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Novel Chiral Water Soluble Phosphines I. Preparation and Characterization of Amine Functionalized DIOP, Chiraphos, and BDPP Derivatives and Quaternization of Their Rhodium Complexes

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Abstract: Synthetic details for the preparation of tetra-amine functionalized derivatives of the ligands BDPP, Chiraphos, and DIOP (2,4-bis(-bis(-p-N,N-dimethylamino-phenyl)phosphino)pentane; 2,3-bis(-bis(-p-N,N-dimethylaminophenyl)-phosphino)butane; and 2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis(-bis(-p-N,N-dimethylaminophenyl)phosphino)-butane; respectively). The ligands are conveniently quaternized in their rhodium diene complexes with $(CH_3)_3OBF_4$. Both the methyl quaternized and proton quaternized versions of the rhodium complexes have unlimited water solubility.

Recently we communicated the synthesis of a derivative of the BDPP (Skewphos)# ligand which contains four cationic ammonium groups, [(S,S)-2,4-bis[-bis(-p-N,N-trimethylammonium)phenyl)phosphino]pentane]$^{4+}$.[1] Rhodium complexes of the cationic ligand are effective for the water phase hydrogenation of prochiral cinnamic acid derivatives.[1,2] The cationic complexes have many similarities to the rhodium complexes of tetra-sulfonated BDPP;[3] both are extremely soluble in water and show virtually no solubility in organic solvents which make them useful for catalysis under two-phase reaction conditions.

The sulfonated ligands are obtained by the direct sulfonation of a chiral ligand that contains phenyl rings. Reaction with H_2SO_4/SO_3 is too severe for the sulfonation of ligands that contain sensitive functional groups such as the acetal ring in DIOP#, however the ligands, Prophos , Skewphos, Chiraphos , and CyclobutaneDIOP# have all been

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chiral ligand abbreviations:
BDPP (Skewphos) = 2,4-bis(diphenylphosphino)pentane
DIOP = 2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane
Prophos = 1,2-bis(diphenylphosphino)propane
Chiraphos = 2,3-bis(diphenylphosphino)butane
CyclobutaneDIOP = 1,2-bis((diphenylphosphino)methyl)cyclobutane

successfully tetra-sulfonated.[3] Direct sulfonation of the phenyl groups places the functional group in a position meta to the phosphorus. [4] In most of the cases with the tetrasulfonated bisphosphines, and specially with the 1,4- and 1,3-bisphosphines, the observed enantioselectivies are lower for the modified ligands than for the unmodified analogues in nonaqueous solvents.[3] The loss in enantioselectivity may be due to either different reaction conditions or to a substituent effect. The available experimental data for aryl substituted DIOP derivatives shows that the nature and position of substituents on the phenyl rings influences the enantioselectivity obtained in nonaqueous solvents.[5]

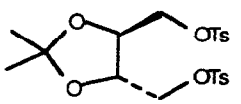
As we previously communicated, the introduction of amino groups to the phenyl rings of a chiral chelating phosphine can be accomplished directly from the reaction of $K(P(C_6H_4NMe_2)_2)$[6] with the appropriate diol-ditosylate. Incorporation of the polar group prior to the assembly of the chiral ligand affords some control over the position of the substituent on the phenyl ring. To minimize the potential effect of the substituent on the orientation of the phenyl rings we have chosen to place the dimethylamino groups in the para position. Here we show that amino functionalized derivatives of the DIOP framework can be prepared via $K(P(C_6H_4NMe_2)_2$; the tetraamine DIOP derivative has been recently reported however the quaternized versions were not prepared.[7] We also describe the details of the synthesis of the corresponding chiraphos derivative and give complete details of the quaternization methods and the characterization of all complexes.

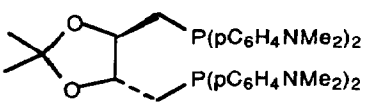
Complete methyl quaternization of all four aryl amino groups of the functionalized ligands is not a routine task. Selective quaternization of aryl amino groups in tertiary or ditertiary phosphines has not been previously reported. Two methods for the quaternization of amino phosphines which contain a single trialkyl amino group have been reported in the literature. Baird et al.[8] have shown that the N-quaternization of $Ph_2PCH_2CH_2NMe_2$ (amphos) can be accomplished by a three step procedure; the phosphine is first oxidized to the corresponding phosphine oxide to protect the phosphorus atom , the amino group is then quaternized with methyliodide, and finally, the phosphine oxide is reduced back to the phosphine. More recently, Nagel and Kinzel[9] reported that the chiral chelating aminophosphine, (3R, 4R)-3,4-bis(diphenylphosphino)-1-methylpyrrolidine can be quaternized by $(CH_3)_3OBF_4$ after protecting the phosphorus

through complexation to rhodium. In this paper the utility of modified versions of these methods are discussed for the consecutive quaternization of the four aryl amino groups in the amine functionalized ligands prepared here.

