Biphosphole: A C_2 Symmetry Chiral Bidentate Ligand. Synthesis and Characterization Of Nickel, Palladium, Platinum, and Rhodium Complexes

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Owing to the C_2 symmetry structure of 1,1′-diphenyl-3,3′,4,4′-tetramethyl-2,2′-biphosphole, **1** (BIPHOS), we investigated the coordination of this chiral bidentate ligand to transition metals in order to explore the potential of these complexes in asymmetric catalysis. Nickel, palladium, and platinum complexes $[M(BIPHOS)X_2]$ (**2** (M = Ni, X = Br), **3** (M = Pd, X = Cl), **4** (M = Pt, X = Cl) were synthesized and fully characterized. Their structures were determined by X-ray crystallography. The cationic palladium complexes $[Pd(BIPHOS)(CH_3CN)_2](BF_4)_2$, **6**, and $[Pd(BIPHOS)(\eta_3\text{-}C_3H_5)]Cl$, **7**, were also synthesized. The π-allyl−palladium complex **7** reveals a potential interest for catalytic allylic substitution. The reaction of **1** with $[Pd(CH_3CN)_4](BF_4)_2$ leads to the formation of the meso diastereoisomer $[Pd(BIPHOS)_2]$ $(BF_4)_2$, **5**, which was fully characterized. Its structure was determined by X-ray crystallography. A bis(BIPHOS) complex of Rh(I), **8**, was also obtained by reaction of **1** with $[Rh(COD)Cl]_2$ or $[Rh(COD)_2]BF_4$.

Introduction

There is increasing interest in enantioselective transition metal-catalyzed reactions.[1] In this field, C_2 symmetry diphosphines[2] are powerful chiral auxiliaries. Focussing our investigations on chiral bidentate ligands and their use in enantioselective synthesis, we were interested by the possibilities offered by the 1,1′-diphenyl-3,3′,4,4′-tetramethyl-2,2′-biphosphole (BIPHOS) first synthesized by F. Mathey in 1986.[3] The coordination chemistry of monophospholes has been extensively studied,[4] and the application of these ligands in homogenous catalysis has been investigated.[5] In particular, it was shown that hydrogenation and hydroformylation of various unsaturated substrates[5c−f] are catalyzed by rhodium−phosphole complexes. In contrast, little work has been done on the 2,2′-biphosphole. The first reported biphosphole complexes $[Mo(BIPHOS)(CO)_4]$ and $[Mn_2(BIPHOS)(CO)_8]$ were isolated by F. Mathey *et al.*,[3] but no information about their structures was obtained. Recently, we have reported[6] the characterization of the diastereoisomers of this diphosphine, in which the axial chirality resulting from a dihedral angle between the two phosphole rings combines with the central chirality of the phosphorus atoms. The aim of this work was to explore the ability of the BIPHOS ligand to coordinate to transition metal atoms and the potential of the corresponding complexes in asymmetric catalysis. We report here the synthesis, X-ray structural characterization of various BIPHOS complexes, and preliminary results concerning the use of this ligand in catalytic reactions.

Results and Discussion

Stereochemical Analysis of the Biphosphole. We have previously reported[6] that in solution at room temperature, 1,1′-diphenyl-3,3′,4,4′-tetramethyl-2,2′-biphosphole, **1**, exists as a mixture of stereoisomers **1a** and **1b** in a 88/12 ratio, as evidenced by ^1H, ^{31}P, and ^{13}C NMR data analysis (Tables 1 and 2). Stereochemical analysis and structural characterizations of these stereoisomers have been investigated. The 2,2′-biphosphole **1** is a particular diphosphine which presents axial chirality generated by the biphosphole framework and central chirality due to phosphorus atoms. The different possibilities of combining axial and central chiralities in BIPHOS are depicted in Figure 1 with a Newman projection along the C−C axis of the bond linking the phosphole rings. This stereochemical analysis shows the existence of six stereoisomers corresponding to three pairs of enantiomers. The structure of the minor stereoisomer **1b** was established by X-ray diffraction studies of the disulfide.[6] In **1b**, the two phosphorus atoms have opposite absolute configuration, and this corresponds to the pair of enantiomers $[\mathbf{1b}]^{S}_{RS}$ + $[\mathbf{1b}]^{R}_{SR}$ (the subscripts correspond to the central chirality of phosphorus and the superscripts to the axial chirality). In **1a**, both phosphorus atoms have the same absolute configuration, and these stereoisomers could exist in solution either as $[\mathbf{1a}]^{S}_{RR}$ + $[\mathbf{1a}]^{R}_{SS}$ form or as

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Table 1. $^{31}P\{^1H\}$ and ^1H NMR (CD_2Cl_2) Spectral Data for Biphosphole Derivatives

	$\delta(^{31}P)$	$\delta(^1H)^a$			
		Me_{21}	Me_{31}	H_4	Ph
1a	17.69	1.87 (s)	2.10 (d, 1.08)^b	6.45 (m, 35.00, 5.00)^c	7.2−7.35
1b	7.07	1.83 (t, 2.50)^c	2.11 (d, 1.10)^b	6.38 (d, 40.00)^c	7.01−7.21
2	46.20	1.77 (s)	2.10 (s)	6.57 (b)	7.47−8.11
3	33.40	1.87 (d, 2.96)^c	2.14 (s, 1.56)^b	6.63 (pdd, 35.00, −3.00)^c	7.40−7.87
4	23.49^d	1.82 (d, 3.75)^c	2.17 (d, 1.56)^b	6.67 (d, 32.00)^c	7.38−7.81
5	33.82	1.79 (s)	2.36 (s)	7.55 (b)	6.95−7.20
8a	46.52^e	1.91 (s)	2.09 (s)	6.35 (b)	7.14−7.36

[a] Biphospholes and complexed biphospholes have the same numbering, referring to X-ray structures. Abbreviations: b, broad; d, doublet; m, multiplet; p, pseudo; t, triplet; s, singlet. [b] J_{HH}. [c] J_{HP}. [d] $^1J_{PPt} = 3409$ Hz, $\delta^{195}Pt = -4357.34$. [e] $^1J_{PRh} = 112.8$ Hz, $\delta^{103}Rh = -731$.

Table 2. $^{13}C\ \{^1H,^{31}P\}$ NMR Data (CD_2Cl_2) of Complexes 3, 4, and 8a, As Compared to 1a^a

	$C_1, C_{1'}$	$C_2, C_{2'}$	$C_3, C_{3'}$	$C_4, C_{4'}$	$C_{21}, C_{21'}$	$C_{31}, C_{31'}$	$C_{111}, C_{111'}$	$C_{112}, C_{112'}$	$C_{113}, C_{113'}$	$C_{114}, C_{114'}$
1a	142.17	140.54	150.10	128.20	14.59	17.64	131.76	132.73	127.63	128.27
3	132.37	147.46	157.90	120.15	14.56	17.70	124.06	132.72	128.48	131.47
4	132.60^b	146.52^c	158.11^d	119.55^e	14.63	17.80	123.89	132.62	128.28	131.36
8a	138.51	147.59	158.37	127.00	17.31	20.09	n.o.	134.95	130.67	132.75

[a] Biphosphole and complexed biphospholes have the same numbering, referring to X-ray structures. Abbreviations: n.o., not observed. [b] $J_{CPt} = 29$ Hz. [c] $J_{CPt} = 26$ Hz. [d] $J_{CPt} = 40$ Hz. [e] $J_{CP} = 18$ Hz.

