Dinuclear Palladium, Nickel, and Rhodium Complexes Based on 1,3-Bis[(2-(diphenylphosphino)benzylidene)-amino]propan-2-ol

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A new dinucleating ligand, 1,3-bis[(2-(diphenylphosphino)benzylidene)amino]-propan-2-ol (L^1H), has been synthesized from 2-(diphenylphosphino)benzaldehyde and 1,3-diaminopropanol in 85% yield. Complexation with palladium, nickel, and rhodium salts gave the following dinuclear complexes: $[M_2(L^1)(OAc)_2](BF_4)$ (**6**, M = Pd; **7**, M = Ni), $[Pd_2(L^1)Me_2](BF_4)$ (**10**), and $[Rh_2(L^1)(CO)_2](BF_4)$ (**11**). In these complexes the two metals are bridged by the secondary alkoxy group of the ligand which keeps them at a fixed distance from each other. X-ray structure determinations of $[Pd_2(L^1)(OAc)_2](BF_4)$ (**6**), $[Pd_2(L^1)Me_2](BF_4)$ (**10**) and $[Rh_2(L^1)(CO)_2](BF_4)$ (**11**) showed that both metals are in a square-planar environment and that the metal−metal distance varies from 3.5 to 3.7 Å. The related complex $Pd_2(L^1H)Me_2Cl_2$ (**9**) has also been characterized crystallographically. In palladium complex **9**, the alkoxy group does not bridge the two metal centers and a much longer metal−metal distance of 7.5 Å is found. Furthermore, the ligand L^1H is capable of forming heterodinuclear complexes. Reaction of L^1H first with $Pd(OAc)_2$ and subsequently with $Rh_2(CO)_4Cl_2$ provided the heterodinuclear complex $[PdRh(L^1H)(Cl)(CO)](BF_4)$.

Introduction

The design of dinucleating ligands which can form homo- or heterodinuclear transition-metal complexes with well defined geometries is of considerable interest, considering the rapidly evolving area of bimetallic catalysis.[1] Especially, dinuclear copper and iron complexes are widely studied for mimicking the bimetallic sites in various enzymes;[2] e.g. Cu_2 sites in hemocyanine or tyrosinase and Fe_2 sites in hemerythrin or methane monooxygenase. Often aminomethylated phenols are used as ligands for these types of dinuclear complexes, in which an additional bridging donor atom, in most cases a phenolic oxygen atom, holds the two metals at a fixed distance from each other.[2] The corresponding thiophenols are also very useful as dinucleating ligands, and Robson and co-workers showed that sulfur functions as a bridging atom in dinuclear copper,[3] nickel,[4] and palladium complexes.[5] Interestingly, the dinuclear palladium complex catalyzes the hydration of acetonitrile to acrylamide via a bimetallic pathway.[6]

Instead of a (thio)phenoxy bridge in dinucleating ligands, it is also possible to use a secondary alkoxy bridge, which furnishes ligands of greater stereochemical flexibility. These ligands can easily be synthesized via a condensation reaction of 1,3-diaminopropan-2-ol or 1,5-diaminopentan-3-ol and aldehydes. The structural and electronic properties of dinuclear copper,[7] manganese,[8] and nickel[9] complexes of these ligands have been studied extensively, and these properties were shown to depend on the metal, the endogenous backbone, the donor atoms, and the exogenous bridging

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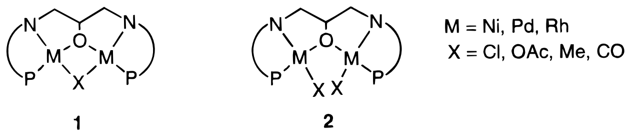
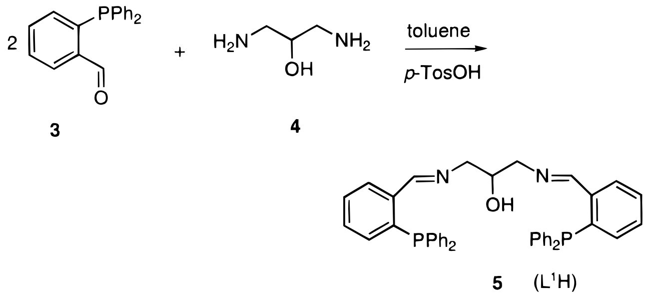


Figure 1. General structure of complexes of dinucleating iminophosphine ligands.

Scheme 1. Synthesis of 5 (L^1H)



ligand. The nature of the exogenous bridging ligand can be a single-atom donor (OR^-, Cl^-, etc.) or a two-atom donor moiety (e.g. pyrazolate or acetate).

Following our interest in bimetallic complexes and catalysis,[10] we have focused on iminophosphine dinucleating ligands with a secondary alkoxy bridging unit. The new ligand **5** contains a N_2P_2O donor set and comprises a compartmental dinucleating ligand system.[2e] Complexation with palladium, nickel, and rhodium generates complexes with the general structures **1** and **2** (Figure 1).

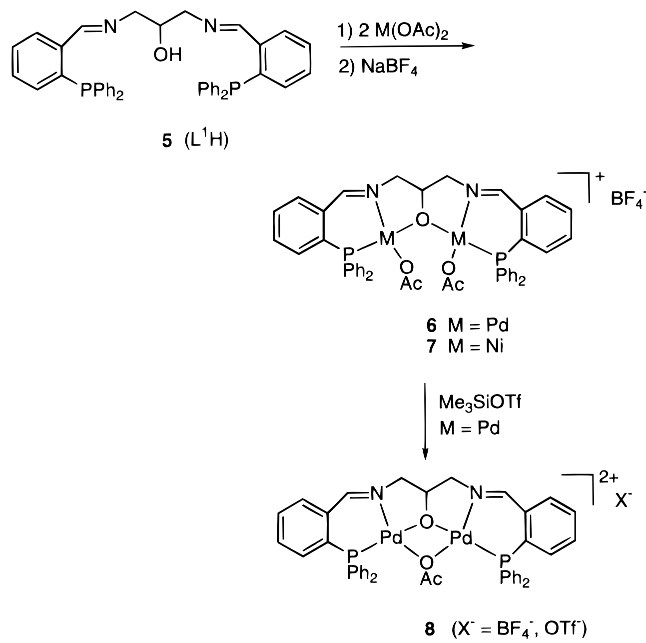
We describe here the synthesis of 1,3-bis[(2-(diphenylphosphino)benzylidene)amino]-propan-2-ol, which is a highly effective ligand for the preparation of homodinuclear palladium, nickel, and rhodium complexes as well as for the preparation of a heterodinuclear rhodium palladium complex. Furthermore, the crystal structures of several new bimetallic complexes of types **1** and **2** and the initial results of these dinuclear complexes in catalysis are reported.

Results

Synthesis of 1,3-Bis[(2-(diphenylphosphino)benzylidene)amino]propan-2-ol (L^1H). The pentadentate ligand 1,3-bis[(2-(diphenylphosphino)benzylidene)-amino]propan-2-ol (**5**; L^1H) was synthesized by condensation of 2 equiv of 2-(diphenylphosphino)benzaldehyde (**3**) and 1,3-diaminopropan-2-ol (**4**) under Dean−Stark conditions in toluene (Scheme 1). Crystallization from dichloromethane/pentane gave **5** in 85% yield as a yellow powder which was air stable. The ^{31}P NMR spectrum showed one absorption at −12.0 ppm. The structure of ligand **5** was further secured by ^1H and ^{13}C NMR spectroscopy, mass spectrometry, and elemental analysis.

Synthesis of $[M_2(L^1)(OAc)_2](BF_4)$ (M = Pd, Ni). Complexation of L^1H with 2 equiv of $Pd(OAc)_2$ in dichloromethane and subsequent anion exchange with $NaBF_4$ provided the dinuclear palladium complex **6**, in which

Scheme 2. Complexation of L^1H with $Pd(OAc)_2$ and $Ni(OAc)_2$



the alkoxy group bridges between the two palladium centers (Scheme 2). Crystals suitable for X-ray analysis were obtained from CH_2Cl_2/pentane (*vide infra*).