Results and Discussion

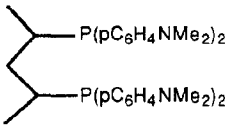
Ligand Synthesis. Potassium bis (p-(dimethylamino)phenyl)phosphide, **1**, has been observed to react cleanly and rapidly with primary alkyl tosylates.[6] Compound **1** appears to be more nucleophilic than potassium diphenylphosphide and the analogues lithium derivative.[6,7] Also it is generated in the absence of any other nucleophiles and can be used directly in substitution reactions. **1** reacts with optically active (-)-2,3,O-isopropylidene-D-threitol-ditosylate to yield the new p-dimethylamino derivative of DIOP, **2a**, (equation 1) with a conversion of 90% as determined by NMR.

1. 

\+ **1** $\xrightarrow[0°C,]{THF}$ 

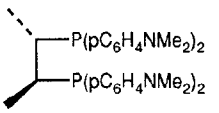
2a

Generally, the application of **1** to the synthesis of chiral ligands can be extended to the S_N2 substitution of other alkylidene dihalides or diol-ditosylates which have been successfully used in the similar reaction with alkali diphenylphosphides.[10,11] In this manner reaction of the 2,4-pentanediol-ditosylate enantiomers with **1** proceeds in greater than 90% conversion to yield p-dimethylamino derivatives of BDPP.



3a

The reaction of 1, 2-alkylidene dihalides or diol-ditosylate with diphenyldiphosphide is reported to be less successful.[11-13] Low yields are also obtained with **1** as the nucleophile in the substitution of 2S,3S-butanediol-ditosylate. Even at -40 °C only about 50% of the reaction mixture was identified by ^{31}P NMR as the p-dimethylamino derivative of Chiraphos.



4a

The remaining 50% of the phosphorus content of the reaction mixture was mainly the product of elimination reactions. Thus $HP(pC_6H_4NMe_2)_2$ and monosubstituted alkylene phosphines were also present in the reaction mixture. The increased susceptibility to elimination compared to those with 1,3 and 1,4 -diol ditosylates is expected from the steric constraints of forming a 1,2-bisphosphine. (The reaction of t-BuCl with **1** leads to elimination to form $HP(pC_6H_4NMe_2)_2$ and isobutene.[6])

Purification of Chiraphos itself is accomplished by the formation of the corresponding $Ni(L\text{^}L)(SCN)_2$ complex. In the present case $Ni(\mathbf{4a})(SCN)_2$ is not formed quantitatively which limited the utility of this method for the purification of **4a**. Fractional crystallization of the crude product obtained from the displacement of the tosylate gives pure **4a** with isolated yields of 11%.

Rhodium complexes of **2a**, **3a**, and **4a** are shown schematically below.

[(4a)Rh(NBD)]$^+$

[(3a)Rh(NBD)]$^+$

[(2a)Rh(NBD)]$^+$

Methyl Quaternization. The method of Nagel and Kinzel for the quaternization of (3R, 4R)-3,4-bis(diphenylphosphino)-1-methylpyrrolidine uses the powerful akylating agent $(CH_3)_3OBF_4$ [9] with protection of the phosphine through coordination to rhodium. When [Rh(NBD)(**3a**)]BF_4 is added to a suspension of $(CH_3)_3OBF_4$ in dichloromethane an orange red solid separates. The solid contains a mixture of partially and fully quaternized complexes. The composition of the separated solid changes very little upon additional stirring. The extent of quaternization can be readily monitored by the NMR spectral differences between the non-quaternized and quaternized complexes.[1] The ^{13}C NMR spectrum of the separated solid showed that less than half of the amino groups were quaternized. Although, the extent of quaternization has little effect on the enantioselectivities provided by these complexes,[14] the solubility requirements for two-phase catalysts and the need for exact spectroscopic characterization of the complexes require nearly complete quaternization.

A solvent more polar than dichloromethane is required to prevent the product from separating prematurely. Unfortunately, the solvents of choice are limited by the extreme reactivity of the quaternizing agent.[15,16] When a slight excess of $(CH_3)_3OBF_4$ was added to a solution of [Rh(NBD)(**3a**)] BF_4 in dry acetonitrile practically all of the amino groups underwent quaternization. However, NMR spectroscopy showed that about 40% of the isolated product was the diacetonitrile complex. Hydrogenation of the mixture obtained in acetonitrile results in the complete formation of the solvent complex.

The acetonitrile complex, was identified by elemental analysis and NMR spectroscopy. Although, this complex yields the same enantioselectivity as other Rh(I) complexes of **2a** [14] the rates are significantly slower. It is likely that acetonitrile is not readily displaced by olefins to form Rh(**2a**)(substrate). Formation of such a complex is necessary for the successful hydrogenation of substrates.[17] Quaternization proceeds in dry acetone solutions without substitution of diene (equation 2).