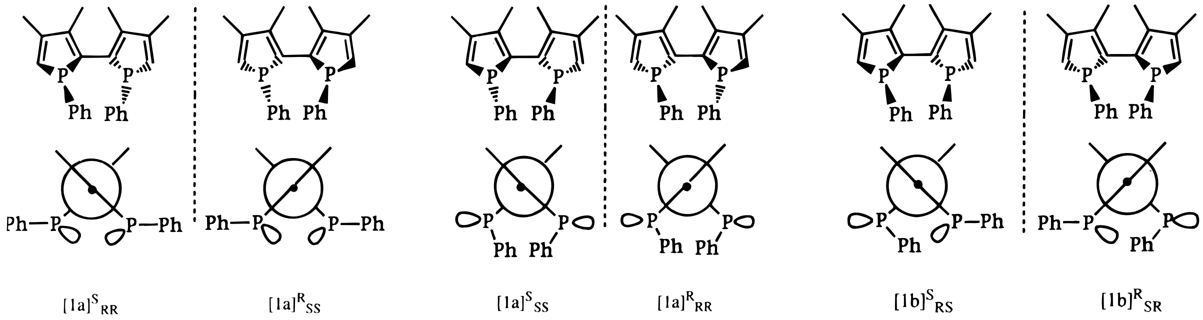
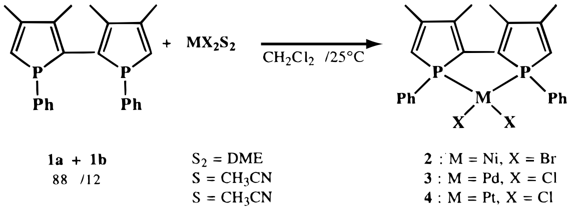


Figure 1. Scheme showing the different stereoisomers. The projection is along the axis of the C−C bond linking the phosphole rings. Superscript refers to axial chirality and subscript to central chirality.

[**1a**]$^R_{RR}$ + [**1a**]$^S_{SS}$ form or as a mixture of these two pairs of enantiomers interconverting rapidly on the NMR time scale, even at low temperature (−70 °C), by rotation around the C−C bridge bond and giving only one sharp ^{31}P resonance ($\delta = 15.7$). In the solid state, the disulfides of **1a** have been identified by X-ray diffraction analysis as the pair of enantiomers [**1a**]$^S_{RR}$ + [**1a**]$^R_{SS}$.[6] Surprisingly, **1a** has been spontaneously resolved by crystallization, and the determined structure corresponds to the enantiomer [**1a**]$^S_{RR}$. In addition, we have studied[6] the kinetics of the **1b** → **1a** isomerization by ^{31}P NMR at low temperature. The free enthalpy of activation, $\Delta G^\ddagger = 16.5$ kcal/mol, corresponds to the inversion barrier for the pyramidal phosphorus center. This low barrier due to extensive electronic delocalization within the planar transition state is comparable to those observed for the monophosphole series.[7]

In the [**1a**]$^S_{RR}$ and [**1a**]$^R_{SS}$ configurations of BIPHOS, **1**, the phosphorus lone pairs are in the right direction to chelate to metal atoms and from these considerations, it appears that BIPHOS should give chiral transition metal complexes.

Synthesis and Characterization of Ni, Pd, and Pt Biphosphole Complexes. The reactions of biphosphole **1** (**1a** + **1b**) in dichloromethane at room temperature with [Ni(DME)Br_2], [Pd($CH_3CN)_2Cl_2$], and [Pt($CH_3CN)_2Cl_2$] produce [Ni(BIPHOS)Br_2], [Pd(BIPHOS)Cl_2] and [Pt(BIPHOS)Cl_2], respectively, in excellent yield (eq 1). The $^{31}P\{^1H\}$ NMR spectra of the reaction mixtures



(1)

exhibit single resonances in each case, showing that the conversion of **1a** + **1b** into the corresponding complexes is quantitative and that the compounds obtained are pure diastereoisomers. Owing to the low pyramidal inversion barrier of the phosphorus atom,[6,7] it is clear that **1b** is quantitatively transformed into **1a** in order to favor coordination onto the metal. These three complexes were characterized by elemental analysis, multinuclear NMR spectroscopy, and mass spectroscopy. They could be obtained as crystals, and they were fully characterized by X-ray structural investigations. The molecular structures of complexes **2**, **3**, and **4**, with atom labeling scheme, are presented in Figures 2, 3, and 4, respectively. Selected bond distances and angles are listed in Tables 3 and 4. They all have a similar structure possessing a C_2 symmetry axis passing through the metal atom and crossing the middle of the C(1)−C(1)′(or C(11)) bond. As a result, all of these complexes are chiral. However, the solid state structure corresponds to the racemic mixture, since all complexes

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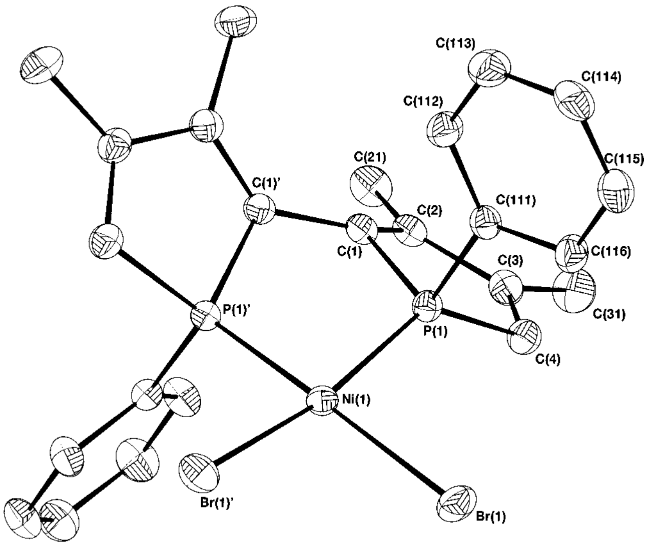

Figure 2. Molecular view of complex **2** showing the atom numbering scheme (30% probability ellipsoids). Hydrogen atoms are omitted.