The ^{31}P NMR spectrum showed one absorption at 30.5 ppm, and the electrospray mass spectrum[11] showed an isotope pattern at *m/z* 963 characteristic for $[Pd_2(L^1)(OAc)_2]^+$ and at *m/z* 453 for $[Pd_2(L^1)(OAc)]^{2+}$. When 1 equiv of trimethylsilyl triflate was added to a solution of **6** in dichloromethane, one acetoxy group was removed from the dinuclear palladium complex. The absorption in the ^{31}P NMR spectrum is shifted to 34.2 ppm and only one signal is shown, which indicates that the two phosphorus atoms are identical. In the ^{19}F NMR spectrum, two absorptions are observed at −152.3 ppm for BF_4 and at −79.7 ppm for OTf. In the electrospray mass spectrum two isotope patterns were observed: one at *m/z* 453 for $[Pd_2(L^1)(OAc)]^{2+}$ and one at *m/z* 462 for $[Pd_2(L^1)(OAc)\cdot H_2O]^{2+}$. No M^+ peaks were found at *m/z* 953. These data are in accordance with dication **8**, in which one exogenous acetate ligand and the oxygen of the endogenous ligand bridge the two palladium centers.

The dinuclear nickel complex was synthesized analogously to the palladium complex **6** from L^1H and $Ni(OAc)_2$ in methanol. Anion exchange with $NaBF_4$ gave $[Ni_2(L^1)(OAc)_2](BF_4)$ (**7**), which is paramagnetic. Electrospray mass spectroscopy showed an isotope pattern at *m/z* 867 characteristic for $[Ni_2(L^1)(OAc)_2]^+$. Complex **7** was furthermore characterized by elemental analysis.

The crystal structure of **6** together with the adopted numbering scheme is shown in Figure 2. Selected bond distances and bond angles are collected in Table 1; details of the X-ray analysis are summarized in Table 5. In Figure 2, the pentadentate binucleating function of the ligand is clearly shown. The palladium centers

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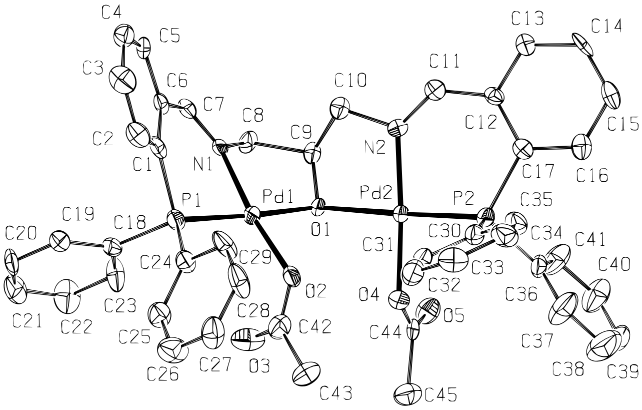


Figure 2. ORTEP plot of **6** at the 50% probability level.

Table 1. Selected Bond Distances (Å) and Bond Angles (deg) of Compound 6 (Standard Deviations in Parentheses)

Pd(1)−O(1)	2.076(4)	Pd(2)−N(2)	2.006(6)
Pd(1)−N(1)	1.978(6)	Pd(2)−P(2)	2.199(3)
Pd(1)−P(1)	2.199(3)	Pd(2)−O(4)	2.017(7)
Pd(1)−O(2)	1.986(6)	Pd(1)···Pd(2)	3.497(2)
Pd(2)−O(1)	2.073(5)		
P(1)−Pd(1)−O(1)	173.56(15)	P(2)−Pd(2)−O(4)	86.6(2)
P(1)−Pd(1)−O(2)	91.22(17)	P(2)−Pd(2)−N(2)	95.36(17)
P(1)−Pd(1)−N(1)	91.04(17)	O(1)−Pd(2)−O(4)	95.2(2)
O(1)−Pd(1)−O(2)	94.7(2)	O(1)−Pd(2)−N(2)	82.5(2)
O(1)−Pd(1)−N(1)	83.4(2)	O(4)−Pd(2)−N(2)	175.6(3)
O(2)−Pd(1)−N(1)	172.3(2)	Pd(1)−O(1)−Pd(2)	114.9(2)
P(2)−Pd(2)−O(1)	175.2(2)		

adopt a square-planar geometry. The two palladium atoms are bridged by the oxygen atom O(1) of the secondary alkoxy substituent from the ligand. The remaining square-planar coordination sites are occupied by P(1), N(1), and O(2) for Pd(1) and P(2), N(2), and O(3) for Pd(2). Remarkably, two terminal acetoxy groups are found, not one bridging acetoxy group as is usually observed in dinuclear nickel and copper complexes with an endogenous secondary alkoxy ligand.[7,9] In the crystal structure, one acetate is disordered by replacement of the acetate group by a chloride atom (Cl:OAc (%) = 10.8(9):89.2(9)). This exchange is probably due to the fact that the initial preparation of crystalline **6** was performed in refluxing chloroform instead of dichloromethane, which may have led to the incorporation of some chloride. Therefore, later experiments were all performed in dichloromethane, in which the probability of halide exchange is smaller. Indeed, analytically pure, chloride-free complex **6** was obtained in this manner.

The intramolecular Pd···Pd distance of 3.497(2) Å is slightly longer than the metal−metal distance found in dinuclear nickel and copper complexes with a secondary alkoxy bridge and a bridging exogenous ligand.[7,9] The deviations from the least-squares plane through the Pd(1), P(1), O(1), O(2), and N(1) atoms are 0.0303(6), 0.079(2), 0.087(4), 0.093(5), and −0.103(5) Å, respectively, and the equivalent values for the Pd(2), P(2), O(1), O(4), and N(2) plane are −0.060(3), 0.021(3), 0.023(4), 0.008(7), and 0.008(6) Å, respectively. The dihedral angle between the two planes is 115.38(19)°, showing a considerable bending of the two square-planar coordination sites toward each other. The Pd−O−Pd angle, which is sensitive to the twisting of the molecule and which becomes smaller upon increased bending,[9c] is 114.9(2)°. The imine moieties are not in the plane of the phenyl rings, and the torsion angle of C(1), C(6), C(7), and N(1) is −15.6(11)°. On the other side of the molecule a smaller torsion angle of −3.3(12)° for C(17), C(12), C(11), and N(2) is found. The Pd−O, Pd−N, and Pd−P distances all are in the normal range.[12]

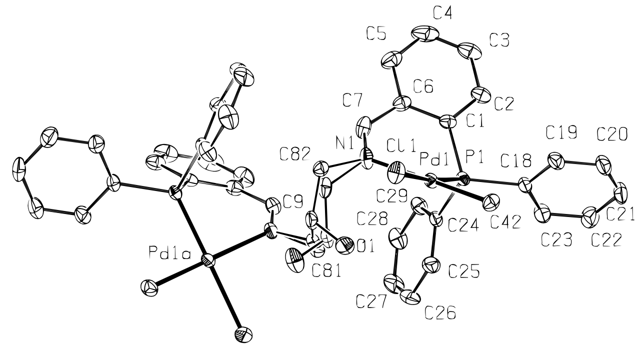
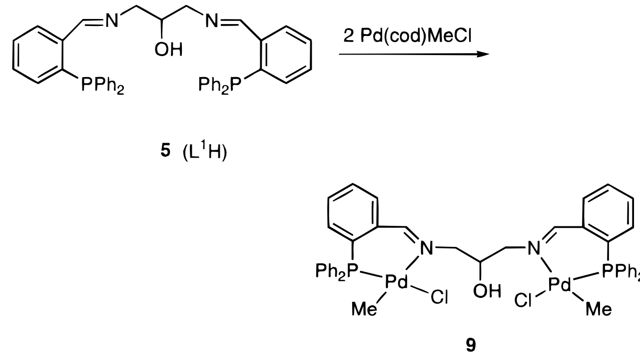


Figure 3. ORTEP plot of **9** at the 50% probability level.

