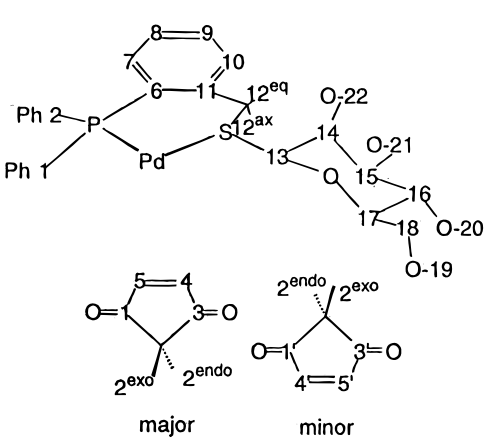
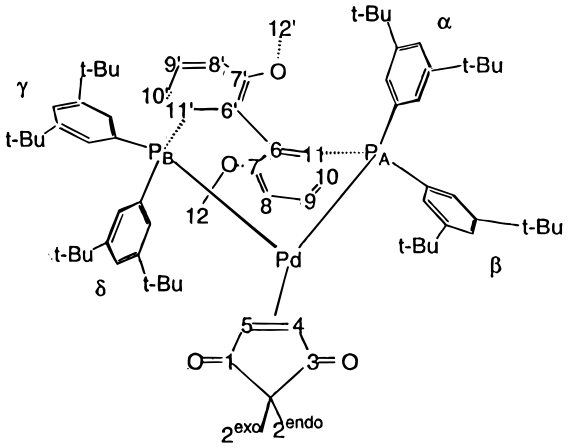
Chart 2. Numbering System



5a 5b



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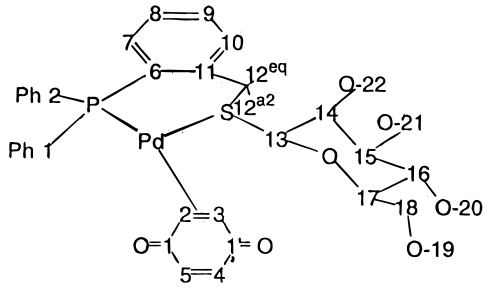
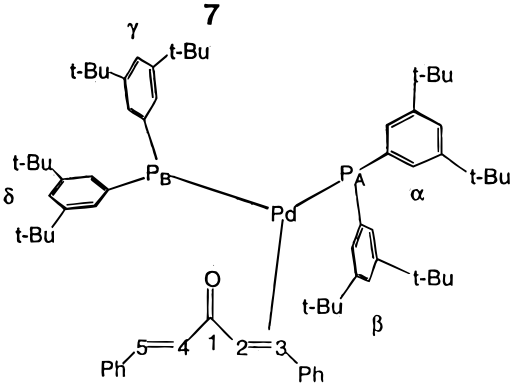


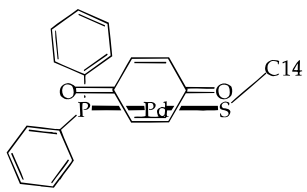
6



8 (BIPHEP same as 7)

distance for Pd−S1 is routine for Pd−S bond lengths in complexes of Pd(II),[22] suggesting no special interaction between the sulfur donor and the zero-valent metal. The two Pd−C bond lengths Pd−C2 and Pd−C3, both at ca. 2.138(6) Å, fall within the normal range. The second double bond of the quinone is remote from the metal (>3.5 Å) and, indeed, tilts away from the palladium atom. There are no unexpected P−C or S−C bond distances, all being ca. 1.8 Å. At 1.411(9) Å, the length of the complexed double bond C2−C3 is, as expected, allowing for some back-bonding from the Pd(0) center to the olefin. The P−Pd−S angle, at 93.73(5)°, is somewhat opened but not unusual. From these seemingly normal data, one obtains the impression that additional Pd(0) complexes with a mixed P,S donor set should be synthetically accessible. A selection of bond lengths and bond angles is given in Table 1 and experimental parameters in Table 2.