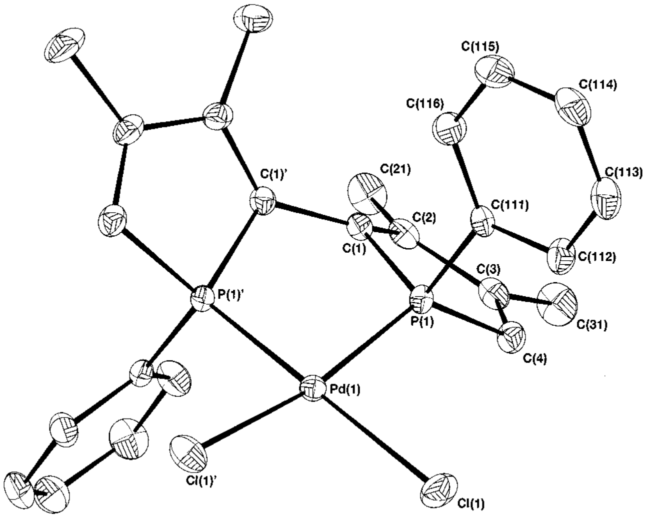

Figure 3. Molecular view of complex **3** showing the atom numbering scheme (30% probability ellipsoids). Hydrogen atoms are omitted.

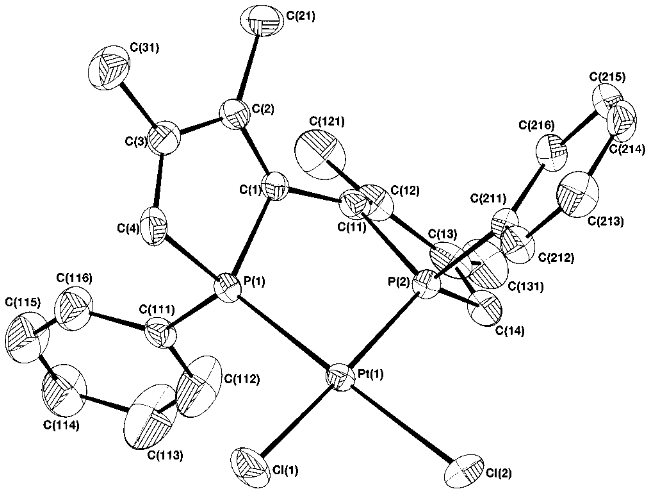

Figure 4. Molecular view of complex **4** showing the atom numbering scheme (30% probability ellipsoids). Hydrogen atoms are omitted.

Table 3. Important Interatomic Distances (Å), with Esd's in Parentheses, for Compounds 2, 3, and 4

	2 (M = Ni, X = Br)	**3** (M = Pd, X = Cl)	**4** (M = Pt, X = Cl)
M(1)–X(1)	2.3394(5)	2.361(1)	2.337(2)
M(1)–X(2),X(1)′[a]	2.3394(5)	2.361(1)	2.345(2)
M(1)–P(1)	2.1511(9)	2.2287(9)	2.227(2)
M(1)–P(2),P(1)′[a]	2.1511(9)	2.2287(9)	2.218(2)
P(1)–C(1)	1.803(3)	1.792(3)	1.812(6)
P(1)–C(4)	1.794(4)	1.787(3)	1.787(7)
P(1)–C(111)	1.821(4)	1.814(3)	1.817(6)
P(2)–C(11)			1.811(6)
P(2)–C(14)			1.783(6)
P(2)–C(211)			1.799(6)
C(1)–C(2)	1.345(5)	1.353(4)	1.36(1)
C(1)–C(11),C(1)′[a]	1.458(7)	1.458(6)	1.446(9)
C(2)–C(3)	1.490(5)	1.497(5)	1.48(1)
C(2)–C(21)	1.493(5)	1.487(5)	1.48(1)
C(3)–C(4)	1.355(5)	1.335(5)	1.34(1)
C(3)–C(31)	1.479(5)	1.503(5)	1.50(1)
C(11)–C(12)			1.35(1)
C(12)–C(13)			1.48(1)
C(12)–C(121)			1.50(1)
C(13)–C(14)			1.32(1)
C(13)–C(131)			1.51(1)

[a] ′ refers to atoms related by the 2-fold axis.

crystallize in a centrosymetric space group. In crystals of **2** and **3**, which belong to the monoclinic *C*2/*c* space group, Ni and Pd atoms lie on the 2-fold axis. As can be seen from the molecular drawings, the chelate rings formed by the coordination of the biphosphole onto the metal atom adopt a puckering conformation. The distances and angles in the phosphole rings are within the range of values reported for related compounds.[8] The phosphole rings are all planar, within experimental error, but they are twisted about each other along the C(1)–C(1′) (or (C11)) bond making dihedral angles of 46.8°, 50.6°, and 53.8° for **2**, **3**, and **4**, respectively. These values compare well with the 46.6° observed for the free ligand **1**.[6] The M–P bond lengths are within the range of values observed in related MP_2X_2 complexes. The Ni–P distance in **2**, 2.1511(9) Å, is comparable with that of 2.151 Å observed in the 1,2-bis(diphenylphosphino)ethane complex [Ni(dppe)Cl_2],[9] but it is slightly longer than the 2.126(1) Å Ni–P distance found in the 2,2′-biphospholene complex [Ni(dpple)Cl_2].[10] Similar observations can be deduced from the comparison of the Pd–P distances of 2.2287(9) Å in **3**, 2.231 Å in [Pd(dppe)Cl_2],[11] and 2.218 Å (mean value) in [Pd(dpple)Cl_2].[10b] It is worth pointing out that in the phosphole complex [Pd(DMPP)$_2$$Cl_2$],[12] the Pd–P bond length is 2.240(3) Å. The Pt–P bonds of 2.223 Å (mean value) in **4** compare well with those of 2.218 Å in [Pt(dppe)Cl_2].[13] It may then be concluded that the BIPHOS ligand behaves as a normal diphosphine ligand, as a good σ-donor and π-acceptor ligand. The P(1), P(1′) (or P(2)), and M atoms have a square planar environment

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Table 4. Important Bond Angles (deg), with Esd's in Parentheses