Scheme 3. Synthesis of 9



Complexation of L^1H with Pd(cod)MeCl (cod = 1,5-Cyclooctadiene). The reaction of L^1H with 2 equiv of Pd(cod)MeCl in THF yielded a white-yellow precipitate (Scheme 3). Crystallization from dichloromethane/pentane provided pale yellow crystals (43% yield) of dinuclear palladium complex **9**, which were suitable for X-ray analysis (vide infra). In the ^{31}P NMR spectrum one absorption was obtained at 35.3 ppm. In the ^1H NMR spectrum, the hydroxyl proton was observed as a broad signal at 4.1 ppm, which indicates that the oxygen atom of the ligand does not bridge the two palladium centers. The methyl resonance appears as a doublet at 0.55 ppm (J = 2.93 Hz). The magnitude of this proton−phosphorus coupling indicates a cis relationship between the methyl group and phosphorus, which is due to the fact that both groups have a large trans influence.[13]

The crystal structure of **9** with adopted numbering scheme is shown in Figure 3, and selected bond distances and bond angles are collected in Table 2. The crystal structure of **9** showed C_2 symmetry. For C(8) and C(9), two orientations are found.

From Figure 3, the extended conformation of the molecule is apparent and the secondary hydroxy group does not bridge the two palladium centers. Therefore, a very large Pd···Pd distance of 7.0529(5) Å is observed. Each palladium is in a square-planar environment, and

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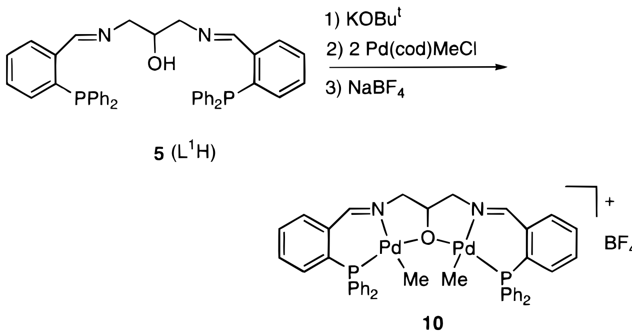
Table 2. Selected Bond Distances (Å) and Bond Angles (deg) of Compound 9 (Standard Deviations in Parentheses)

Pd(1)−Cl(1)	2.3837(9)	Pd(1)−N(1)	2.172(3)
Pd(1)−P(1)	2.2024(9)	Pd(1)−C(42)	2.037(4)
Cl(1)−Pd(1)−P(1)	172.89(3)	P(1)−Pd(1)−N(1)	86.50(9)
Cl(1)−Pd(1)−N(1)	90.97(9)	P(1)−Pd(1)−C(42)	93.86(11)
Cl(1)−Pd(1)−C(42)	88.76(11)	N(1)−Pd(1)−C(42)	179.11(12)

Scheme 4. Synthesis of 10



the four coordination sites are occupied by P(1), N(1), Cl(1), and C(42). The chloride atom is situated trans to phosphorus, and the methyl group is trans to nitrogen, as was also indicated by NMR spectroscopy (*vide supra*). The deviations of the least-squares plane of Pd(1), P(1), N(1), Cl(1), and C(42) are 0.04672(19), −0.0887(9), 0.062(3), −0.0821(9), and 0.062(3) Å, respectively. The crystal structure shows intramolecular hydrogen bonds of 3.139(5) Å between the hydroxy hydrogen and both chlorides. Only one of the hydrogen bridges is shown. The Pd−N, Pd−P, Pd−C, and Pd−Cl bond distances in dinuclear complex **9** are all in the normal range found for mononuclear Pd−Me complexes.[14]

To obtain $[Pd(L^1)Me_2](BF_4)$ (**10**), in which the alkoxide moiety bridges the two palladium centers, the hydroxy group of L^1H was first deprotonated with potassium *tert*-butoxide in dichloromethane. Subsequently, 2 equiv of Pd(cod)MeCl was added and, after an anion exchange reaction with $NaBF_4$, complex **10** was isolated (Scheme 4). Crystals suitable for X-ray analysis were obtained via crystallization from dichloromethane/pentane. In the ^{31}P NMR spectrum, one absorption was seen at 39.8 ppm, which is shifted significantly compared to the absorption for the phosphine moiety found in $Pd_2(L^1H)Me_2Cl_2$ (**9**). In **10**, the methyl group is also positioned cis toward the phosphorus atom and in the ^{1}H NMR spectrum a doublet for the methyl group was obtained at 0.49 ppm with $J_{PH} = 1.96$ Hz.

The crystal structure of **10** together with the adopted numbering scheme is shown in Figure 4, and selected bond distances and angles are collected in Table 3. In complex **10**, the two palladium centers are indeed bridged by the oxygen atom of the endogenous ligand. Therefore, the Pd···Pd distance of 3.7598(5) Å is much shorter than that found in complex **9** (7.0529(5) Å) with the nonbridging hydroxyl group. The Pd···Pd distance is slightly longer than that found in the corresponding complex $[Pd_2(L^1)(OAc)_2](BF_4)$ (**6**). The two palladium atoms are in a square-planar environment, and the

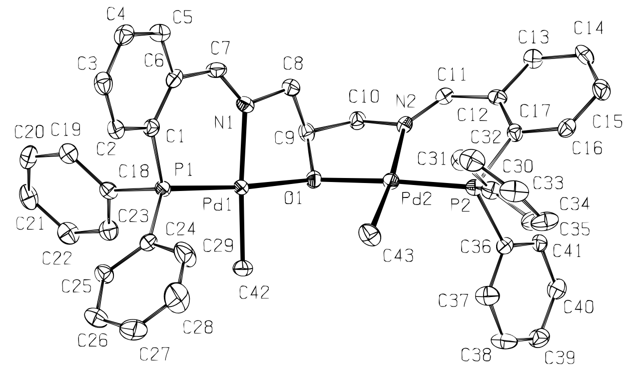
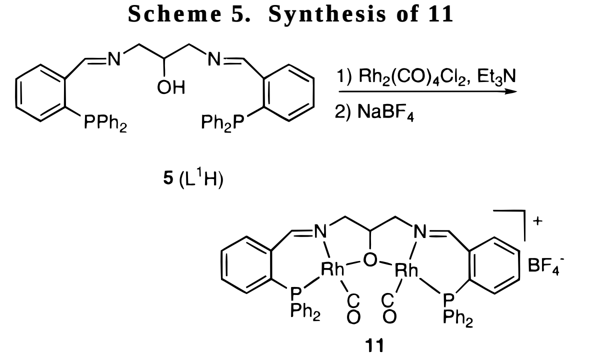


Figure 4. ORTEP plot of **10** at the 50% probability level. The bridging moiety is disordered. O(1) is hydrogen-bonded to Cl(1).

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) of Compound 10 (Standard Deviations in Parentheses)

Pd(1)−O(1)	2.093(4)	Pd(2)−N(2)	2.076(4)
Pd(1)−N(1)	2.087(4)	Pd(2)−P(2)	2.1763(14)
Pd(1)−P(1)	2.1758(14)	Pd(2)−C(43)	2.040(5)
Pd(1)−C(42)	2.041(5)	Pd(1)···Pd(2)	3.7598(5)
Pd(2)−O(1)	2.096(4)		
P(1)−Pd(1)−O(1)	173.99(10)	P(2)−Pd(2)−N(2)	94.47(11)
P(1)−Pd(1)−N(1)	93.78(11)	P(2)−Pd(2)−C(43)	91.06(15)
P(1)−Pd(1)−C(42)	91.62(15)	O(1)−Pd(2)−N(2)	82.32(14)
O(1)−Pd(1)−N(1)	81.75(14)	O(1)−Pd(2)−C(43)	92.33(17)
O(1)−Pd(1)−C(42)	92.73(18)	N(2)−Pd(2)−C(43)	174.38(18)
N(1)−Pd(1)−C(42)	174.25(18)	Pd(1)−O(1)−Pd(2)	127.66(17)
P(2)−Pd(2)−O(1)	172.18(11)		

Scheme 5. Synthesis of 11



maximum deviation from the least-squares plane of Pd(1), P(1), O(1), N(1), and C(42) is 0.0434(3) Å. The related value for the Pd(2), P(1), N(2), O(1), and C(43) plane is 0.0839(11) Å. The bending of the two coordination planes with respect to each other is 118.02(14)°, and the Pd−O−Pd angle of 127.66(17)° is slightly larger than that found in $[Pd_2(L^1)(OAc)_2](BF_4)$. The imine moieties are not in the plane of the phenyl rings, and the torsion angles for C(1), C(6), C(7), and N(1) and for C(17), C(12), C(11), and N(2) are −12.4(8) and 3.0(7)°, respectively.