Perhaps the most interesting feature of the structure concerns the relative placement of the various organic fragments of the three donors. As suggested by the sketch below, one finds the sugar substituent, the axial P−phenyl, and the remaining six atoms of the benzoquinone, all on one side of the metal atom. This aspect of the structure is illustrated in Figure 1b. This leaves



the sulfur lone pair in a rather open area, in keeping with Gillespie's ideas[23] on electron pair domains. We

Table 2. Experimental Data for the X-ray Diffraction Study of 6

formula	$C_{39}H_{39}O_{11}PPdS$
mol wt	853.18
data collection T, °C	23
cryst syst	monoclinic
space group	$P2_1$ (No. 4)
a, Å	9.1405(5)
b, Å	22.0595(77)
c, Å	10.2021(29)
β, deg	107.64(1)
V, Å^3	1960.4(9)
Z	4
ρ (calcd), g cm^{-3}	1.445
μ, cm^{-1}	6.128
radiation	Mo Kα (graphite monochromated $\lambda = 0.710\ 69$ Å)
θ range, deg	$2.5 < \theta < 27.0$
no. of indep data coll	4086
no. of obs reflns (n_o)	3170 ($\|F_o\| > 3.0\sigma(\|F\|)$)
transmission coeff	0.9998−0.9521
R^a	0.029
$R_w{}^a$	0.038
GOF	1.171

[a] $R = \Sigma(|F_o - (1/k)F_c|)/\Sigma|F_o|$; $R_w = [\Sigma_w(F_o - (1/k)F_c)^2/\Sigma_w|F_o|^2]^{1/2}$; where $w = [\sigma^2(F_o)]^{-1}$; $\sigma(F_o) = [\sigma^2(F_o^2) + f^4(F_o^2)]^{1/2}/2F_o$ and $f = 0.050$.

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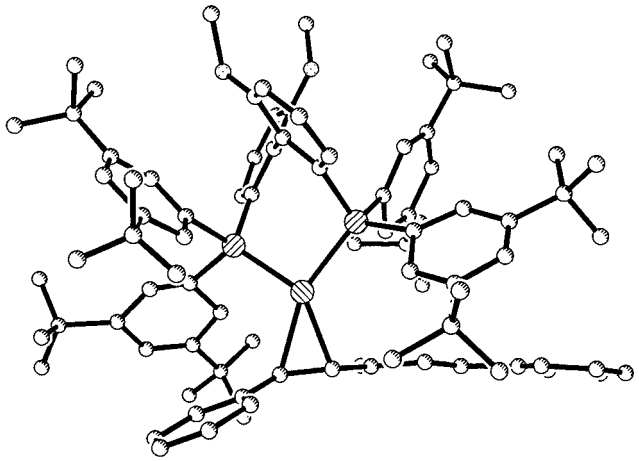
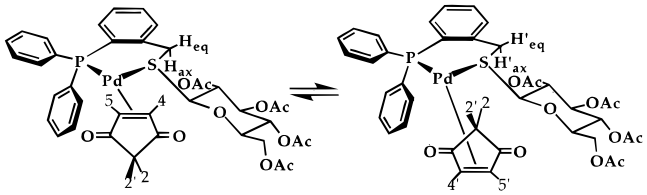


Figure 2. Structure of **8**.

have noted previously[10,24] that in P,S-chelate complexes there is a tendency to have pseudoaxial substituents on sulfur, thus leaving the sulfur lone pair in a relatively open area of the structure.

We have also grown crystals of Pd(dba)(**1**), **8**, and collected data for this complex. Unfortunately, the crystal was of poor quality; however, the structure is, as expected, the immediate coordination sphere consisting of the metal, two P-donors, and one double bond of the dba (Figure 2), although the data do not warrant a detailed analysis.[25]

NMR Studies. The Pd(0) P,S complexes, **5** and **6**, each reveal interesting dynamics in solution. Complex **5** exists in two isomeric forms **5a,b** in a ratio of 3.2:1.



5a **5b**

The relative position of the sugar moiety is not determined.

All the proton resonances in **5** are relatively sharp. Nevertheless, two-dimensional exchange spectroscopy[26,27] (Figure 3), shows that there is slow intramolecular exchange. The exchange spectrum shows that the olefinic protons pseudotrans to the P donors exchange *selectively* with the olefinic protons pseudotrans to the S donors in the corresponding isomer. This is consistent