2. $[Rh(diene)(\mathbf{2\text{-}4a})]BF_4 + 4.5\ (CH_3)_3OBF_4 \xrightarrow[R.T.]{acetone} [Rh(diene)(\mathbf{2\text{-}4b})][BF_4]_5$

diene = NBD or COD

2b = $[DIOP(pNMe_3)_4]^{4+}$

3b = $[BDPP(pNMe_3)_4]^{4+}$

4b = $[Chiraphos(pNMe_3)_4]^{4+}$

The quaternized complexes separate from acetone as orange red solids or red oils. ^{13}C and ^{31}P NMR spectra of the separated complexes show that, on average, 90 to 95% of the dimethylamino groups are quaternized. At 95% quaternization approximately 81% of the complexes are tetra-quaternized and 17% are tri-quaternized. Recrystallization from aqueous methanol (95%) yields the pure tetra-quaternized derivative.

Some protonation will always occur since $(CH_3)_3OBF_4$ reacts slowly with acetone[16] to liberate HBF_4. Thus the quaternizing agent should be added to acetone solutions of the rhodium complexes to maximize the yield of tetra-quaternized product. In one experiment in which the order of addition was reversed quantitative protonation at the amino groups was observed. Protonation was not observed in acetonitrile solution although acetonitrile is also reported to be methylated by $(CH_3)_3OBF_4$,[16] Apparently acetonitrile is less reactive than acetone towards $(CH_3)_3OBF_4$.

The acetal ring in the DIOP derivative was not affected by the addition of stoichiometric amounts of $(CH_3)_3OBF_4$. Also for short periods of time (2h or less) the DIOP ligand showed no reaction with excess of fluoroboric acid (see below) although acetals are sensitive toward acid hydrolysis .[18]

Protonation. The fact that the protonation above occurred exclusively at the amino group leads to a method for the direct protonation of the complexes with non-coordinating acids.[2,19] Thus complete protonation of the four dimethyl amino groups is possible by the addition of aqueous HBF_4 to acetone or methanol solutions of $[Rh(diene)(\mathbf{2\text{-}4a})]BF_4$ (equation 3).

3. $[Rh(diene)(\mathbf{2\text{-}4a})]BF_4 + 10\ HBF_4 \rightarrow [Rh(diene)(\mathbf{2\text{-}4c})][BF_4]_5$

diene = NBD or COD

2c = $[DIOP(p\text{-}NHMe_2)_4]^{4+}$

3c = $[BDPP(p\text{-}NHMe_2)_4]^{4+}$

4c = $[Chiraphos(p\text{-}NHMe_2)_4]^{4+}$

The protonation is also completely reversible by the addition of weak bases such as Et_3N which leads to a versatile catalyst system.[2] Quaternization by protonation is more convenient than methyl quaternization however the complexes obtained are less applicable for two phase reactions.[14]

Reaction with HCl and H_2. Protonation of $[Rh(\mathbf{2\text{-}4a})(NBD)]^+$ with coordinating acids such as HCl follows the literature expectations [20] and results in protonation of the metal and substitution of the diene ligand. [19] The reaction of the methyl-quaternized complex, $[Rh(\mathbf{3b})(NBD)]^{5+}$ with aqueous HCl proceeds similarly to displace the diene, as judged by the ^{31}P NMR spectrum of the reaction solution. (equation 4.)

4. $[Rh(\mathbf{3b})(NBD)]^{5+} \xrightarrow[MeOH]{HCl/H_2O} [Rh(\mathbf{3b})(H_2O)_2(H)(Cl)]^{5+}$

As expected from the literature,[3, 21] the methyl quaternized diene complexes react with hydrogen to form planar solvent complexes (equation 5). The solvent complexes formed by hydrogenation are readily identified from their large Rh-P coupling constants (Table 1).

5. $[Rh(\mathbf{3b})(NBD)]^{5+} \xrightarrow[H_2O]{H_2} [Rh(\mathbf{3b})(H_2O)_2]^{5+}$

It is important to note that the diene ligands in the rhodium-diene complexes of **2-4b** and **2-4c** are not substituted by water in the absence of a coordinating acid. This is in

contrast to what was observed for the rhodium complexes of sulfonated chiral phosphines.[3]

Formation of a substrate complex is considered to be the first intermediate in catalytic asymmetric hydrogenation.[17] The addition of N-acetyl amino cinnamic acid to aqueous solutions of $[Rh(\mathbf{3b})(H_2O)_2]^{5+}$ caused the doublet at 52.5 ppm to disappear. However only a broad signal at 40-46 ppm was obtained for the expected substrate complex .