Synthesis of $[Rh_2(L^1)(CO)_2](BF_4)$ (11). Complexation of L^1H with $Rh_2(CO)_4Cl_2$ in dichloromethane in the presence of 1 equiv of diisopropylethylamine and subsquent anion exchange with $NaBF_4$ gave the dinuclear rhodium dicarbonyl complex $[Rh_2(L^1)(CO)_2](BF_4)$ (**11**) in 73% yield (Scheme 5). Crystals suitable for X-ray analysis were obtained via crystallization from dichloromethane/pentane.

In the ^{31}P NMR spectrum a doublet was observed at 51.7 ppm with a rhodium−phosphorus coupling of 159

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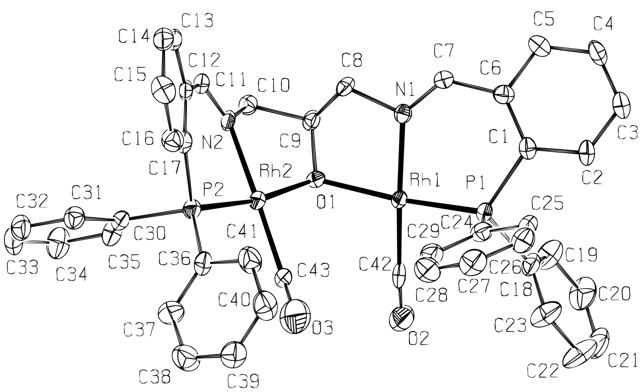


Figure 5. ORTEP plot of **11** at the 50% probability level.

Table 4. Selected Bond Distances (Å) and Bond Angles (deg) of Compound 11 (Standard Deviations in Parentheses)

Rh(1)−O(1)	2.088(4)	Rh(2)−N(2)	2.054(5)
Rh(1)−N(1)	2.054(5)	Rh(2)−P(2)	2.1938(17)
Rh(1)−P(1)	2.1962(16)	Rh(2)−C(43)	1.954(7)
Rh(1)−C(42)	1.882(6)	Rh(1)···Rh(2)	3.4605(7)
Rh(2)−O(1)	2.104(4)		

P(1)−Rh(1)−O(1)	171.43(12)	P(2)−Rh(2)−N(2)	89.13(16)
P(1)−Rh(1)−N(1)	92.33(13)	P(2)−Rh(2)−C(43)	91.74(18)
P(1)−Rh(1)−C(42)	89.40(18)	O(1)−Rh(2)−N(2)	81.78(19)
O(1)−Rh(1)−N(1)	81.70(17)	O(1)−Rh(2)−C(43)	97.2(2)
O(1)−Rh(1)−C(42)	97.5(2)	N(2)−Rh(2)−C(43)	176.5(2)
N(1)−Rh(1)−C(42)	170.2(3)	Rh(1)−O(1)−Rh(2)	111.27(18)
P(2)−Rh(2)−O(1)	171.07(12)		

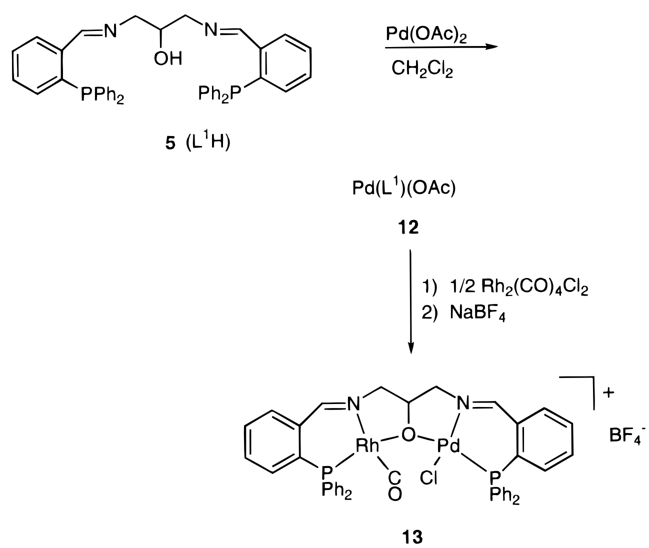
Hz. The coordination of the carbonyl to rhodium was evident from IR spectroscopy, which gave a vibration at 2016 cm^{-1}, and from ^{13}C NMR spectroscopy, which gave a CO absorption at 190.0 ppm ($J_{Rh-C} = 75.2$ Hz, $J_{P-C} = 20.2$ Hz).

The crystal structure of **11** together with the adopted numbering scheme is shown in Figure 5. Selected bond distances and bond angles are collected in Table 4. The two rhodium atoms are bridged by the secondary alkoxy group of the endogenous ligand O(1), and the Rh···Rh distance is 3.4605(7) Å. Both rhodium centers adopt a square-planar geometry, and the other coordinating atoms to the rhodium atoms are P(1), N(1), and C(42) for Rh(1) and P(2), N(2), and C(43) for Rh(2). The maximum deviation from the Rh(1), P(1), N(1), O(1), and C(42) least-squares plane is 0.144(5) Å, and the deviation for the Rh(2), P(2), N(2), O(1), and C(43) plane is 0.038(5) Å. The angle between the square-planar rhodium coordination sites is 109.0(2)°, and the Rh−O−Rh angle is 111.27(18)°, which is the highest bending thus found in these types of complexes.[9c]

The torsion angles of C(1), C(6), C(7), N(1), and C(17), C(12), C(11), N(2) are −10.1(12), and −16.6(9)°, respectively. The Rh−P, Rh−N, Rh−O, and Rh−C distances all are in the normal range for rhodium complexes.[15]

Synthesis of the Heterodinuclear Complex [PdRh(L[1])(CO)Cl](BF_4) (13). So far, it has been shown that L[1]H is an excellent ligand for the synthesis of homodinuclear transition-metal complexes. In catalytic reactions two similar metals might cooperate with each other, lowering the transition states during catalysis. Complexes with two distinct metals are also interesting because of the different functions which can be performed by the two metals in the catalytic cycle. An elegant example has been published by Sawamura and co-workers, in which a two-component rhodium palladium system catalyzes the allylic alkylation of activated nitriles.[16] To investigate the feasibility of obtaining a heterodinuclear complex with the ligand L[1]H, we focused on the synthesis of a rhodium palladium mixed system.

Scheme 6. Synthesis of 13



For the synthesis of rhodium palladium complex **13**, L[1]H was first complexed with 1 equiv of $Pd(OAc)_2$ in dichloromethane (Scheme 6). This reaction probably results in the mononuclear complex Pd(L[1])(OAc) (**12**), for which the coordination mode is not known at the present. In the ^{31}P NMR spectrum one broad signal was obtained at 30.7 ppm. Subsequently, 0.5 equiv of $Rh_2(CO)_4Cl_2$ was added and finally an anion exchange was performed with $NaBF_4$ to provide complex **13**. In dinuclear complex **13**, the acetate group is replaced by a chloride which is derived from $Rh_2(CO)_4Cl_2$. In a reverse sequence, where L[1]H was first complexed with $Rh(CO)_4Cl_2$, a mononuclear rhodium complex was formed which did not react with $Pd(OAc)_2$.