	2 (M = Ni, X = Br)	**3** (M = Pd, X = Cl)	**4** (M = Pt, X = Cl)
X(1)−M(1)−X(2), X(1)′[a]	98.64(3)	98.54(6)	92.84(8)
X(1)−M(1)−P(1)	87.97(3)	88.29(3)	92.33(7)
X(2)−M(1)−P(1)			172.59(6)
X(1)−M(1)−P(2), P(1)′[a]	168.32(3)	169.36(4)	175.59(7)
X(2)−M(1)−P(2)			88.33(6)
P(1)−M(1)−P(2)	87.22(5)	86.18(4)	86.90(6)
M(1)−P(1)−C(1)	109.5(1)	108.3(1)	107.0(2)
M(1)−P(1)−C(4)	130.6(1)	129.3(1)	130.1(2)
C(1)−P(1)−C(4)	92.4(2)	93.1(2)	91.9(3)
M(1)−P(1)−C(111)	108.5(1)	108.8(1)	112.2(2)
C(1)−P(1)−C(111)	107.6(2)	109.2(1)	104.4(3)
C(4)−P(1)−C(111)	105.8(2)	106.2(1)	106.7(3)
M(1)−P(2)−C(11)			107.4(2)
M(1)−P(2)−C(14)			126.5(2)
C(11)−P(2)−C(14)			92.1(3)
M(1)−P(2)−C(211)			113.8(2)
C(11)−P(2)−C(211)			108.6(3)
C(14)−P(2)−C(211)			105.4(3)
P(1)−C(1)−C(2)	110.1(3)	109.8(2)	109.6(5)
P(1)−C(1)−C(11),C(1)′[a]	111.5(1)	112.7(1)	111.4(4)
C(2)−C(1)−C(11),C(1)′[a]	135.1(3)	134.1(3)	137.6(6)
C(1)−C(2)−C(3)	113.2(3)	112.4(3)	113.2(6)
C(1)−C(2)−C(21)	125.1(4)	125.6(3)	123.8(8)
C(3)−C(2)−C(21)	121.6(3)	121.9(3)	122.9(7)
C(2)−C(3)−C(4)	115.0(3)	115.8(3)	115.4(6)
C(2)−C(3)−C(31)	121.1(4)	119.8(3)	120.9(8)
C(4)−C(3)−C(31)	123.9(4)	124.3(4)	123.8(8)
P(1)−C(4)−C(3)	109.0(3)	108.7(3)	109.8(6)
P(2)−C(11)−C(1)			112.3(4)
P(2)−C(11)−C(12)			109.1(6)
C(1)−C(11)−C(12)			133.8(6)
C(11)−C(12)−C(13)			113.3(6)
C(11)−C(12)−C(121)			124.2(9)
C(13)−C(12)−C(121)			122.3(7)
C(12)−C(13)−C(14)			115.5(6)
C(12)−C(13)−C(131)			120.6(7)
C(14)−C(13)−C(131)			123.9(8)
P(2)−C(14)−C(13)			109.8(6)

[a] ′ refers to atoms related by the 2-fold axis.

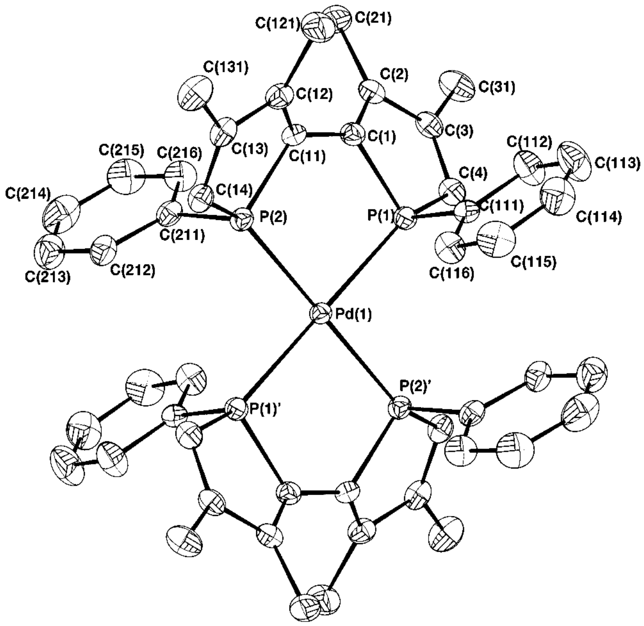

Figure 5. Molecular view of complex **6** showing the atom numbering scheme (30% probability ellipsoids). Hydrogen atoms are omitted.

Table 5. Coordination Chemical Shifts Δ(δ^{31}P) for LMX_2, $L'MX_2$, and L''_2MX_2

	$\delta(^{31}P)$	$\Delta(\delta^{31}P)$
[Ni(BIPHOS)Br$_2$]	46.20	28.51
[Pd(BIPHOS)Cl$_2$]	33.40	15.71
[Pt (BIPHOS)Cl$_2$]	23.49	5.8
[Ni(dpple)Br$_2$][10b]	87.7	116
[Pd(dpple)Cl$_2$][10b]	88.3	116.6
[Pt(dpple)Cl$_2$][10b]	63.1	91.4
[Pd-cis-(DMPP)$_2$Cl$_2$][12]	26.36	28.86
[Pt-cis-(DMPP)$_2$Cl$_2$][4]	8.1	10.6

[a] $\Delta(\delta^{31}P) = \delta^{31}P(\text{complex}) - \delta^{31}P(\text{ligand})$. L = 2,2′-biphosphole **1a**. dpple = 2,2′-bis(1-phenyl-3,4-dimethyl-2,5-dihydro-1*H*-phosphole). DMPP = 1-phenyl-3,4-dimethylphosphole.

with, however, a slight distorsion from the idealized situation. The Ni compound has the largest tetrahedral distorsion. This can be seen by comparing the values of the dihedral angles between the P(1)−P(1′)−M and X(1)−X(1′)−M planes for these three compounds, which are 14.1° for **2**, 12.07° for **3**, and 7.0° for **4**.

These complexes give well-resolved ^{1}H, ^{31}P, and ^{13}C NMR spectra (Tables 1 and 2), except the nickel complex **2** which exhibits broad signals. This indicates the existence of a tetrahedral−square planar interconversion in solution, as observed for some phosphole[4] and diphosphine nickel complexes.[14] The ^{1}H NMR spectra of compounds **3** and **4**, which exhibit only two resonance signals for the two nonequivalent methyl groups in the 1.8−2.2 region, confirm the formation of pure diastereoisomer complexes. The assignments of methyl 21 and 31 were made by a ^{31}P-decoupling experiment and comparison with the spectrum of the ligand. In contrast, the resonance of proton H(4) is more complicated, due to an AA′XX′system (A = ^{1}H, X = ^{31}P) as observed in the spectrum of the ligand **1a**. According to the analysis of this system, the $^2J_{PP}$ coupling constants are small (**3**, 7.5 Hz; **4**, 0.0 Hz), the $^2J_{HP}$ coupling constants are in usual range (**3**, 35 Hz; **4**, 32 Hz) and the $^4J_{HP}$ coupling constants are small (**3**, −3.0 Hz; **4**, 0.0 Hz). The $^{13}C\{^1H\}$ spectra of compounds **3** and **4** are more complicated, each carbon resonance displayed AA′XX′ multiplets (A = ^{13}C, X = ^{31}P). In order to facilitate assignment, $^{13}C\{^1H,^{31}P\}$ spectra were recorded. In addition, ^{2}D GE-HMQC(^{1}J, L. R.) $^1H-^{13}C\{^{13}C,^{31}P\}$ NMR spectra allowed the complete assignment of all resonances to be made (Table 2). The ^{31}P chemical shifts of complexes **2**, **3**, and **4** lie downfield relative to the ligand (Table 1). From these data, we have calculated the ^{31}P coordination chemical shifts $\Delta\delta^{31}P$ ($\Delta\delta^{31}P = \delta^{31}P_{complex} - \delta^{31}P_{ligand}$). These values, smaller than those observed for five-membered chelate phosphorus ligands like the biphospholene ligand (dpple),[10] are comparable to those found for similar phosphole complexes [Pd(DMPP)$_2$X$_2$] or [Pt(DMPP)$_2$X$_2$][4,12] (Table 5). According to the observations of F. Mathey,[4] these smaller coordination chemical shifts may not result from weaker M−P bonds, as evidenced by the X-ray structural results, but rather from the existence of some π-back-bonding between the transition metal and the biphosphole. This suggest that biphosphole, like phosphole, is softer and more polarizable than phosphines.[4]