Experimental Section

Microanalyses were performed by Galbraith Laboratories, Knoxville, Tennessee and by Atlantic Microlab, Inc., Norcross, Georgia. ^1H, ^{13}C and ^{31}P NMR spectra were run at 25°C on Bruker WP-200 and WP-270 instruments. ^{31}P NMR chemical shifts are referenced to external 85% H_3PO_4. Integrated ratios on ^1H NMR spectra were consistent with the given formulae. Optical rotations were determined on a Perkin-Elmer 241 polarimeter. Direct probe mass spectra were recorded on a VG Analytical 7070 E-HF spectrometer at 70 eV. All preparations and operations were carried out under an atmosphere of dry deoxygenated argon. Solvents were degassed before use. (-)-_,3-O-isopropylidene-D-threitol, 2,4-pentanediol enantiomers, (2R, 3R)-butanediol, p-toluenesulfonyl chloride, trimethyloxonium tetrafluoroborate were purchased from Aldrich and used as received. A loan of $RhCl_3 \cdot 3H_2O$ was provided by Johnson-Matthey and the complexes, $[Rh(NBD)Cl]_2$,[22] and $[Rh(COD)Cl]_2$,[23] and the diolditosylates[11,24,25] were prepared by the literature methods. Potassium bis-(p-(N,N-dimethylamino)phenyl)phosphide,**1**, solutions were prepared in situ as previously described.[6]

Preparation of (-),2,3-O-Isopropylidene-2,3-dihydroxy-1,4-bis-[bis-((p-N,N-dimethylamino)phenyl)phosphino]butane, DIOP-$(pNMe_2)_4$, **2a**. A solution of **1** prepared from 10.0 g (25.5 mmol) of tris-[p-(dimethylamino)phenyl] phosphine in 200 ml of THF

was cooled to 0°C. 5.97 g (12.7 mmol) of (-)-2,3-O-isopropylidene-D-threitol-ditosylate was added in portions to this solution with intensive stirring. The dark red solution gradually turned into a light orange suspension . After the ditosylate addition the ice bath was removed and the mixture was stirred for an additional half hour. Then 200 ml degassed water was added and the bulk of the THF was pumped off. The separated, crude, oily phosphine was extracted with a mixture of 200 ml ether and 200 ml dichloromethane. The organic phase was washed with water and dried over $MgSO_4$. The $MgSO_4$ and a small amount of bisphosphine impurity (~0.5 g of tetrakis[(p-N,N-dimethylamino)phenyl] bisphosphine) were filtered off and the solvents removed under vacuum. The residue was crystallized from 100 ml ethanol yielding 5.2 g (61%) white crystalline product. Mp. 78°C, $[\alpha]_b^{20}$=-18.7 (c 1.94; benzene), -2.2° (c 2.30; $CHCl_3$). Anal. calc. for $C_{39}H_{52}N_4O_2P_2$: C, 69.79; H, 7.75; N, 8.35; P, 9.24. Found: C, 69.73; H, 7.74; N, 7.84; P, 9.18. ^1H NMR (200.1 MHz, $CDCl_3$): 7.39, 7.30 dd; dd ($^3J_{HH}$=8.7 Hz, $^3J_{PCCH}$=7.5 Hz), 6.66; 6.64 dd; dd ($^3J_{HH}$=8.2 Hz; $^4J_{PCCCH}$<1 Hz), 3.80 m (not res.), 2.91, 2.90 s; s, 2.30 m (not res.); 1.36 s. Mass spectrum (70 eV): M^+, m/e 670 (15%), $[M-((CH_3)_2C(O))]^+$ 612 (4%), $[M-P(C_6H_4\text{-}pN(CH_3)_2)_2]^+$ 399 (30%), $[P(C_6H_4\text{-}pN(CH_3)_2)_2]^+$ 271 (100%), $[PC_6H_4\text{-}pN(CH_3)_2]^+$ 151 (70%), $[C_6H_4\text{-}pN(CH_3)_2]^+$ 120 (20%).

2,4-Bis[-bis((p-N,N-dimethylamino)phenyl)phosphine] pentane, BDPP-$(pNMe_2)_4$, **3a**. Both antipodes of the ligand were prepared in a manner identical to that of above. In reactions with 5.23 g (12.7 mmol) of either 2R, 4R- or 2S, 4S-pentanediol-ditosylate a typical yield of 5.8 g (75%) was obtained. Analytical data for **3a** were given in a previous short communication.[1] Mass spectrum (70 eV): M^+, m/e 612 (80%), $[M-(C_6H_4\text{-}pN(CH_3)_2)]^+$ 492 (40%), $[P(C_6H_4\text{-}p(CH_3)_2)_3]^+$ 391 (50%), $[M-P(C_6H_4\text{-}pN(CH_3)_2)_2]^+$ 341, (30%); $[C_2H_4P(C_6H_4\text{-}pN(CH_3)_2)_2]^+$ 299 (40%), $[P(C_6H_4\text{-}pN(CH_3)_2)_2]^+$ 271 (100%), $[PC_6H_4\text{-}pN(CH_3)_2]^+$ 151 (90%), $[C_6H_4\text{-}pN(CH_3)_2]^+$ 120 (40%).