In the ^{31}P NMR spectrum, two absorptions were observed: i.e. a singlet at 33.7 ppm derived from the phosphorus atom which coordinates to palladium and a doublet at 52.1 ppm with $J_{Rh-P} = 162$ Hz, which is derived from the phosphorus atom coordinating to rhodium. In the ^{1}H NMR spectrum, the five hydrogen atoms from the propanol backbone are observed separately, which shows clearly the dissymmetry of complex **13**. In contrast, in the symmetric homodinuclear complexes (*vide supra*) the methylene groups were identical. For **13** four doublets of doublets (at 4.38, 4.15, 4.05, 3.85 ppm) were obtained which are derived from the CH_2 groups and one broad absorption (4.27 ppm) was due to the CH moiety. Furthermore, the two imine protons were found at 8.80 and 8.51 ppm. In the electrospray mass spectrum a M^+ peak was obtained at *m/z* 907, which is in agreement with $[PdRh(L^1)(CO)Cl]^+$. In addition, one peak was observed at *m/z* 879, which

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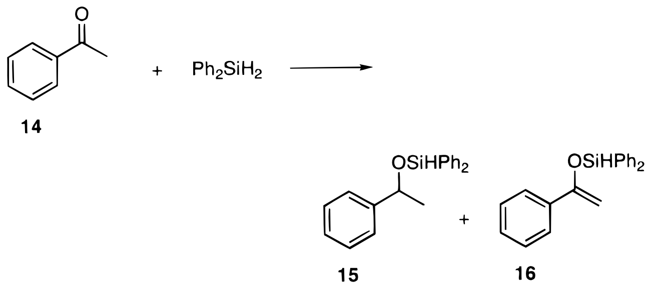
Scheme 7. Hydrosilylation of Acetophenone



corresponds to the M$^+$ complex minus a carbon monoxide, i.e. [PdRh(L^1)Cl]$^+$. In the IR spectrum a strong carbonyl absorption was observed at 2012 cm^{-1}.

Catalysis. The palladium complexes [Pd_2(L^1)(OAc)$_2$]-(BF_4) (**6**) and [Pd_2(L^1)(Me)$_2$](BF_4) (**10**) were unfortunately not active in oligomerization reactions of ethylene.[17] Also, no activity was found in the copolymerization reaction of ethylene and carbon monoxide.[18]

The dinuclear rhodium complex **11** was used in the hydrosilylation reaction[19] of acetophenone (Scheme 7). In this catalytic reaction, one of the Si−H moieties of diphenylsilane adds to the carbonyl carbon to give silyl ether **15**, which can be hydrolyzed to 1-phenylethanol. As a byproduct a small amount of silyl enol ether **16** might be obtained, which after hydrolysis is converted to the starting material. The hydrosilylation reaction of **14**, catalyzed by **11** (0.5 mol %), gave after 3 days in toluene a conversion of 93%, which is rather slow compared to reported catalytic systems.[19] Unexpectedly, a 3:7 ratio of the products **15** and **16** was found, which implies that **16** is the main product. Therefore, complex **11** is not very effective for the reduction of ketones to alcohols by hydrosilylation. However, it appears that a very mild catalytic method has been found for the synthesis of enol ethers.[20]

Furthermore, the homodinuclear rhodium complex **11** and the heterodinuclear rhodium palladium complex **13** were tested in the hydroboration reaction of alkenes with catecholborane (Scheme 8). Additions of catecholborane to alkenes without catalyst are generally very slow, but they are accelerated enormously using a catalytic amount of transition-metal complexes.[21] Furthermore, the selectivity changes such that addition occurs exclusively at the C═C bond, instead of addition at more reactive functional groups such as ketones and nitriles.[22]

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(20) The scope and limitations will be investigated and the results published separately.

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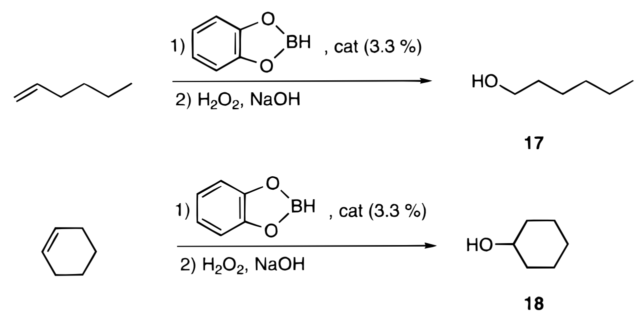
Scheme 8. Hydroboration of 1-Hexene and Cyclohexene



The hydroboration reaction of 1-hexene catalyzed by **11** gave, after 20 min of reaction time followed by a standard workup procedure (NaOH, H_2O_2), 80% conversion to 1-hexanol. Due to the isomerization reaction also catalyzed by **11**, 20% of internal hexenes was obtained. The rhodium palladium complex **13** gave even more isomerization, and the ratio of internal hexenes to 1-hexanol was 1:1.

Because of the relatively high isomerization activity of **11** and **13**, cyclohexene was used, as it remains unchanged upon isomerization. In comparison to 1-hexene, the hydroboration reaction of cyclohexene is much slower because cyclohexene is an internal alkene. The hydroboration reaction of cyclohexene catalyzed by **11** gave after oxidative workup 90% conversion to cyclohexanol after 24 h. The rates are comparable with hydroboration reactions by mononuclear catalysts known in the literature.[17]

Conclusions

The new compartmental dinucleating ligand **5** (L^{1}H) with a PNONP donor set has been synthesized in 85% yield. Complexation with palladium, nickel, and rhodium gave the dinuclear complexes [M_2(L^1)(OAc)$_2$](BF_4) (M = Pd, **6**; M = Ni, **7**), [Pd_2(L^1)(Me)$_2$](BF_4) (**10**), and [Rh_2(L^3)(CO)$_2$](BF_4) (**11**). In these complexes, the oxygen atom of the dinucleating ligand functions as a bridging atom between the two metals and binds them at a fixed distance with respect to each other, i.e. 3.5−3.8 Å, as confirmed by X-ray analysis. In the related complex Pd_2(L^{1}H)(Me)$_2Cl_2$, in which the oxygen atom of the ligand does not bridge, the two metal centers have a much larger M···M distance of 7.5 Å. Finally, the highly interesting heterodinuclear complex [PdRh(L^1)-(CO)Cl](BF_4) has been synthesized by sequential complexation with Pd(OAc)$_2$ and with $Rh_2(CO)_4Cl_2$. Preliminary results on applications of these new dinuclear complexes in catalysis are also given.

Experimental Section

All operations were carried out under an atmosphere of argon. 2-(Diphenylphosphino)benzaldehyde[23] and Pd(cod)-MeCl[24] were prepared by literature procedures. 1,3-Diaminopropan-2-ol was obtained from Fluka, and Pd(OAc)$_2$, Ni(OAc)$_2$, $Rh_2Cl_2(CO)_4$, and Me_3SiOTf were obtained from Aldrich and

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were used as received. ^1H, ^{31}P, and ^{13}C NMR spectra were recorded at 200, 81, and 50 MHz, respectively, with a Varian Gemini 200 FT NMR spectrometer. Chemical shifts are reported in ppm and referenced to the residual deuterated solvent signals for ^1H and ^{13}C and external triphenyl phosphate (δ −18 ppm) for ^{31}P. IR spectra were measured using a Perkin-Elmer 841 spectrometer. Electron ionization mass spectra (EI-MS) were measured on a AEI-MS-902 spectrometer; for electrospray MS (ES-MS) we used a Nermag-R-30-10 spectrometer. Elemental analyses were determined in the microanalytical department of the University of Groningen.

1,3-Bis[(2-(diphenylphosphino)benzylidene)amino]-propan-2-ol (5). A solution of 1,3-diaminopropan-2-ol (564 mg, 6.25 mmol) and 2-(diphenylphosphino)benzaldehyde (4.0 g, 13.8 mmol) in toluene (50 mL) was refluxed under Dean−Stark conditions for 5 h. The solution was evaporated to dryness, and the product was crystallized from CH_2Cl_2/pentane, yielding a yellow powder. Yield: 3.39 g (85%). Mp: 153.9−154.0 °C. Anal. Calcd for $C_{41}H_{36}N_2OP_2$: C, 77.59; H, 5.72; N, 4.41; P, 9.76. Found: C, 77.32; H, 5.74; N, 4.38; P, 9.62. ^{31}P NMR ($CDCl_3$): δ −12.0 (s). ^1H NMR ($CDCl_3$): δ 8.7 (d, J = 3.9 Hz, 2 H, HC=N), 7.8 (m, 2H, Ar H), 7.5−7.2 (m, 24H, Ar H), 6.9 (m, 2H, Ar H), 3.8 (m, 1H, CH), 3.4 (d, J = 6.0 Hz, 4H, CH_2), 2.5 (d, J = 5.1 Hz, 1H, OH). ^{13}C NMR: δ 161.6 (d, $^3J_{PC}$ = 14.9 Hz, CH), 139.2 (d, $^1J_{PC}$ = 16.8 Hz, C), 137.2 (d, $^2J_{PC}$ = 11.8 Hz, C), 137.0 (t, $^1J_{PC}$ = 9.2 Hz, C), 134.0 (d, $^2J_{PC}$ = 3.8 Hz, CH), 133.6 (CH), 133.5 (CH), 130.0 (CH), 128.8 (d, $^2J_{PC}$ = 4.2 Hz, CH), 128.6 (CH), 128.4 (d, $^3J_{PC}$ = 6.9 Hz, CH), 70.3 (CH), 64.2 (CH_2). EI-MS: *m*/*z* 634 (M^+). HRMS: calcd *m*/*z* 634.230, found *m*/*z* 634.230.