Attempted Synthesis of [Pd(BIPHOS)(CH$_3$CN)$_2$]-(BF$_4$)$_2$ Complex. Palladium complexes [Pd(L)$_2$(solvent)$_2$] have been shown to be catalysts or catalyst precursors

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Table 6. Important Interatomic Distances (Å) and Bond Angles (deg), with Esd's in Parentheses, for Compound 5

Pd(1)−P(1)	2.339(1)	C(2)−C(3)	1.480(9)
Pd(1)−P(2)	2.337(1)	C(2)−C(21)	1.499(9)
P(1)−C(1)	1.798(6)	C(3)−C(4)	1.345(9)
P(1)−C(4)	1.781(6)	C(3)−C(31)	1.499(9)
P(1)−C(111)	1.805(6)	C(5)−C(6)	1.352(8)
P(2)−C(5)	1.806(6)	C(6)−C(7)	1.488(9)
P(2)−C(8)	1.784(6)	C(6)−C(61)	1.489(9)
P(2)−C(211)	1.805(6)	C(7)−C(8)	1.330(9)
C(1)−C(2)	1.341(8)	C(7)−C(71)	1.497(9)
C(1)−C(5)	1.453(8)		
P(1)−Pd(1)−P(2)	84.51(5)	C(1)−C(2)−C(3)	113.1(5)
P(1)−Pd(1)−P(2)	95.49(5)	C(1)−C(2)−C(21)	123.6(6)
Pd(1)−P(1)−C(1)	106.1(2)	C(3)−C(2)−C(21)	123.3(5)
Pd(1)−P(1)−C(4)	128.7(2)	C(2)−C(3)−C(4)	115.1(5)
C(1)−P(1)−C(4)	92.0(3)	C(2)−C(3)−C(31)	120.8(6)
Pd(1)−P(1)−C(111)	110.9(2)	C(4)−C(3)−C(31)	124.1(6)
C(1)−P(1)−C(111)	105.6(3)	P(1)−C(4)−C(3)	109.5(5)
C(4)−P(1)−C(111)	109.4(3)	P(2)−C(5)−C(1)	113.9(4)
Pd(1)−P(2)−C(5)	107.0(2)	P(2)−C(5)−C(6)	109.6(4)
Pd(1)−P(2)−C(8)	132.3(2)	C(1)−C(5)−C(6)	134.2(5)
C(5)−P(2)−C(8)	92.4(3)	C(5)−C(6)−C(7)	112.7(5)
Pd(1)−P(2)−C(211)	107.1(2)	C(5)−C(6)−C(61)	124.2(6)
C(5)−P(2)−C(211)	109.4(3)	C(7)−C(6)−C(61)	123.0(6)
C(8)−P(2)−C(211)	106.5(3)	C(6)−C(7)−C(8)	115.8(5)
P(1)−C(1)−C(2)	110.3(4)	C(6)−C(7)−C(71)	119.7(6)
P(1)−C(1)−C(5)	112.7(4)	C(8)−C(7)−C(71)	124.5(6)
C(2)−C(1)−C(5)	136.1(5)	P(2)−C(8)−C(7)	109.3(5)

for olefin isomerisation[15] and CO−olefin copolymerization.[16,17] In addition, they are also useful starting materials for the synthesis of a variety of complexes because the weakly coordinated solvent molecules are readily displaced.[18] Accordingly, we have attempted to synthesize an analogous complex using $[Pd(CH_3CN)_4](BF_4)_2$ as the starting material. Addition of 1 equiv of a toluene solution of biphosphole **1** (**1a** + **1b**) to a dichloromethane solution of $[Pd(CH_3CN)_4](BF_4)_2$ at room temperature led to the immediate formation of an orange complex **5**, which could be isolated by evaporation of the solvent (eq 2). A similar reaction conducted

$$\begin{tikzcd} \mathbf{1a} + \mathbf{1b} + 0.5[Pd(CH_3CN)_4](BF_4)_2 \arrow[r, "-CH_3CN"'] \arrow[d] & {[Pd(BIPHOS)_2](BF_4)_2} \ \mathbf{5} \\ \mathbf{3} + 2AgBF_4 \arrow[r, "-2AgCl"'] & {[Pd(BIPHOS)(CH_3CN)_2](BF_4)_2} \ \mathbf{6} \end{tikzcd} \qquad (2)$$

at −50 °C give the same complex. The ^1H and ^{31}P NMR spectra are consistent with the formation of the pure diastereoisomer complex (Tables 1 and 2). This stable complex **5** was not the expected complex, as indicated by elemental analysis, mass spectroscopy, and X-ray crystallography. The molecular view of the cation is shown in Figure 5. Important bond distances and bond angles are given in Table 6. The Pd atom lies on an inversion center, which relates the two parts of the molecule. Thus, this compound contains the $[\mathbf{1a}]^S_{RR}$ and $[\mathbf{1a}]^R_{SS}$ absolute configurations of BIPHOS and is the meso diastereomer. It is worth pointing out that similar complexes, $[Ni(dpple)_2](BF_4)_2$, have been reported.[19] In this case, the meso and racemic diastereoisomers were obtained in roughly equivalent amounts. Owing to its location on the inversion center, the Pd atom has a perfect square planar geometry. The Pd−P distances of 2.38(1) Å (mean value) are longer than those found for **3**. This lengthening results from the combined effects of the increased steric hindrance within the palladium coordination sphere and the greater trans influence of P than that of Cl. The phosphole rings are planar, within experimental error, but as in complexes **2**, **3**, and **4**, they are twisted along the C(1)−C(1′) bond making a dihedral angle of 53.3°. This structure proves that biphosphole is a rather good ligand.

As the $[Pd(BIPHOS)(CH_3CN)_2](BF_4)_2$ complex is not accessible by the procedure described above, we tried another method starting from complex **3** (eq 2). Chloride abstraction with $AgBF_4$[20] in acetonitrile solution at ambient temperature affords a new orange complex **6**, which has only been analyzed by ^1H and ^{31}P NMR spectroscopy. According to the ^1H NMR spectrum, complex **6** should be the expected complex but we have not obtained further evidence yet. Indeed, this complex is rather unstable and decomposes within 2 h at room temperature in solution. Isolation by evaporation of the solvent gives an orange powder that is extremely air and moisture sensitive.