2S, 3S-Bis[-bis-((p-N,N-dimethylamino)phenyl)phosphines] butane, Chiraphos-(pNMe2)4, **4a**. 2R, 3R-butanediol-ditosylate was added in portions to a solution of **1** prepared from 16.6 g (42.5 mmol) of tris-[p-(dimethylamino) phenyl]phosphine in 300 ml of THF 6.9 g (17 mmol) at -40°C. After the addition the cooling bath was removed and the deep orange suspension was left to stand overnight. The remaining phosphide was then destroyed by the cautious addition of 300 ml degassed water. A significant amount of unsoluble diphosphine side product (~2-3 g) was filtered off before work up as above. The crude phosphine (purity ~50%) that was obtained after the evaporation of CH_2Cl_2/ether solvents was repeatedly crystallyzed (~3 times) from ethanol resulting in 1.1 g (11% yield) white crystalline product. Mp. 186 °C, $[a]_D^{20}$=-149.2 (c, 1.22; $CHCl_3$). Anal. calc. for $C_{36}H_{48}N_4P_2$; C, 72.20; H, 8.02, N, 9.36, Found: C, 72.50; H, 7.91, N, 9.18. ^1H NMR (200.1 MHz, $CDCl_3$): 7.26; 7.15 dd; dd, ($^3J_{HH}$=7.9 Hz, $^3J_{PCCH}$=7.1 Hz), 6.63; 6.60 dd; dd ($^3J_{HH}$=8.20 Hz), 2.97; 2.90 s;s, 2.47 quart. ($^3J_{HH}$=7.0 Hz, $^2J_{PCH}$=-$^3J_{PCCH}$) 1.10 d,d ($^3J_{HH}$=7.0 Hz, $^3J_{PCCH}$=14.2 Hz) .

Ni(**4a**)(SCN)2 . A solution of 7.0 g crude **4a** (purity ~50%) in 10 ml of CH_2Cl_2 was added to a solution of 2.5 g $NiClO_4 \cdot 6H_2O$ and 2.5 g NaSCN in 40 ml of ethanol. A reddish brown oily crystalline solid separates and was collected and dried under vacuum. The crude complex was then suspended in a mixture of 50 ml of THF and 50 ml of ether, filtered and dried again, 1.3 g (28% of **4a**) of bronze colored solid was obtained. Anal. calc. for $C_{38}H_{48}N_6P_2S_2Ni$; C, 59.01; H, 6.21%, N, 10.87; S, 8.02. Found: C, 61.8; H, 6.20, N, 10.18; S, 7.63. ^1H NMR (200.1 MHz, d_6-acetone, d_6-DMSO): 7.98, 7.51 dt; dt ($^3J_{HH}$=8.5 Hz, $^3J_{PCCH}$=$^5J_{PNiPCCH}$=5.5 Hz), 6.95; 6.90 d; d ($^3J_{HH}$=8.9 Hz), 3.08 s; s; 2.15 m (not res.) 0.94 m ($^3J_{HH}$=6Hz, $^3J_{PCCH}$=8Hz, $^4J_{PCCCH}$=6Hz.) IR (mmol): ν_{N-H} 3420 (s), ν_{C-H} 2890, ν_{as} C-N,S 2100 (s), 2094 (s), ν_{P-Ar} 1596 (s), 1532, 1520 (s), 1449 ν_S C-N,S 1372. The addition of NaCN to the aqueous ethanol suspension of Ni (**4a**)(SCN)2 by the method of Bosnich and coworkers[13,25] resulted in the liberation of the ligand.

[Rh(diene)(**2-4a**)]BF_4 complexes (diene = NBD or COD). The rhodium norbornadiene or cyclooctadiene complexes of **2-4a** were prepared in the manner previously described in reference 25b. Elemental analyses for [Rh(NBD)(**3a**)]BF_4 and [Rh(COD)(**3a**)] were provided in references 1 and 2.

[Rh(NBD)(**3a**)]BF_4: ^1H NMR (200.1 MHz, d_6-acetone): 7.62; 7.39 m; m ($^3J_{HH}$=8.6 Hz, $^3J_{PCCH}$=9.1 Hz), 6.91; 6.82 d; d ($^3J_{HH}$=8.6 Hz), 4.86 br. s, 4.38 br. s, 3.92 br. s, 3 05; 3.04 s; s, 2.80 m (not res.), 1.81 tt ($^3J_{HH}$=6.8 Hz, $^3J_{PCCH}$=19.2 Hz) 1.14 dd ($^3J_{HH}$=6.8 Hz, $^3J_{PCCH}$=12.8 Hz).