[$Pd_2(L^1)(OAc)_2$](BF_4) (6). $Pd(OAc)_2$ (177 mg, 0.79 mmol) was added to a solution of L^1H (250 mg, 0.39 mmol) in CH_2Cl_2 (5 mL), and the mixture was refluxed for 2 h. Then $NaBF_4$ (43.3 mg, 0.39 mmol) was added and the solution was refluxed for another 30 min. The solution was cooled and filtered, and the filtrate was added dropwise to hexane (30 mL). The resulting precipitate was filtered off, washed with hexane, and dried under vacuum, yielding a yellow-brown powder (373 mg, 91%). Suitable crystals for X-ray analysis were obtained by crystallization from CH_2Cl_2/pentane. Anal. Calcd for $C_{45}H_{41}BF_4N_2O_5P_2Pd_2\cdot 2CH_2Cl_2$: C, 46.22; H, 3.71; N, 2.29. Found: C, 46.18; H, 3.84; N, 2.40. ^{31}P NMR ($CDCl_3$): δ 30.5 (s). ^1H NMR ($CDCl_3$): δ 8.5 (s, 2 H, HC=N), 7.9 (m, 2H, Ar H), 7.8−7.2 (m, 28 H, Ar H), 4.5 (m, 1H, CH), 3.2 (m, 4H, CH_2), 1.4 (s, 6H, CH_3). ES-MS: *m*/*z* 963 (M^+), 453 [($M^+ - OAc)^{2+}$].

[$Ni_2(L^1)(OAc)_2$](BF_4) (7). $Ni(OAc)_2\cdot 4H_2O$ (225 mg, 0.79 mmol) was added to a solution of L^1H (250 mg, 0.39 mmol) in methanol (10 mL), and the mixture was refluxed for 1 h. Then $NaBF_4$ (43.3 mg, 0.39 mmol) was added, and the solution was refluxed for another 30 min. Cooling the solution to −20 °C yielded **7** as a red-brown powder. Yield: 212 mg (56%). Anal. Calcd for $C_{45}H_{41}BF_4N_2O_5P_2Ni_2\cdot CH_3OH$: C, 55.92; H, 4.59; N, 2.83. Found: C, 56.04; H, 4.53; N, 2.76. ES-MS: *m*/*z* 867 (M^+).

[$Pd_2(L^1)(OAc)$](BF_4)(OTf) (8). Me_3SiOTf (8.1 μL, 42 μmol) was added to a solution of [$Pd_2(L^1)(OAc)_2$](BF_4) (45 mg, 42 μmol) in CH_2Cl_2 (3 mL). The reaction mixture was stirred for 1 h, filtered, and poured in pentane. The resulting precipitate was collected, washed with pentane, and dried under vacuum, yielding a brown powder. Yield: 40 mg (83%). ^{31}P NMR ($CDCl_3$): δ 30.5 (s). ^{19}F NMR ($CDCl_3$): δ −152.3 (s), −79.7 (s). ^1H NMR ($CDCl_3$): δ 8.78 (s, 2H, CH=N), 8.12 (m, 2H, Ar H), 7.78−7.38 (m, 26H, Ar H), 4.54−4.20 (m, 5H, CH_2, CH), 2.03 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 181.9 (C), 168.3 (d, $^3J_{PC}$ = 6.5 Hz, CH), 139.5 (d, $^3J_{PC}$ = 9.2 Hz, CH), 135.9 (d, $^2J_{PC}$ = 17.6 Hz, C), 135.2 (d, $^2J_{PC}$ = 8.0 Hz, CH), 134.0 (CH), 133.4 (d, $^2J_{PC}$ = 12.2 Hz, CH), 133.3 (d, $^2J_{PC}$ = 12.2 Hz, CH), 133.1 (CH), 129.7 (d, $^3J_{PC}$ = 6.1 Hz, CH), 129.4 (d, $^3J_{PC}$ = 5.7 Hz, CH), 124.7 (d, $^1J_{PC}$ = 60.3 Hz, C), 124.2 (d, $^1J_{PC}$ = 60.3 Hz, C), 117.8 (d, $^1J_{PC}$ = 56.1 Hz, C), 73.1 (CH), 71.2 (CH_2), 23.5 (CH_3); 2 CH's were not resolved due to overlap. ES-MS: *m*/*z* 462 ($M^{2+} + H_2O$), 453 (M^{2+}).

$Pd_2(L^1H)Me_2Cl_2$ (9). Pd(cod)MeCl (84 mg, 0.32 mmol) was added to a solution of L^1H (100 mg, 0.16 mmol) in THF (2 mL), and the mixture was stirred for 1 h. The white precipitate was collected and crystallized from CH_2Cl_2/pentane, yielding crystals suitable for X-ray analysis. Yield: 65 mg (43%). Anal. Calcd for $C_{43}H_{42}Cl_2N_2OP_2Pd_2\cdot 0.5CH_2Cl_2$: C, 52.72; H, 4.37; N, 2.82. Found: C, 53.06; H, 4.43; N, 2.80. ^{31}P NMR ($CDCl_3$): δ 35.3 (s). ^1H NMR ($CDCl_3$): δ 8.36 (s, 2H, HC=N), 7.65−7.03 (m, 28H, Ar H), 4.55 (br d, J = 11.7 Hz, 2H, CH_2), 3.89 (br, 2H, CH, OH), 3.87 (dd, J = 10.5 Hz, J = 5.86 Hz, 2H, CH_2), 0.55 (d, J = 2.93 Hz, 6H, CH_3). ^{13}C NMR ($CDCl_3$): δ 165.6 (d, $^3J_{PC}$ = 4.9 Hz, CH), 137.2 (d, $^2J_{PC}$ = 14.9 Hz, C), 136.5 (d, $^2J_{PC}$ = 9.2 Hz, CH), 134.0 (d, $^2J_{PC}$ = 12.9 Hz, CH), 133.9 (CH), 133.7 (d, $^2J_{PC}$ = 12.3 Hz, CH), 132.1 (d, $^3J_{PC}$ = 6.9 Hz, CH), 131.5 (d, $^3J_{PC}$ = 1.5 Hz, CH), 131.2 (d, $^4J_{PC}$ = 1.9 Hz, CH), 131.0 (d, $^4J_{PC}$ = 1.9 Hz, CH), 128.8 (d, $^1J_{PC}$ = 53.2 Hz, C), 128.6 (d, $^1J_{PC}$ = 55.0 Hz, C), 128.8 (d, $^3J_{PC}$ = 7.6 Hz, CH), 128.6 (d, $^3J_{PC}$ = 7.6 Hz, CH), 125.3 (d, $^1J_{PC}$ = 42.7 Hz, C), 71.0 (CH), 66.5 (CH_2), 1.9 (CH_3).