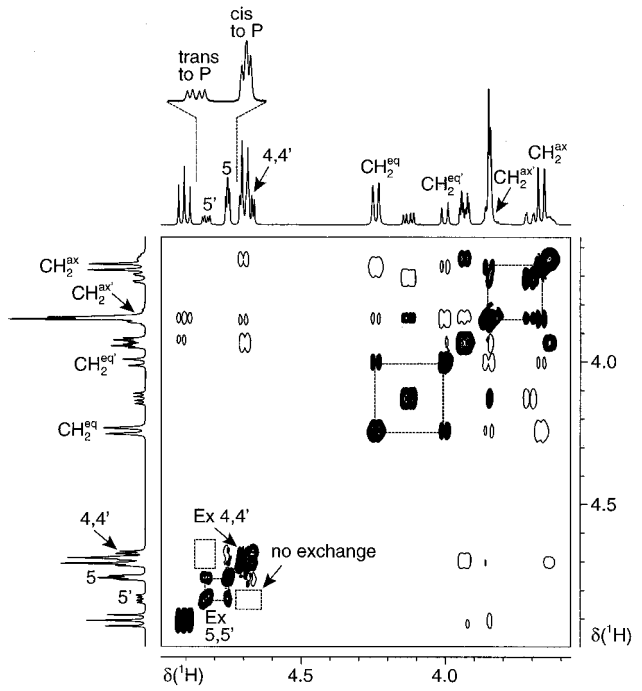


Figure 3. Section of the NOESY spectrum of **5** revealing the selective exchange (lower left corner) of the olefinic protons of the dione in **5** (500 MHz, CD_2Cl_2).

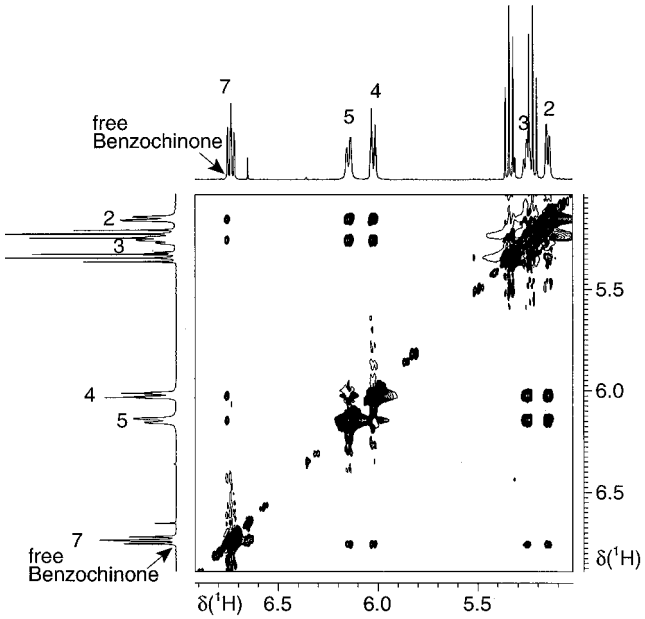


Figure 4. Section of the NOESY spectrum of **6** revealing the random exchange of the olefinic protons of the benzoquinone (500 MHz, CD_2Cl_2).

with a rotation of coordinated **3** without dissociation. The protons of the dione in both isomers are readily assigned using $^{13}C,^{1}H$-correlation characteristics together with $J(^{31}P,^{1}H)$ values (trans > cis, see top-left of Figure 3) and a $^{31}P,^{1}H$ 2-dimensional correlation.

Complex **6** shows only one ^{31}P signal. All four olefinic benzoquinone ^{13}C signals for **6** are quite broad, whereas the analogous proton signals are only slightly broadened. However, it is clear from the exchange spectrum (Figure 4) that the benzoquinone in **6** dissociates and then recombines. This conclusion is based on the presence of exchange cross peaks stemming from traces of free **4** (not visible in the conventional 1-dimensional spectrum), as well as the observed *lack* of selectivity in

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Table 3. NMR Data for the Isomers of Pd(1,3-cyclopent-4-enedione)(2), 5[a]

5a (major)			**5b** (minor)		
	^{1}H	^{13}C		^{1}H	^{13}C
1	(C=O, trans to S)	200.9	1′	(C=O, trans to S)	201.2
2^{endo}	2.97	46.5	2′ ^{endo}	2.97	46.1
2^{exo}	2.46	46.5	2′ ^{exo}	2.42	46.1
3	(C=O, trans to P)	199.9	3′	(C=O, trans to P)	199.9
4	4.71	80.6	4′	4.70	
5	4.76	72.2	5′	4.83	
o-1	7.43		*o*-1′	7.44	
m-1			*m*-1	7.46	
o-2	7.27		o-2′	7.42	
m-2	7.35				
7	6.67	132.9	7′	6.73	132.9
8	7.29		8′	7.30	
10	7.45		10′	7.33	
12^{ax}	3.67	33.5	12$^{ax′}$	4.00	38.7
12^{eq}	4.24	33.5	12$^{eq′}$	3.84	38.7
13	4.70	81.6	13′	4.69	
14	5.22	68.0	14′	5.43	69.0
15	5.33	73.3	15′	4.70	73.5
16	4.91		16′	5.27	
17	3.93		17′	3.63	
18	3.84	33.5			
18	3.99	33.5			

^{31}P, **5a** 18.2 ppm
^{31}P, **5b** 17.6 ppm

[a] CD_2Cl_2, AMX 500, ambient temperature; *o* = *ortho*, *m* = *meta*.