Synthesis of the $[Pd(BIPHOS)(\eta^3\text{-}C_3H_5)]X$ Complex. (η^3-Allyl)palladium complexes of various bidentate ligands are efficient catalysts for allylic subtitution.[21] It has been reported that these complexes can be prepared by reaction of the dimeric allylpalladium chloride $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ with a bidentate ligand, in the presence of sodium or silver salts.[22] A similar reaction conducted with **1**, in the presence of either $AgBF_4$ or $NaBPh_4$, leads to a mixture of at least four products, as evidenced by ^{31}P NMR analysis. From this mixture we cannot isolate the expected complex. However, the corresponding chloro complex $[Pd(BIPHOS)(C_3H_5)]Cl$, **7**, was obained from $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ and **1** (**1a** + **1b**) without adding salt (eq 3). According to ^{31}P NMR analysis (δ = 32.04), the formation of complex **7** is quantitative, but a fast decomposition occurs in solution.

$$\mathbf{1a} + \mathbf{1b} + 0.5[Pd(\eta^3\text{-}C_3H_5)Cl)_2 \xrightarrow{CH_2Cl_2} [Pd(BIPHOS)(\eta^3\text{-}C_3H_5)]Cl \ \mathbf{7} \qquad (3)$$

This allylpalladium complex generated *in situ* was used in the catalytic allylic substitution of 1,3-diphenylprop-2-enyl acetate with the anion of dimethyl malonate and proved to be as effective as the best previously

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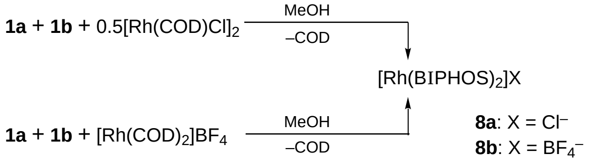
reported catalytic systems for this reaction.[23] At 35 °C in dichloromethane, working on a 2 mmol scale and using 0.02 equiv of catalyst, the formation of $Ph-CH{=}CH-CHPh-CH(CO_2Me)_2$ is quantitative (99%) in 10 min.

Synthesis and Characterization of Rhodium Complexes. $[Rh(COD)Cl]_2$ and $[Rh(COD)_2]BF_4$ are good precursors for the preparation of cationic complexes of rhodium(I), which are useful in hydrogenation reactions.[24] Surprisingly, the reaction of 1 equiv of **1a** + **1b** with 0.5 equiv of $[Rh(COD)Cl]_2$ at room temperature in methanol gives a mononuclear complex **8a** by substitution of the two 1,5-cyclooctadiene (COD) ligands (eq 4). Complex **8a** was identified by mass spectroscopy and multinuclear spectroscopy (Tables 1 and 2). As observed for complex **5**, only one diastereoisomer is obtained, but so far we have not been able to determine if it is the meso or the racemate. This complex is best prepared by mixing the rhodium precursor (1 equiv) and **1a** + **1b** (4 equiv). Similary, **1a** + **1b** reacts rapidly with $[Rh(COD)_2]BF_4$ at room temperature, with displacement of two COD ligands.



(4)

Biphosphole **1a** + **1b** and $[Rh(COD)_2]BF_4$ were used as the catalytic system for the hydrogenation of α-acetamidocinnamic acid. At room temperature and under 1 atm of H_2, working on a 2.5 mmol scale of the substrate and using 0.01 equiv of catalyst, 20% of *N*-acetylphenylalanine was obtained after 22 h. The formation of complex **8b** may explain this poor yield.

Conclusion

The biphosphole ligand coordinates transition metals to give chiral complexes with a $[\mathbf{1a}]^{\mathrm{S}}_{\mathrm{RR}} + [\mathbf{1a}]^{\mathrm{R}}_{\mathrm{SS}}$ configuration. New nickel, palladium, and platinum complexes $[M(BIPHOS)X_2]$ have been synthetized and fully characterized. The biphosphole is a rather good ligand. Thus, bis(BIPHOS) complexes of Pd(II) and Rh(I) can be easily prepared by displacement of the weakly bonded ligands of $[Pd(CH_3CN)_4](BF_4)_2$ and $[Rh(COD)Cl]_2$, respectively. The cationic palladium complexes synthesized appear to be more reactive than the neutral palladium complexes. Specifically, the π-allylpalladium complex reveals a potential interest for catalytic allylic substitution. We are presently investigating the optical resolution of these chiral biphosphole complexes in order to explore their performance in asymmetric catalysis.

Experimental Section

General Comments. All reactions were carried under an inert atmosphere of dry argon by using Schlenk glassware and vacuum line techniques. Solvents were freshly distilled from standard drying agents.

^1H, $^{13}C\{^1H,^{31}P\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker WMX 400 instrument operating at 400, 162, and 100 MHz, respectively. Chemical shifts are reported in parts per million (ppm) relative to Me_4Si (^1H and ^{13}C) or 85% H_3PO_4 (^{31}P). ^{195}Pt (85 MHz) and ^{103}Rh (12.6 MHz) NMR spectra were recorded on a Bruker WMX 400 instrument relative to H_2PtCl_6 and Rh metal ($\Xi = 12.644338$ MHz) as references, respectively.

Elemental analyses were performed by the "Service d'Analyse du Laboratoire de Chimie de Coordination" at Toulouse and the "Service Central d'Analyse du CNRS" at Lyon, France. Mass spectra were obtained on a Nermag R10-10 instrument. Infrared spectra (KBr pellet) were recorded on a Perkin-Elmer 1725X FT-IR spectrometer.

$[Ni(DME)Br_2]$, $[Pd(\eta_3\text{-}C_3H_5)Cl]_2$, and $[Rh(COD)Cl]_2$ were purchased from Aldrich Chemical Co. The starting materials biphosphole **1**,[25] $[Pd(CH_3CN)_2Cl_2]$,[26] $[Pt(CH_3CN)_2Cl_2]$,[27] $[Pd(CH_3CN)_4](BF_4)_2$,[28] and $[Rh(COD)_2]BF_4$[29] were prepared as described in the literature.

X-ray Structure Determination. For three of the four compounds, **3**, **4**, and **5**, data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer equipped with a graphite-oriented monochromator, utilizing Mo Kα radiation ($\lambda = 0.710\ 73$). The final unit cell parameters were obtained by the least-squares refinement of the setting angles of 25 reflections that had been accurately centered on the diffractometer. Only statistical fluctuations were observed in the intensities monitored over the course of data collections. Data for **2** were collected on a Stoe IPDS (imaging plate diffraction system) using Mo Kα radiation. Final unit cell parameters were derived from the least-squares refinement of 2000 reflections.