[$Pd_2(L^1)Me_2$](BF_4) (10). $KOBu^t$ (17.6 mg, 0.16 mmol) was added to a solution of L^1H (100 mg, 0.16 mmol) in CH_2Cl_2 (5 mL). After the mixture was stirred for 30 min, Pd(cod)MeCl (84 mg, 0.32 mmol) was added and this mixture was stirred for 1 h. Then, $NaBF_4$ (17.6 mg, 0.16 mmol) was added and the reaction mixture was stirred for another 12 h. The solution was added dropwise to pentane (25 mL). The resulting precipitate was collected, washed with pentane and dried under vacuum, yielding a yellow powder. Crystals suitable for X-ray analysis were obtained by crystallization from CH_2Cl_2/pentane. Yield: 52 mg (34%). Anal. Calcd for $C_{43}H_{41}BF_4N_2OP_2Pd_2\cdot CH_2Cl_2$: C, 50.41; H, 4.31; N, 2.78. Found: C, 49.99; H, 4.12; N, 2.61. ^{31}P NMR ($CDCl_3$): δ 39.8 (s). ^1H NMR ($CDCl_3$): δ 8.73 (s, 2H, HC=N), 7.87 (m, 2H, Ar H), 7.67 (t, J = 7.6 Hz, 2H, Ar H), 7.63−7.23 (m, 24H, Ar H), 4.5 (br, 1H, CH), 4.1 (m, 4H, CH_2), 0.49 (d, J = 1.97 Hz, 6H, CH_3). ^{13}C NMR ($CDCl_3$): δ 162.9 (CH), 137.9 (d, $^2J_{PC}$ = 9.8 Hz, CH), 136.8 (d, $^2J_{PC}$ = 15.8 Hz, C), 135.0 (CH), 133.6 (d, $^2J_{PC}$ = 13.4 Hz, CH), 132.6 (d, $^3J_{PC}$ = 7.3 Hz, CH), 132.2 (CH), 131.2 (CH), 131.0 (CH), 130.2 (d, $^1J_{PC}$ = 29.3 Hz, C), 129.4 (d, $^1J_{PC}$ = 28.1 Hz, C), 128.8 (d, $^3J_{PC}$ = 11.0 Hz, CH), 128.7 (d, $^2J_{PC}$ = 12.2 Hz, CH), 123.8 (d, $^1J_{PC}$ = 46.4 Hz, C), 76.8 (CH), 66.4 (CH_2), 2.3 (CH_3); 1 CH was not resolved due to overlap. ES-MS: *m*/*z* 877 (M^+).

[$Rh_2(L^1)(CO)_2$](BF_4) (11). $Rh_2(CO)_4Cl_2$ (50 mg, 0.13 mmol) and Et_3N (18 μL, 0.13 mmol) were added to a solution of L^1H (82 mg, 0.13 mmol) in CH_2Cl_2 (2 mL), and the mixture was stirred for 1 h. Then $NaBF_4$ (14.1 mg, 0.13 mmol) was added and the mixture was stirred for another 12 h. Crystals suitable for X-ray analysis were obtained by crystallization from CH_2Cl_2/pentane. Yield: 72 mg (73%). Anal. Calcd for $C_{43}H_{35}BF_4N_2O_3P_2Rh_2$: C, 52.58; H, 3.59; N, 2.85. Found: C, 52.51; H, 3.74; N, 2.83. ^{31}P NMR ($CDCl_3$): δ 51.7 (d, J_{Rh-P} = 159 Hz). ^1H NMR ($CDCl_3$): δ 9.1 (2H, s, HC=N), 7.9−7.2 (28H, m, Ar H), 4.3 (1H, br, CH), 4.1 (4H, br, CH_2). ^{13}C NMR ($CDCl_3$): δ 190.0 (dd, $^1J_{RhC}$ = 75.2 Hz, $^2J_{PC}$ = 20.2 Hz, C), 166.6 (d, $^3J_{PC}$ = 6.9 Hz, CH), 137.8 (d, $^2J_{PC}$ = 8.4 Hz, CH), 136.0 (dd, $^1J_{PC}$ = 16.8 Hz, $^2J_{RhC}$ = 1.9 Hz, C), 133.4 (d, $^2J_{PC}$ = 12.2 Hz, CH), 133.0 (CH), 132.5 (d, $^1J_{PC}$ = 14.5 Hz, C), 131.8 (d, $^3J_{PC}$ = 1.5 Hz, CH), 131.4 (d, $^2J_{PC}$ = 14.1 Hz, C), 131.1 (CH), 128.8 (d, $^3J_{PC}$ = 2.7 Hz, CH), 128.5 (d, $^3J_{PC}$ = 2.7 Hz, CH), 124.6 (d, $^1J_{PC}$ = 44.6 Hz, C), 73.7 (CH), 67.5 (CH_2). 1 CH was not resolved. IR ($CHCl_3$): ν_{max}/cm^{-1} (CO) 2016 (s). ES-MS: *m*/*z* 895 (M^+).

PdRh(L^1)(CO)(Cl)(BF_4) (13). $Pd(OAc)_2$ (58 mg, 0.26 mmol) was added to a solution of L^1H (163 mg, 0.26 mmol) in CH_2Cl_2 (5 mL). The solution was refluxed for 1 h. Then $Rh_2(CO)_4Cl_2$ (50 mg, 0.13 mmol) was added and the mixture was stirred for 1 h. Finally $NaBF_4$ (28.2 mg, 0.26 mmol) was added and the reaction mixture was stirred for another 30 min. The solution was added dropwise to hexane (25 mL). The resulting precipitate was collected, washed with hexane, and dried under

Table 5. Summary of Crystallographic Data

	6	9	10	11
		Crystal Data		
chem formula	$C_{45}H_{41}N_2O_5P_2Pd_2BF_4 \cdot 2CH_2Cl_2$ [−0.108 ($C_2H_3O_2$) + 0.108 (Cl)]	$C_{43}H_{42}Cl_2N_2OP_2Pd_2$	$C_{43}H_{41}N_2OP_2Pd_2BF_4 \cdot 2CH_2Cl_2$	$C_{43}H_{35}N_2O_3P_2Rh_2BF_4 \cdot 2CH_2Cl_2$
mol wt	1218.74	948.51	1133.27	1152.19
cryst syst	triclinic	monoclinic	triclinic	triclinic
space group	$P\bar{1}$ (No. 2)	$C2/c$ (No. 15)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a, Å	13.4207(12)	22.0020(14)	11.0224(15)	13.0693(9)
b, Å	13.7895(8)	10.4889(6)	11.884(4)	13.4963(9)
c, Å	14.0514(8)	17.4192(11)	18.862(3)	14.0695(9)
α, deg	102.068(4)	90	105.34(2)	101.822(5)
β, deg	99.063(6)	92.643(5)	99.845(11)	97.726(5)
γ, deg	100.789(6)	90	97.54(2)	100.113(5)
V, Å^3	2445.1(3)	4015.7(4)	2306.8(10)	2353.6(3)
D_{calcd}, g cm^{-3}	1.655	1.569	1.632	1.626
Z	2	4	2	2
$F(000)$	1221	1912	1136	1152
μ(Mo Kα), cm^{-1}	10.9	11.4	11.3	10.5
color	yellowish	yellowish	colorless	red
cryst size, mm	0.10 × 0.18 × 0.50	0.15 × 0.25 × 0.40	0.15 × 0.40 × 0.65	0.30 × 0.30 × 0.30
		Data Collection		
T, K	150	150	150	150
radiation (Mo Kα), Å	0.710 73	0.710 73	0.710 73	0.710 73
θ_{min}, θ_{max}, deg	1.5, 26.0	1.9, 27.5	1.1, 27.6	1.5, 27.5
scan type and range, deg	ω, 0.71 + 0.35 tan θ	ω, 0.64 + 0.35 tan θ	ω, 1.54 + 0.35 tan θ	ω, 1.39 + tan θ
data set	−17 to +17; −17 to +17; 0−18	−28 to +28; 0−13; 0−22	−14 to +14; −15 to +10; −23 to +24	−16 to +16; 0−17; −18 to +17
total and unique no. of data	10 018, 9602	4748, 4605	12 574, 10 623	10 933, 10 494
no. of obsd data ($I > 2.0\sigma(I)$)	5536	3725	7697	7255
		Refinement		
N_{ref}, N_{par}	8950, 615	4605, 256	10 622, 589	10 493, 568
R^a	0.0646	0.0363	0.0473	0.0598
wR2^b	0.1298	0.0849	0.1072	0.1560
w^c	$1/[\sigma^2(F_o^2) + (0.0351P)^2]$	$1/[\sigma^2(F_o^2) + (0.0377P)^2 + 4.1816P]$	$1/[\sigma^2(F_o^2) + (0.0428P)^2 + 3.0562P]$	$1/[\sigma^2(F_o^2) + (0.0677P)^2 + 6.9539P]$
S	1.04	1.06	1.01	1.03
max and av shift/error	0.00, 0.00	0.001, 0.000	0.01, 0.00	0.001, 0.000
min, max resd dens e/Å^3	−0.91, 0.74	−0.43, 0.64	−0.72, 0.87	−1.06, 1.75