[Rh(COD)(**3a**)]BF_4: ^1H NMR [270.1 MHz, $CDCl_3$). 7.99; 7.10 m; m ($^3J_{HH}$=8.1 Hz, $^3J_{PCCH}$, 8.6 Hz); 6.92; 6.73 d; d ($^3J_{HH}$=8.1 Hz), 4.63 m (not res.), 3.96 quart.(J=7.9 Hz), 3.17; 3.04 s; s, 2.63 hept. (J=7.5 Hz), 2.54; 1.96 m, m (not res.), 1.65 m ($^3J_{PCCH}$=22.5 Hz, $^3J_{2PCCH}$=10.5 Hz, $^3J_{HH}$=9 Hz) 0.97 m ($^3J_{HH}$=7.5 Hz, $^3J_{PCCH}$=12 Hz).

[Rh(NBD)(**2a**)]BF_4: Anal. calc. for $C_{46}H_{60}BF_4N_4O_2P_2Rh$; C, 58.00; H, 6.30; N, 5.88; P, 6.51; Rh, 10.81. Found: C, 56.49; H, 6.31; N, 5.63; P, 6.01; Rh, 10.99. ^1H NMR (270 MHz, d_6 acetone): 7.72; 7.28 br. d,d; br. d,d ($^3J_{HH}$ = 8.5 Hz, $^3J_{CCH}$ =10.5Hz, $^5J_{PRhPCCH}$<4Hz), 6.90; 6.86 d;d ($^3J_{HH}$ = 8.5 Hz), 4.57 br. s.; 4.36 br.s; 3.89 br.s; 3.73 m (not res), 3.08; 3.03 s;s, 2.68 t($^2J_{HH}$=-13.5 Hz, $^2J_{PCH}$=13.5Hz); 2.57 d,d($^3J_{HH}$=9.1Hz, $^2J_{HH}$=-13.5Hz), 1.50 br. s; 1.11 s.

[Rh(NBD)(**4a**)]BF_4: Anal calc. for $C_{43}H_{56}BF_4N_4P_2Rh$:C, 58.6; H, 6.36; N, 6.36; Found: C, 56.53, H, 6.26, N, 6.91. ^1H NMR (200.1 MHz, CD_3OD): 7.59; 7.17 m;m ($^3J_{HH}$ = 8.6 Hz, $^3J_{PCCH}$ = 8.6 Hz, $^5J_{PRhPCCH}$<4.0 Hz), 6.88; 6.83 d;d($^3J_{HH}$=8.6Hz); 5.22 br.s, 4.83 br. s, 3.97 br. s, 3.04; 3.02 s; s. 2.09 m (not res.), 1 67 br. s., 0.97 m (not res.)

[Rh(COD)(**4a**)]BF_4: ^1H NMR (200.1 MHz, $CDCl_3$): 7.78; 7.32 m;m ($^3J_{HH}$ = 8.5 Hz, $^3J_{PCCH}$=9.3 Hz, $^5J_{PRhPCCH}$<4 Hz), 6.79; 6.78 d;d ($^3J_{HH}$=8.5 Hz), 4.95 m,

4.38 quart (J = 6.7 Hz), 3.10; 3.06 s;s, 2.39; 2.09 m;m, 2.06 m (not res.), 0.95 m ($^3J_{HH}$ = 6 Hz, $^3J_{PCCH}$ = 11.7 Hz, $^4J_{PCCCH}$ = $^4J_{RhPCCH}$ = 4.5Hz).

Rh(**3b**)($CH_3CN)_2$. 470 mg (0.525 mmol) of [Rh(NBD)(**3a**)]BF_4 was dissolved in 5 ml of acetonitrile followed by the addition of 318 mg (2.15 mmol) of $(CH_3)_3OBF_4$. During the addition a slight increase in temperature was observed, but the color of the solution remained unchanged. The dark orange red solution was stirred for an additional 20 minutes, then hydrogenated for 5 minutes under an atmosphere of dry hydrogen. After the hydrogenation the product was precipitated as a red oil by the addition of 20 ml of ether. The solvents were decanted and the residue was dried under vacuum. The orange solid was then suspended in a few ml of dichloromethane, filtered and dried under vacuum. 510 mg (75%) orange solid. Anal. calc. for $C_{41}H_{68}B_5F_{20}N_6P_2Rh$: C, 41.8%, H, 5.26, N, 6.50; P, 4.80. Found C, 41.17; H, 5.48; N, 6.46, P, 4.25. ^1H NMR (270 MHz, CD_3CN): 8.02; 7.80 m,m, 8.02 m, 3.67; 3.58 s;s, 2.78 m (not res.), 2.44 br. s, 1.92 m (not res) 1.09 dd ($^3J_{HH}$ = 7.2 Hz, $^3J_{PCCH}$ = 13.8 Hz).