Table 4. Selected ^{1}H NMR Data[a] for Pd(benzoquinone)(2), 6

2	5.15	12^{eq}	4.22
3	5.26	12^{ax}	3.62
4	6.02	13	4.56
5	6.15	14	5.23
7	6.73	15	5.35
8	7.30	16	5.00
9	7.43	17	3.93
10	7.42	18	4.12
		18′	3.87

^{31}P 24.9 ppm

[a] CD_2Cl_2, AMX 500, ambient temperature. [b] Ph *o*-1, 7.37; Ph *m*-1, 7.46; Ph *o*-2, 7.37.

the exchange between the four olefinic benzoquinone protons, i.e., all four are exchanging with each other and the free benzoquinone. Again, the various coordinated olefinic protons are recognized using their $^3J(^{31}P,^1H)$ values, the consequent differing multiplicities, and a ^{31}P,^{1}H 2-dimensional correlation. We have no satisfactory explanation for this change of mechanism relative to **5** . We do note that **4** is slightly larger than **3** and that in the solid-state structure of **6** (discussed above), one finds a large number of atoms on one side of the coordination plane placed fairly close together.

The most pertinent NMR results for **5** and **6** are given in Tables 3 and 4. From an analysis of the NOESY spectra for both **5** and **6** it seems that the six-membered chelate ring conformation is fixed; however, extensive overlap in the aromatic region prevents a decision as to the relative position of the stereogenic *S* center.

The chiral Pd(0) MeO-BIPHEP complexes **7** and **8** exist as single isomers in solution and give simple AX (or AB) type ^{31}P spectra. We have previously noted[28] that coordinated **1** is somewhat unusual in that it often shows restricted rotation about the P−C bonds associated with the 3,5-di-*tert*-butyl aryl groups at ambient

(28) Currao, A.; Feiken, N.; Macchioni, A.; Nesper, R.; Pregosin, P. S.; Trabesinger, G. *Helv. Chim. Acta* **1996**, *79*, 1587.

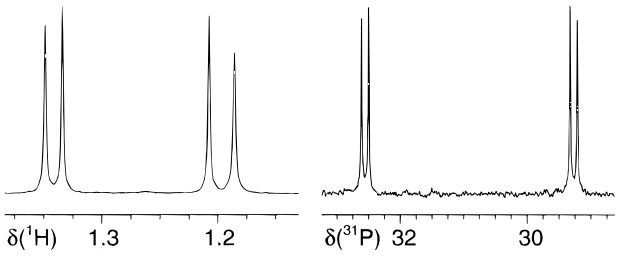


Figure 5. ^{1}H *tert*-butyl region (left) and ^{31}P spectrum of **7** (right).

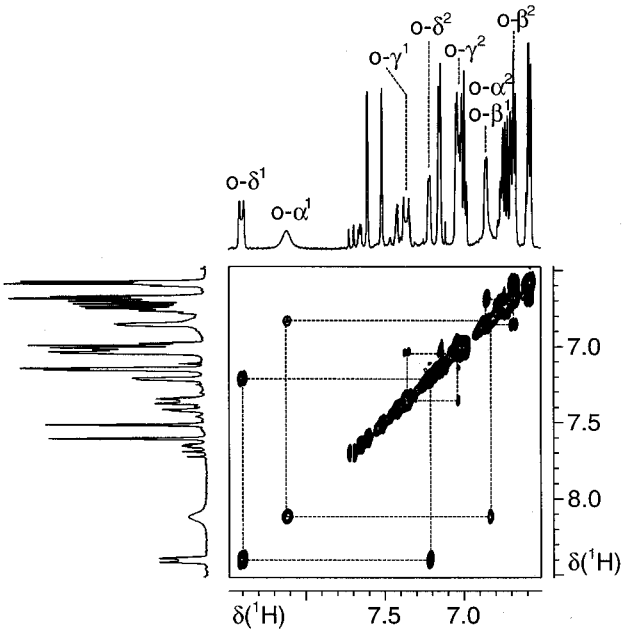
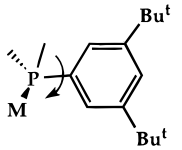