^{a} $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. ^{b} wR2 = $\{\sum w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. ^{c} $P = (F_o^2 + 2F_c^2)/3$.

vacuum, yielding a red powder which was crystallized from CH_2Cl_2/pentane. Yield: 64 mg (25%). ^{31}P NMR ($CDCl_3$): δ 52.1 (d, J_{Rh-P} = 162 Hz), 33.7 (s). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.80 (d, J_{PC} = 2.3 Hz, 1H, CH=N), 8.50 (s, 1H, CH=N), 8.12 (m, 1H, Ar H), 7.81−7.76 (m, 2H, Ar H), 7.67−7.36 (m, 23H, Ar H), 7.26−7.16 (m, 2H, Ar H), 4.38 (dd, J = 13.5 and 3.7 Hz, 1H, CH_2), 4.27 (br, 1H, CH), 4.15 (dd, J = 13.4 and 5.2 Hz, 1H, CH_2), 4.05 (dd, J = 13.4 and 3.9 Hz, 1H, CH_2), 3.86 (dd, J = 13.4 and 7.5 Hz, 1H, CH_2). ^{13}C NMR ($CDCl_3$, 500 MHz): δ 189.8 (d, $^1J_{RhC}$ = 56.0 Hz, C), 166.8 (CH), 165.2 (CH), 139.4 (d, $^3J_{PC}$ = 8.6 Hz, CH), 138.3 (d, $^3J_{PC}$ = 8.6 Hz, CH), 136.7 (d, $^2J_{PC}$ = 17.1 Hz, C), 136.6 (d, $^2J_{PC}$ = 14.7 Hz, C), 135.4 (CH), 135.4 (CH), 135.0 (d, $^2J_{PC}$ = 8.6 Hz, CH), 134.7 (d, $^2J_{PC}$ = 12.3 Hz, CH), 134.6 (d, $^2J_{PC}$ = 11.0 Hz, CH), 134.5 (d, $^2J_{PC}$ = 12.3 Hz, CH), 134.3 (d, $^2J_{PC}$ = 12.3 Hz, CH), 134.2 (CH), 134.1 (CH), 133.9 (CH), 132.9 (CH), 132.7 (d, $^1J_{PC}$ = 56.3 Hz, C), 132.5 (CH), 131.8 (CH), 129.8 (d, $^3J_{PC}$ = 11.0 Hz, CH), 129.7 (d, $^3J_{PC}$ = 12.3 Hz, CH), 129.4 (d, $^3J_{PC}$ = 11.0 Hz, CH), 129.3 (d, $^3J_{PC}$ = 11.0 Hz, CH), 128.0 (d, $^1J_{PC}$ = 62.5 Hz, C), 127.8 (d, $^1J_{PC}$ = 62.5 Hz, C), 126.0 (d, $^1J_{PC}$ = 42.9 Hz, C), 120.4 (d, $^1J_{PC}$ = 50.2 Hz, C), 75.5 (CH), 71.9 (CH_2), 67.6 (CH_2); 1 C and 1 CH were not resolved due to overlap. IR ($CHCl_3$): ν_{max}/cm^{-1} (CO) 2012 (s). ES-MS: m/z 907 (M^+) 879 (M^+ − CO).

Hydrosilylation of Acetophenone. A mixture of acetophenone (0.25 mL, 2 mmol) and rhodium complex **11** (9.8 mg, 0.01 mmol) in toluene (0.5 mL) was stirred for 10 min. Then, diphenylsilane (0.4 mL, 2 mmol) was added and the mixture was stirred for 3 days at room temperature and analyzed by NMR. δ_H ($CDCl_3$): 1.5 (d, J = 7.0 Hz, 3H, CH_3),[a] 2.4 (s, 3H, CH_3),[e] 2.6 (s, 3H, CH_3),[c] 4.5 (d, J = 2.5 Hz, 1H, CH_2),[b] 4.8 (d, J = 2.5, 1H, CH_2),[b] 4.9 (s, 2H, H_2Si),[d] 5.0 (q, J = 7.0, 1H, CH),[a] 5.5 (s, 1H, SiH),[a] 5.8 (s, 1H, SiH),[b] 7.1−8.0 (m, Ar H) (a = **15**, b = **16**, c = **14**, d = diphenylsilane, e = toluene).

Hydroboration of Alkenes. A 5-mm NMR tube was charged with olefin (0.30 mmol), catecholborane (64 μL, 0.60 mmol), benzene-d_6 (0.3 mL), and catalyst precursor **11** or **13** (10 μmol). The progress of the reaction was monitored by ^{1}H NMR spectroscopy. After all alkene had been consumed, the mixture was quenched with 3 M NaOH (0.25 mL) and 30% H_2O_2 (0.50 mL) and subsequently heated to 50 °C for 3 h. The organic layer was separated and analyzed by ^{1}H NMR spectroscopy and GC, and the products were compared with independent samples.

X-ray Structure Determinations. X-ray data were collected on an Enraf-Nonius CAD4-T diffractometer on a rotating anode (Mo Kα, graphite monochromator). Unit-cell dimensions were derived from the SET4[25] setting angles of 25 reflections. Unit cells were checked for higher symmetry with the program LEPAGE.[26] All structures were refined on F^2 with SHELXL.[27] Geometrical calculations and the ORTEP illustrations were done with PLATON.[28] Crystal data are presented in Table 5.

X-ray Structure Determination of 6. The structure was solved by automated Patterson techniques using DIRDIF.[29] One of the Pd coordination sites shows substitutional disorder. A 0.892/0.108 C_2H_3O/Cl disorder model (including a corresponding splitting of the Pd site, to accommodate the slightly

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deviating Pd coordination plane) was used in the refinement. The minor Cl disorder form is found in the usual square-planar position at 2.28 Å from Pd. The chlorine sits in the pocket occupied by an acetate anion for the major disorder form. The low occupancy (0.11) of the Cl site excludes detection of other scattering matter in the "acetate pocket". Hydrogen atoms were introduced at calculated positions and refined riding on their carrier atoms. The largest residual density in the final difference map is near Pd.

X-ray Structure Determination of 9. The structure was solved by direct methods using SHELXS86.[30] The central part (between the two N atoms) of the molecule appears to be disordered and was refined with a disorder model (50:50). Additional data were collected to investigate the possibility that the unit cell is primitive and not C-centered. The result was negative: the average $I/\sigma(I)$ was found to be 0.44 (i.e. well below the noise level), and the maximum $I/\sigma(I)$ was only 5.9 for reflection (0,7,−3). Attempts to refine the structure in the spacegroup $P2_1/c$ were, as was expected, unstable and point to the same disorder described above. Hydrogen atoms were included in calculated positions. The structure contains small voids (at 0.5, 0.177, 0.250 and symmetry-related sites) of 28 Å^3. However, no residual electron density was found there.

X-ray Structure Determination of 10. The structure was solved by automated Patterson techniques using DIRDIF.[25] An empirical correction for absorption was done with PLATON/DELABS (correction range 0.799−1.188). Reflection profiles were structured and were found unsuitable for the collection of reliable ψ-scan data and their use for a ψ-scan-based correction for absorption. Hydrogen atoms were included in calculated positions.

X-ray Structure Determination of 11. The structure was solved by automated Patterson techniques using DIRDIF.[25] Hydrogen atoms were included in calculated positions. The highest residual density in the difference map is found in the CH_2Cl_2 solvent area (indicating some unresolved disorder) and near rhodium (absorption artifacts).

Supporting Information Available: X-ray crystallographic files for **6** and **9**−**11**, in CIF format, are available. Access information is given on any current masthead page.

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