[Rh(diene)(**2-4b**)]$(BF_4)_5$ complexes: The following procedure was used for the quaternization of [Rh(diene)(**2-4a**)]BF_4: 2 mmol of [Rh(diene)(**2-4a**)]BF_4 was dissolved in 15 ml of dry acetone to form a dark orange red solution. 1.33 g (9 mmol) of $(CH_3)_3$ OBF_4 was added to the solution with vigorous stirring at room temperature. The reaction is exothermic and a red oil quickly separates from solution. The mixture was stirred for an additional 10 minutes, then the solvent was decanted. The oil was washed with a mixture of 1 ml of Et_3N and 10 ml of CH_2Cl_2. The solvents were repeatedly removed by decanting and the complex was dried under vacuum. The obtained orange red solid was then dissolved in 10 ml of water. The insoluble residues (~100-200 mg) were filtered off and the orange red solution was dried under vacuum. The orange red solid (~1.85 mmol, 92%) contained ~20% triquaternized complex. Pure tetraquaternized complexes were obtained following the manner. The crude complex was suspended in 20-30 ml of hot MeOH. Then, a few drops of water (1-2 ml) was added to the suspension

until a clear orange red solution formed. The solution was left to crystallize at 5°C to give ~ 0.7 mmol (35%) deep orange crystalline tetraquaternized complex. The crystals were collected and dried under vacuum. Cooling to -20°C led to the separation of some triquaternized complex.

[Rh(NBD)(**2b**)](BF4)5: Anal calc. for $C_{50}H_{72}B_5F_{20}N_4O_2P_2Rh$: C 44.13, H, 5.15, N, 4.11, Found: C, 41.80, H, 5.33, N, 4.01. ^1H NMR (200. 1 MHz, D_2O): 8 19; 7.76 m; m (not res), 8.06; 8.04 d;d ($^3J_{HH}$ = 8.1 Hz), 4.83 br.s, 4.53 m (not res), 4 00 br. s., 3.90 m, 3.72; 3.68 s;s, 3.07; 2.95 m, m (not res), 1.61 br. s.; 1.21 s.

[Rh(NBD)(**3b**)](BF4)5. Elemental analysis is provided in ref. 1. ^1H NMR (270 MHz, D_2O): 8.14 ; 7.82 m;m ($^3J_{HH}$ = 9.1 Hz, $^3J_{PCCH}$ = 9.1 Hz, $^5J_{PRhPCCH}$ = 3.6 Hz) 8.08; 8.05 d;d ($^3J_{HH}$ = 9.1 Hz), 5.06 br. s, 4.60 br. s, 4.00 br.s, 3.76; 3.75 s;s, 2.98 m (not res.), 1.99 t,t ($^3J_{HH}$ = 6.5 Hz, $^3J_{PCCH}$ = 22.0 Hz), 1.16 br. d,d (J_{HH} = 6.5 Hz, $^3J_{PCCH}$ = 14.2 Hz, $^5J_{PH}$,$^4J_{RhH}$ <4 Hz.)

[Rh(NBD)(**4b**)](BF4)5: Anal. calc. for $C_{47}H_{68}B_5F_{20}N_4P_2Rh$: C, 43.82; H, 5.28; N, 4.35. Found: C, 43.24; H, 5.41; N, 4.36. ^1H NMR (200.1 MHz, D_2O): 8.04; 7.71 m; m ($^3J_{HH}$ = 8.7 Hz, $^3J_{PCCH}$ = 8.6 Hz, $^5J_{PRhPCCH}$ < 4 Hz), 8.05; 8.04 d;d ($^3J_{HH}$ = 8.7 Hz), 5.65 br.s, 5.13 br.s, 4.08 br.s, 3.74; 3.73 s;s, 2.47 m (not res), 1.77 br. s, 1.07 m (not res).

[Rh(COD)(**4b**)](BF4)5. Anal calc. for $C_{48}H_{72}B_5F_{20}N_4P_2Rh$: C, 44.2; H, 5.52; N, 4.29. Found: C, 42.10, H, 5.46; N, 4.19. ^1H NMR (200.1 MH_2, D_2O): 8.26; 7.83 m;m ($^3J_{HH}$ = $^3J_{PCCH}$ = 8.6 Hz, $^5J_{PRhPCCH}$ = 5.5 Hz) 8.10; 8.08 d;d ($^3J_{HH}$= 8.6 Hz), 5.34 m (not res); 4.61 m (not res), 3.77; 3.75 s;s; 2.44; 2.21m;m, 2.14 m, 1.07 m ($^3J_{HH}$ = 6 Hz, $^3J_{PCCH}$= 12.0 Hz, $^4J_{PCCCH}$ = $^4J_{RhPCCH}$~ 5 Hz).

[Rh(diene)(**2-4c**)](BF4) complexes were prepared in situ by the method reported in reference 2. Elemental analyses were also provided for [Rh(NBD)(**3c**)](BF4)5 and [Rh(COD)(**3c**)](BF4)5 complexes.