Figure 6. Section of the ROESY spectrum of **8** revealing the four pairs of exchanging *ortho* protons. The lines indicate these four selective processes (243 K, 500 MHz, CD_2Cl_2**)**.

temperature. For **7**, with its relatively small 1,3-



M = Pd, Ru

pentenedione, we observe free rotation around these P−C bonds, as demonstrated by the appearance of the *tert*-butyl region (Figure 5). One finds four nonequivalent rings each with two equivalent *tert*-butyl resonances.[29]

However, for the dba complex, **8**, at ambient temperature, one observes a larger number of aromatic and *tert*-butyl signals due to this restricted rotation. The ROESY spectrum for **8** at 243 K (Figure 6) shows the eight nonequivalent *ortho* ring protons which undergo the expected four selective exchange processes as the rings slowly rotate (we choose to show these resonances

(29) Close inspection of the aromatic region of **7** reveals two broad signals, with very similar chemical shifts. One of these broad signals lies almost completely under a different sharp resonance. We assign these broad resonances to two nonequivalent *ortho* protons of one P−aryl ring, so that one of the four rings is indeed, exhibiting restricted rotation. Nevertheless, the rotational barriers for **7** are smaller than those for **8**.

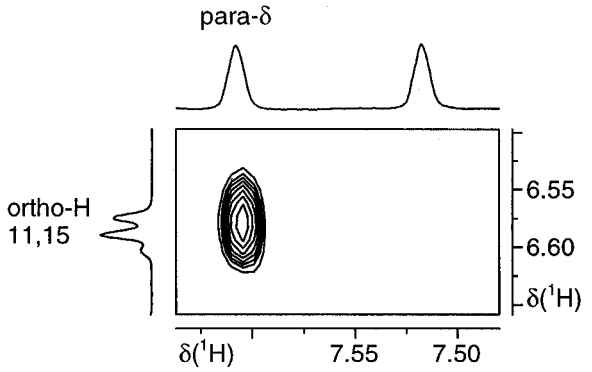


Figure 7. Section of the NOESY spectrum of **8** revealing the NOE from the *ortho* proton of the dba ring to the *para* proton of the δ ring (243 K, 500 MHz, CD_2Cl_2).

Table 5. Selected NMR Data[a] for 7 and 8[a]

7			8		
	^{1}H	^{13}C		^{1}H	^{13}C
2^{endo}	2.89	46.4	2	5.03	72.4
2^{exo}	2.22	46.4			
			3	4.40	67.6
4	4.30	73.0	4	6.20	124.3
5	4.76	70.1	5	7.04 (ca.)	
8	6.32	111.7	8	6.20	112.6
9	6.76	128.2			
10	6.46	123.7	10	6.75	
12	3.38	56.4	12	3.38	57.5
8′	6.32	112.8	8′	6.07	111.1
9′	6.85	128.2	9′	6.72	
10′	6.66	123.3	10′	6.08	123.4
12′	3.50	56.3	12′	3.23	56.5
o-α	7.59		*o*-α	8.12, 6.88	132.9
			p-α	7.52	
t-α	1.34		*t*-α	1.16, 1.57	
o-*β*	7.11		*o*-*β*	6.88, 6.68	131.3
p-*β*	7.33		*p*-*β*	7.15	126.3
t-*β*	1.21		*t*-*β*	1.15, 0.95	31.6, 30.8
o-*γ*	7.29		*o*-*γ*	7.36, 7.06	128.9
p-*γ*	7.24		*p*-*γ*	7.16	125.1
t-*γ*	1.19		*t*-*γ*	1.22, 1.19	31.5, 31.6
o-*δ*	7.42		*o*-*δ*	8.41, 7.22	132.5, 126.3
p-*δ*	7.51		*p*-*δ*	7.61	132.2
t-*δ*	1.35		*t*-*δ*	1.60, 1.01	31.8, 31.4

[a] CD_2Cl_2, DRX 400, ambient temperature; *t* = *tert*-butyl resonance. See Chart 2 for α, *β*, *δ*, and *γ* rings. $P_A = 29.3$ ppm, $^2J(P-P) = 18.3$ Hz; $P_B = 32.6$ ppm.