The four structures were solved by direct methods (SIR92[30]) and refined by least-squares procedures on F_{obs}. In compound **5**, the BF_4 anion is disordered with three of the fluorine atoms distributed on six sites. In a first step, it was assumed that the thermal parameters of the corresponding F atoms in the disordered positions were equal, and the occupancies were allowed to vary with the constraint that the sum of the occupancies equals unity. Additional distance and angle restraints (mean B−F and F−B−F values) were used during this procedure. When the occupancy factors were well-defined, all of the restraints were released and the disordered F atoms were refined isotropically. For all compounds, H atoms could be located by difference Fourier syntheses, but for compounds **2**, **4**, and **5**, they were introduced in the calculations in their idealized positions (d(CH) = 0.96 Å) and their atomic coordinates were recalculated after each cycle. They were given isotropic thermal parameters 20% higher than those of the carbon to which they are attached. For **3**, a constrained refinement (d(C−H) = 0.98 Å) of H coordinates was used, whereas they were given equivalent isotropic thermal parameters. Least-squares refinements were carried out by minimizing the function $\sum w(|F_o| - |F_c|)^2$, where F_o and F_c are the observed and calculated structure factors. The weighting scheme used in the last refinement cycle was $w = w'[1 - (\Delta F/6\sigma(F_o)^2]_2$, where $w' = 1/\sum_1^n A_r T_r(x)$ with three coefficients A_r for the Chebyshev polynomial $A_r T_r(x)$, where x was $F_c/F_c(\max)$.[31] Models reached convergence with $R = \sum(||F_o| - |F_c||)/\sum(|F_o|)$

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Table 7. Crystal Data

	3	4	5
		Crystal Parameters	
formula	$C_{24}H_{24}P_2Cl_2Pd$	$C_{24}H_{24}P_2Cl_2Pt$	$[(C_{24}H_{24}P_2)_2Pd][BF_4]_2$
fw, g	551.7	640.40	487.8
shape (color)	flat (yellow)	platelet (yellow)	box (yellow)
size, mm	0.5 × 0.5 × 0.05	0.80 × 0.35 × 0.15	0.5 × 0.4 × 0.38
crystal system	monoclinic	orthorhombic	Rhombohedral
space group	*C*2/*c*	*Pbca*	$R\bar{3}$
a, Å	13.236(7)	10.713(3)	31.179(6)
b, Å	10.058(2)	17.585(3)	31.179(6)
c, Å	17.892(5)	26.040(3)	14.416(4)
β, deg	102.18(3)		120.0
V, Å^3	2328(2)	4905(2)	12138(5)
Z	4	8	9
F(000)		2465	4508
ρ (calcd), g·cm^{-3}	1.574	1.734	1.20
μ (Mo Kα), cm^{-1}	11.62	61.37	3.51
		Data Collection	
diffractometer	Enraf-Nonius CAD4F	Enraf-Nonius CAD4	Enraf-Nonius CAD4F
monochromator	graphite	graphite	graphite
radiation	Mo Kα (λ = 0.710 73)	Mo Kα (λ = 0.710 73)	Mo Kα (λ = 0.710 73)
scan type	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
scan range θ, deg	1.0 + 0.345 tan θ	1.0 + 0.345 tan θ	0.9 + 0.345 tan θ
2θ range,deg	$3 < 2\theta < 54$	$3 < 2\theta < 50$	$3 < 2\theta < 50$
no. of rflns collected	5049 ($\pm h,k,\pm l$)	4836(h,k,l)	5026 ($h,k,\pm l$)
no. of unique rflns	2527	4836	4739
merging *R* factor	0.0252		0.022
rflns used ($I > 3\sigma(I)$)	1799	2726	2669
		Refinement	
R	0.023	0.0277	0.0547
R_w	0.026	0.0330	0.0615
weighting scheme	Chebyshev	Chebyshev	Chebyshev
coeff. Ar	2.21, −0.498, 1.33	3.01, −0.502, 2.33	7.49, −2.34, 5.62
goodness of fit	1.12	1.05	1.05
no. of least-squares parameters	171	264	274

	2		2
		Crystal Parameters	
compound	$C_{24}H_{24}P_2Br_2Ni$	c, Å	17.828(3)
fw, g	593	β, deg	103.00(1)
shape (color)	prismatic (dark red)	*V*, Å^3	2356(1)
size, mm	0.6 0.45 0.38	*Z*	4
crystal system	monoclinic	*F*(000)	1183
space group	*C*2/*c*	ρ (calcd), g·cm^{-3}	1.671
a, Å	13.228(2)	μ (Mo Kα), cm^{-1}	43.30
b, Å	10.254(1)		
		Data Collection	
diffractometer	IPdS Stoe	ϕ increment, deg	2
monochromator	graphite	exposure time, min	2
radiation	Mo Kα (λ = 0.710 73)	2θ range, deg	$3.8 < 2\theta < 56.3$
scan mode	ϕ	no. of rflns collected	10678
detector distance, mm	60	no. of independent rflns (R_m)	2736 (0.022)
scan range ϕ, deg	$0 < \phi < 200$	reflections used ($I > 3\sigma(I)$)	1925
		Refinement	
R	0.0413	coeff. Ar	2.18, −0.047, 1.70
R_w	0.0482	goodness of fit	1.012
weighting scheme	Chebyshev	no. of least-squares parameters	133

and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$, having the values listed in Table 7. Criteria for a satisfactory complete analysis were that the ratios of the root mean square shift to standard deviation were less than 0.1 and that there were no significant features in final difference maps. Details of the data collection and refinement are given in Table 7.

The calculations were carried out with the CRYSTALS package program[32] running on a PC486 DX266. Molecular views were drawn using CAMERON.[33]

Dibromo(1,1′-diphenyl-3,3′,4,4′-tetramethyl-2,2′-biphosphole)nickel(II), 2. $[Ni(DME)Br_2]$ (0.16 g, 0.51 mmol) was added to a solution of biphosphole **1** (0.19 g, 0.51 mmol) in 10 mL of CH_2Cl_2 and 20 mL of toluene. The reaction mixture was stirred for 24 h at room temperature, during which time it slowly changed from yellow to dark red. After evaporation of the solvents, the residue was washed with pentane and then extracted with dichloromethane. After the resulting solution was filtered, the dichloromethane solution was slowly evaporated to yield 0.25 g (83%) of red crystals. Anal. Found (Calcd) for $C_{24}H_{24}Br_2NiP_2$: C, 47.51 (48.62); H, 4.18 (4.08); Br, 26.78 (26.95); P, 10.21 (10.45).

Dichloro(1,1′-diphenyl-3,3′,4,4′-tetramethyl-2,2′-biphosphole)palladium(II), 3. To a solution of biphosphole **1** (0.13 g, 0.35 mmol) in toluene (20 mL) was added solid $[Pd(CH_3CN)_2Cl_2]$ (0.09 g, 0.35 mmol), and the mixture was stirred for 1 h at room temperature. The solvent was removed under vacuum to give an orange residue, which was dissolved in

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dichloromethane. The resulting solution was filtered through a 0.45 μm PTFE filter, then slow addition of pentane gave the complex as an orange microcrystalline solid, which was filtered, washed with pentane, and dried under vacuum (0.18 g, 94%). Orange crystals were obtained by slow evaporation of a dichloromethane solution. Anal. Found (Calcd) for $C_{24}H_{24}Cl_2P_2Pd$: C, 51.77 (52.25); H, 4.26 (4.38); Cl, 13.74 (12.85); P, 10.62 (11.23). MS (DCI, CH_4), *m*/*z*: 552 (M^+, 18), 515 ($(M - Cl)^+$, 100).