Table 1. ^{31}P NMR Data[a]

compound	solvent	δ (ppm)	$^{1}J_{RhP}$(Hz)	$^{2}J_{PP}$(Hz)
2a	$CDCl_3$	-27.9 s	- -	- -
3a[b]	$CDCl_3$	-5.8 s	- -	- -
4a	$CDCl_3$	-12.8 s	- -	- -
[Rh(NBD(**2a**)] BF_4	CD_3OD	14.1 d	152.7	- -
[Rh(NBD(**3a**)] BF_4[b,c]	CD_3OD	24.4 d	152.1	- -
[Rh(NBD(**4a**)] BF_4	CD_3OD	55.5 d	152.7	- - -
[Rh(COD(**3a**)] BF_4[c]	CD_3OD	23.7 d	142.4	- -
[Rh(COD(**4a**)] BF_4	CD_3OD	52.4 d	141.9	- - -
[Rh(**3b**)$(CH_3CN)_2$]$(BF_4)_5$	CD_3CN	47.9 d	162.9	- - -
[Rh(NBD)(**2b**)]$(BF_4)_5$	D_2O	17.1 d	152.4	- - -
[Rh(NBD)(**3b**)]$(BF_4)_5$[b]	D_2O	28.9 d	152.3	- - -
[Rh(NBD)(**4b**)]$(BF_4)_5$	D_2O	57.6 d	153.3	- - -
[Rh(COD)(**4b**)]$(BF_4)_5$	D_2O	56.5 d	147.5	- - -
[Rh(NBD)(**2c**]$(BF_4)_5$	CD_3OD	17.5 d	152.7	- - -
[Rh(NBD)(**3c**)]$(BF_4)_5$[c]	CD_3OD	29.1 d	151.6	- - -
[Rh(COD)(**3c**)]$(BF_4)_5$[c]	CD_3OD	28.7 d	146.8	- - -
[Rh(**3b**)HCl$(H_2O)_2$]$(BF_4)_5$[d]	CD_3OD	35.6 d, d; 39.5 d, d	108; 122	40.3
[Rh(**3c**)HCl$(H_2O)_2$]$(BF_4)_5$[c,d]	CD_3OD	35.7 d, d; 39.6 d, d	106, 119	40.1
[Rh(**3b**) $(H_2O)_2$]$(BF_4)_5$	D_2O	52.5 d	190.7	- - -
[Rh(**4b**) $(H_2O)_2$]$(BF_4)_5$	D_2O	76.2 d	198	- - -
Ni(**4a**)$(SCN)_2$	d_6-acetone	59.9 s	- - -	- - -

a. at 81.01 MHz and 298 K.

b. reference 1.

c. reference 2.

d. at 245 K.

[Rh(NBD)(**3c**)](BF4)5: ^{1}H NMR (270 MH2, d6-acetone): 8.00; 7.93 t;t ($^3J_{HH}$ = $^3J_{PCCH}$ = 9.1 Hz), 8.06; 8.03 d;d ($^3J_{HH}$ = 9.1 Hz), 5.10 br.s, 4.64 br. s, 4.03 br. s, 3.58; 3.51 s;s, 3.16 m (not res.) 2.03 m (not res), 1.57 br. s, 1.25 br. dd ($^3J_{HH}$ = 6.5 Hz, $^3J_{PCCH}$ = 14.0 Hz).

[Rh(COD)(**3c**)](BF4)5: ^{1}H NMR (200.1 MHz, CD3OD): 8.45; 7.70 m;m ($^3J_{HH}$ = 8.3 Hz, $^3J_{PCCH}$ not res), 7.94; 7.84 d;d ($^3J_{HH}$ = 8.30 Hz), 4.76 m (not res), 4.12 quart (J = 5.6 Hz); 3.46; 3.40 s;s, 2.82 m (not res), 2.52; 206 m,m (not res). 1.82 (not res), 1.06 m ($^3J_{HH}$ = 6.8 Hz, $^3J_{PCCH}$= 12.7 Hz).

[Rh(NBD)(**2c**)](BF4)5: (27.0 MHz, d6-acetone): 8.17; 7.92 m,m(not res.), 7.95, 7.93 d,d ($^3J_{HH}$= 8.1Hz), 4.80 br. s, 4.67, br. s, 4.04 br. s, 3.99 m, 3.48; 3.47 s;s, 3.08; 2.93 m;m (not res), 1.57 br.s, 1.16 s.

[Rh(**3c**))(HCl)(H2O)2]Cl5 was isolated and characterized as previously described.[2]

[Rh(**3b**)(HCl)(H2O)2]Cl5 was generated similarly by the reaction of [Rh(NBD)(**3b**)](BF4)5 with an excess of HCl in aqueous methanol solution. This complex and the aquo-complexes were not isolated.

[Rh(**3-4b**)(H2O)2](BF4)5 complexes were obtained by a short time (5 min.) hydrogenation of [Rh(diene)(**3-4b**)](BF4)5 complexes in aqueous solution at 14 bar of H2.

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