as opposed to the *tert*-butyl signals as there is less overlap). Once again,[28,30,31] the highest barriers to rotation are associated with the pseudoaxial P−aryl groups, with the full sequence being $\alpha < \delta < \beta < \gamma$. Coordination of a larger ligand, such as dba, compresses the BIPHEP framework, with the squeeze most pronounced between the two pseudoaxial rings and the biphenyl moiety. Not surprisingly, the pseudoequatorial BIPHEP ring, *δ*, closest to the uncoordinated double bond of dba, is more hindered than its α counterpart (see fragment above). In support of this, we note the unexpected NOE between the *para* proton of the *δ*-ring and the *ortho* protons of one dba ring (Figure 7), thus confirming that these molecular fragments are in close contact. Table 5 contains a summary of the NMR parameters for **7** and **8**.

We have previously shown[28,30] in bis(3,5-di-*tert*-butyl) Pd(allyl)(MeO-BIPHEP)$^+$ and RuH(arene)(MeO-BIPHEP)$^+$ type complexes that this restricted rotation around the P−C bonds effectively produces a more rigid chiral pocket. Further, we have suggested that this increased rigidity is associated with improved enantioselectivity in several catalytic reactions where the substrate has substantial bulk.[31] We consider that our observations for **8** represent additional support for this conclusion.

Although Pd(benzoquinone)(**1**), **9**, was readily prepared (Experimental Section), it was not sufficiently stable in solution for the length of time necessary to make the kinds of detailed studies described above.

In summary (a) one can prepare and isolate new chiral complexes of Pd(0) containing a chelating phosphine−sulfur donor, together with an olefin, (b) these complexes have interesting dynamics, e.g., olefin dissociation or olefin rotation, and (c) the bis(3,5-di-*tert*-butyl) MeO-BIPHEP Pd(0) complexes show hindered rotation around the aryl P−C bonds, in keeping with previous observations.

Experimental Section

General Considerations. The *R*(+) and *S*(−) MeO-BIPHEP compounds were provided by F. Hoffmann-La Roche AG, Basel. (2,3,4,6-tetra-*O*-acetyl-1-{(2-diphenylphosphino)-benzyl)thio}-*β*-D-glucopyranose, (2-$Ph_2PC_6H_4CH_2$)−S−CH-CH(OAc)CH(OAc)CH(OAc)CH(CH_2OAc)O, **2**, was prepared as described by us previously.[10] All reactions were performed in an atmosphere of Ar using standard Schlenk techniques. Dry and oxygen-free solvents were used. Routine ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded with Bruker DPX-250 and 300 MHz spectrometers unless otherwise specified. Chemical shifts are given in parts per million (ppm), and coupling constants (*J*) are given in Hertz. The 2-dimensional studies were carried out at 500 MHz for ^{1}H NMR studies. NOESY and ^{31}P,^{1}H-correlation experiments measurements were carried out as reported previously.[27,28] The ROESY spectra for **8** (500 MHz, CD_2Cl_2, 243 K), were obtained with a 0.4 s spin lock. The carrier frequency was set in the middle of the proton spectrum. IR spectra were recorded with a Perkin-Elmer 882 infrared spectrophotometer. Elemental analyses and mass spectroscopic studies were performed at ETHZ.

Crystallography. A suitable crystal was mounted on a glass fiber on a CAD4 diffractometer that was used for the space group determination and for the data collection. Unit cell dimensions were obtained by a least-squares fit of the 2*θ* values of 25 high-order reflections ($9.5 \le \theta \le 15.4°$). Selected crystallographic and other relevant data are listed in Table 2 and Supporting Information.

Data were measured with variable scan speed to ensure constant statistical precision on the collected intensities. Three standard reflections were used to check the stability of the crystal and of the experimental conditions and measured every 90 min; no significant variation was detected. Data were corrected for Lorentz and polarization factors using the data reduction programs of the MOLEN crystallographic package.[32] An empirical absorption correction was also applied (azimuthal (Ψ) scans of three reflections having $\chi > 85°$).[33] The standard deviations on intensities were calculated in terms of statistics alone, while those on F_o were calculated as shown in Table 2.

The structure was solved by a combination of direct and Fourier methods and refined by full-matrix least squares.