Dichloro(1,1′-diphenyl-3,3′,4,4′-tetramethyl-2,2′-biphosphole)platinium(II), 4. Starting from $[Pt(CH_3CN)_2Cl_2]$, complex **5** was synthesized in a similar way to **3** and was obtained as a yellow powder (88%). Crystals were grown from a dichloromethane/pentane solution of the compound. Anal. Found (Calcd) for $C_{24}H_{24}Cl_2P_2Pt$: C, 45.12 (45.02); H, 3.61 (3.78); Cl, 12.42 (11.07); P, 9.10 (9.67). MS (DCI, CH_4), *m*/*z*: 640 (M^+, 22), 604 ($(M - Cl)^+$, 100).

Bis(1,1′-diphenyl-3,3′,4,4′-tetramethyl-2,2′-biphosphole)palladium(II) Tetrafluoroborate, 5. To a solution containing 0.14 g (0.32 mmol) of $[Pd(CH_3CN)_4](BF_4)_2$ in 5 mL of dichloromethane was added, at room temperature, a solution of biphosphole **1** (0.12 g, 0.32 mmol) in 10 mL of toluene. After 1 h of stirring, the solvents were removed under vacuum. The orange residue was extracted with dichloromethane which, after filtering through Celite, was slowly evaporated to yield 0.29 g (89%) of orange crystals. Anal. Found (Calcd) for $C_{48}H_{48}B_2F_8P_4Pd$: C, 56.58 (56.04); H, 4.49 (4.67). MS (FAB, MNBA matrix), *m*/*z*: 941 ($(M^+ - BF_4)$, 33.6], 854 ($(M^+ - B_2F_8)$, 100).

Bis(acetonitrile)(1,1′-diphenyl-3,3′,4,4′-tetramethyl-2,2′-biphosphole)palladium(II) Tetrafluoroborate, 6. Complex **3** (0.10 g, 0.18 mmol) was mixed with $AgBF_4$ (0.07 g, 0.36 mmol) in acetonitrile (20 mL). The reaction mixture turned orange immediately. After 1h at room temperature, the resulting AgCl precipitate was removed by filtration through a 0.45 mm PTFE filter and the solution was evaporated under reduced pressure. Complex **6** is obtained as an orange powder (0.13 g, 97%) and is extremely air and moisture sensitive. ^{31}P NMR (CD_3CN): δ 36.61. ^1H NMR (CD_3CN): δ 2.02 (s, 12H, CH_3), 2.25 (s, 6H, CH_3), 6.81 (broad, 2H, CH), 7.40−7.85 (m, 10H, Ph).

(η^3-Allyl)(1,1′-diphenyl-3,3′,4,4′-tetramethyl-2,2′-biphosphole)palladium(II) Chloride, 7. A solution of biphosphole **1** (0.07 g, 0.19 mmol) in 2 mL of dichloromethane was added to a solution of $[Pd(\eta_3-C_3H_5)Cl]_2$ (0.04 g, 0.10 mmol) in 2 mL of dichloromethane at room temperature. The resulting mixture turned yellow and then red after 10 min of stirring. After 1 h, the mixture was filtered and washed with pentane. A red powder (0.10 g, 96%) was obtained after evaporation of the solvent. ^{31}P NMR (CD_2Cl_2): $\delta = 32.04$. MS (FAB, MNBA matrix), *m*/*z*: 521 ($(M - Cl)^+$, 100).

Allylic Substitution Catalyzed by $[Pd(\eta_3-C_3H_5)Cl]_2$/BIPHOS. $[Pd(\eta_3-C_3H_5)Cl]_2$ (3.6 mg 9.8 μmol) biphosphole **1** (11.0 mg 29.5 μmol, 1.5 equiv/Pd), and 1,3-diphenylprop-2-enyl acetate (248 mg 0.98 mmol) were dissolved in 4 mL of dichloromethane. The yellow solution was stirred for 15 min and then slowly added to a suspension of sodium malonate, prepared from dimethylmalonate (0.340 mL, 2.95 mmol) and dry NaH (70 mg, 2.95 mmol) in 4 mL of dichloromethane. The homogeneous red reaction mixture was stirred for 10 min at 35 °C and subsequently quenched by addition of 5 mL of saturated NH_4Cl. The aqueous layer was separated and extracted with dichloromethane, and the combined organic extracts were dried over $MgSO_4$. Evaporation of the solvent led, in quantitative yield, to crude $Ph-CH{=}CH-CHPh-CH(CO_2Me)_2$, as determined by ^1H NMR.

Bis(1,1′-diphenyl-3,3′,4,4′-tetramethyl-2,2′-biphosphole)rhodium(I) Chloride, 8a. To a solution of 0.03 g of $[Rh(COD)Cl]_2$ (0.06 mmol) in 4 mL of methanol was added a solution of 0.09 g of biphosphole **1** (0.24 mmol, 4 equiv) in 2 mL of methanol, at room temperature. The mixture turned red immediately. The solution was stirred for 1 h and then filtered. After removal of the solvent, the brown solid obtained was washed with pentane and dried in vacuo. Yield: 0.10 mg (93%) of a brown powder. MS (FAB, MNBA matrix), *m*/*z*: 851 ($(M - Cl)^+$, 100).

Bis(1,1′-diphenyl-3,3′,4,4′-tetramethyl-2,2′-biphosphole)rhodium(I) Tetrafluoroborate, 8b. Complex **8b** was prepared as described for **8a**, starting from $[Rh(COD)_2]BF_4$ (0.03 g, 0.08 mmol) and biphosphole **1** (0.06 g, 0.16 mmol, 2 equiv). Yield: 0.06 mg (87%). MS (FAB, MNBA matrix), *m*/*z*: 851 ($(M - BF_4)^+$, 100).

Hydrogenation of α-Acetamidocinnamic Acid Catalyzed by $[Rh(COD)_2]BF_4$/BIPHOS. Under an argon atmosphere, $[Rh(COD)_2]BF_4$ (0.10 g, 0.25 mmol), biphosphole **1** (0.09 g, 0.25 mmol), α-acetamidocinnamic acid (0.51g, 2.5 mmol), and degassed methanol were introduced into a Schlenk vessel. The atmosphere was then replaced with hydrogen, and the solution was allowed to react under 1 atm of H_2 at room temperature for 22 h. After filtration through a 0.45 μm PTFE filter, evaporation of the solvent gave an orange solid. The ^1H NMR spectrum of the solid indicated a mixture of α-acetomidocinnamic acid/ *N*-acetylphenylalanine in a ratio of 80/20. The ^{31}P NMR spectrum exhibits a doublet characteristic of complex **8b**.

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Supporting Information Available: Tables of fractional atomic coordinates, anisotropic thermal parameters for non-hydrogen atoms, and atomic coordinates for H atoms (8 pages). Ordering information is given on any current masthead page. These data have also been deposited at the Cambridge Crystallographic Data Center. Copies of the data can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K.

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