(30) Feiken, N.; Pregosin, P. S.; Trabesinger, G.; Scalone, M. *Organometallics* **1997**, *16*, 537.
(31) Trabesinger, G.; Albinati, A.; Feiken, N.; Kunz, R.; Pregosin, P. S.; Tschoerner, M. *J. Am. Chem. Soc.* 1997, submitted for publication.
(32) *MOLEN*, Enraf-Nonius Structure Determination Package; Enraf-Nonius: Delft, The Netherlands, 1990.
(33) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A* **1968**, *24*, 351.

Anisotropic displacement parameters were used for all atoms, except for the carbon atoms of the phenyl rings. The contribution of the hydrogen atoms in their calculated positions (C−H = 0.95 Å, $B_{iso}(H) = 1.3 \times B_{eq}(C_{bonded})$ Å^2) was taken into account but not refined. As can be expected, the terminal acetate substituents are undergoing large amplitude motion.

The function minimized was: $[\sum w(|F_o| - 1/k|F_c|)^2])$ with $w = [\sigma^2(F_o)]^{-1}$. No extinction correction was deemed necessary. The scattering factors used, corrected for the real and imaginary parts of the anomalous dispersion, were taken from the literature.[34] The handedness of the structure was tested by refining both enantiomorphs; the coordinates giving the significantly[35] lower R_w factor were used. Upon convergence, the final Fourier difference map showed no significant peaks. All calculations were carried out by using the Enraf-Nonius MOLEN crystallographic programs.[32]

Pd(4-cyclopentene-1,3-dione)(2), 5. Ligand **2**, (64 mg, 100 μmol) and $Pd_2(dba)_3$·$CHCl_3$ (52 mg, 50 μmol) were suspended in ca. 1 mL of acetone. The brown-violet suspension slowly dissolves to give an orange solution (ca. 120 min). 4-Cyclopentene-1,3-dione, **3**, (10 mg, 104 μmol) was added with stirring. The orange solution changes color within 60 min to bright yellow. After 24 h of stirring, the solution was filtered through Celite and evaporated to dryness. The residue was washed with ether (2 × 1 mL). Recrystallization from acetone/hexane gave 33 mg (39%) of yellow crystals. Anal. Calcd for $C_{38}H_{39}O_{11}PSPd$ (841.2): C, 54.26; H, 4.67. Found: C, 54.21; H, 4.53. Mp: 149 °C. FAB-MS: *m/e* 841 (M + 1), 744 (M + 1 − $C_5H_4O_2$), 413 (M + 1 − ($C_5H_4O_2$ + glucopyranosetetraacetate)). IR (KBr pellet): $\nu_{C=O}$ 1753 (vs), 1690 (vs), 1673 (s), 1644 (vs). ^{31}P NMR (CD_2Cl_2) δ: 18.8 (77% isomer **5a**), 18.3 (23% isomer **5b**).

Pd(benzoquinone)(2), 6. Ligand **2,** (32.2 mg, 50.4 μmol) and $Pd_2(dba)_3$·$CHCl_3$ (25.9 mg, 25 μmol) were suspended in ca. 1 mL of acetone. The brown-violet suspension slowly dissolves to give an orange solution (ca. 60 min). Benzoquinone (6.5 mg, 1.2 equiv) was added to the solution. The color changes to red-orange, and stirring was continued for 24 h. The solution was filtered through Celite and taken to dryness. The residue was washed with ether (3 times), redissolved in acetone, filtered, and reduced to a small volume. Addition of pentane gave red-orange crystals, which were collected by filtration. Yield: 17.5 mg (41.0%). Anal. Calcd for $C_{39}H_{39}O_{11}PSPd$ (853.2): C, 54.9; H, 4.61. Found: C, 54.7; H, 4.67. FAB-MS: *m/e* 853 (M + 1), 744 (M + 1 − $C_6H_4O_2$), 413 (M + 1 − ($C_6H_4O_2$ + glucopyranosetetraacetate)). IR (KBr pellet): $\nu_{C=O}$ 1752 (vs), 1737 (vs), 1632 (s), 1612 (vs), 1574 (s). ^{31}P NMR (CD_2Cl_2) δ: 23.6.

Pd(4-cyclopentene-1,3-dione)(1), 7. (*R*)(+)-**1** (51.7 mg, 50 μmol) was added to a stirrred suspension of $Pd(dba)_2$ (28.7 mg, 25 μmol) in 2 mL of CH_2Cl_2. The deep violet suspension dissolves during 20 h of stirring to afford a brown-orange solution. Addition of **3** (30 mg, 0.31 mmol) induces a slow color change to yellow over 18 h. Filtration and evaporation to dryness gave a yellow powder. This crude product was purified by column chromatography using 18 g of silica gel in a 10 mm column and pentane/ether 1/1 to 2/1 as eluent (R_f = 0.4). Evaporation of the eluent gave 59 mg (95.6%) of the pure complex as a yellow solid. Anal. Calcd for $C_{75}H_{100}O_4P_2Pd$ (1233.98): C, 73.00; H, 8.17. Found: C, 72.8; H, 7.97. Mp: 250−252 °C (dec). FAB-MS: *m/e* 1234 (M + 1), 1137 (M − $C_5H_4O_2$). ^{31}P NMR (CD_2Cl_2) δ: 29.3 (d, J = 18 Hz), 32.6 (d, J = 18 Hz). ^{1}H-NMR (CD_2Cl_2) δ: 1.18 (s, 18H), 1.21 (s, 18H), 1.34 (s, 18H), 1.35 (s, 18H), 2.22 (d, J = 20.4 Hz, 1H), 2.87 (d, J = 20.4 Hz, 1H), 3.37 (s, 3H), 3.49 (s, 3H), 4.30 (m, 1H), 4.76 (m, 1H), 6.32 (m, 2H^{ar}), 6.46 (m, 1H^{ar}), 6.66 (m, 1H^{ar}), 6.75 (m, 1H^{ar}), 6.85 (m, 1H^{ar}), 7.1 (m, 2H^{ar}), 7.2−7.4. (m, 4H^{ar}), 7.44 (m, 2H^{ar}), 7.51 (m, 2H^{ar}), 7.64−7.67 (m, 2H^{ar}). IR (CsI pellet): $\nu_{C=O}$ 1708 (s), 1694 (s), 1674 (vs), 1648 (s).

This complex can also be prepared from the usual $Pd_2(dba)_3$·$CHCl_3$.

Pd(dba)(1), 8. $Pd_2(dba)_3$·$CHCl_3$ (51.7 mg, 50 μmol) and (*S*)-(−) **1** (103.1 mg, 100 μmol) were placed in a Schlenk flask. Upon addition of 5 mL of THF, the dark violet suspension dissolves to give a brown-orange solution, which was stirred at 40 °C for 3 h. Filtration of the resulting reaction mixture was followed by removal of the solvent to afford the crude product as a dark orange solid. Purification via column chromatography on 20 g of silica gel using pentane/ether 8.5/1.5 as eluent led to 102 mg (74.7%) of analytically pure complex. Anal. Calcd. for $C_{87}H_{110}O_3P_2Pd$ (1372.19): C, 76.15; H, 7.84. Found: C, 76.21; H, 7.84. FAB-MS: *m/e* 1372 (M + 1), 1137 (M − dba). IR (KBr pellet): $\nu_{C=O}$ 1637 (m).

Pd(benzoquinone)(1), 9. $Pd_2(dba)_3$·$CHCl_3$ (36 mg, 34.8 μmol) and (*S*)-**1** (71.7 mg, 69.6 μmol) were suspended in 2 mL of CH_2Cl_2 and stirred for 16 h. **4** (45 mg, 6 equiv) was then added to the resulting orange-brown solution. A red-orange solution was formed within ca. 2 h and then stirred for an additional 18 h. Workup by filtration and evaporation to dryness followed by column chromatography using 14 g of silica gel gave the pure compound. The complex was obtained as orange-red solid by evaporation of the pentane/ether 2/1 eluent (R_f = 0.45). Yield: 68 mg (78.4%). Mp: 180 °C (dec). The ligands dba and excess benzoquinone were eluted with CH_2Cl_2. Anal. Calcd for $C_{76}H_{100}O_4P_2Pd$ (1245.99): C, 73.26; H, 8.09. Found: C, 73.5; H, 8.24. FAB-MS: *m/e* 1246 (M + 1), 1137 (M − $C_6H_4O_2$). ^{31}P NMR (CD_2Cl_2) δ: 34.8. IR (CsI pellet): $\nu_{C=O}$ 1623 (vs).

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Supporting Information Available: Tables of bond lengths, bond angles, torsion angles, final positional parameters, and anisotropic displacement parameters and an ORTEP plot with a full numbering scheme (10 pages). Ordering information is given on any current masthead page.

OM970185R

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