Transition Metal Complexes of Lower Rim 1,3-Diphosphinite and 1,3-Diphosphino Calix[4]arenes

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5,11,17,23-Tetra-*tert*-butyl-25,27-bis((diphenylphosphino)oxy)-26,28-dipropoxycalix[4]arene, **3**, is easily prepared from chlorodiphenylphosphine and 1,3-dipropoxycalix[4]arene in exclusively the cone conformation. 5,11,17,23-Tetra-*tert*-butyl-25,27-bis((diphenylphosphino)ethoxy)-26,28-dipropoxycalix[4]arene, **5** (also in the cone conformation), is obtained from the reaction of KPPH_2 with the 1,3-ditosylate calix[4]arene derivative. The coordination properties of calix[4]arene ligands **3** and **5** with Rh^{I} , Cu^{I} , and Pt^{II} have been investigated. Isolation of both bimetallic ($\text{Rh}_2(\text{3})(\text{COD})_2\text{Cl}_2$) and monometallic ($\text{Rh}(\text{3(P=O)})(\text{COD})\text{Cl}$) complexes proved that the ligand binds to the Rh^{I} ion in a monodentate fashion. However, in the case of the Cu^{I} complex, a bidentate coordination is observed. Compound **5** coordinates to both Cu^{I} and Pt^{II} in a bidentate fashion, in which the two phosphorus atoms coordinate in a *cis* arrangement to the Pt^{II} center.

Introduction

Tetra-*tert*-butylcalix[4]arene,¹ (1, Scheme 1), a cyclic tetramer composed of phenolic units linked *via* the ortho positions by methylene bridges, is an important building block in supramolecular chemistry.^{1,2} It has been well established that the calix[4]arenes can adopt four extreme, different conformations³ (the cone, partial cone, 1,2-alternate, and the 1,3-alternate) rendering different, potentially useful geometries of the building block. Selective functionalization⁴ at the phenolic OH groups (lower rim) and at the *para* positions of the phenol rings (upper rim) has led to the development of calix[4]arene hosts capable of recognizing neutral molecules,⁵ cations,⁶ and more recently anions.⁷

We,^{4a,8} and others,⁹ have had a continued interest in the use of calix[n]arenes as platforms for artificial molecular receptors. However, despite the importance of the calix[4]arenes in supramolecular chemistry,

examples of transition metal complexes of calix[4]arenes are rare.^{10–12,14,18,20} Those with transition metals of catalytic interest (e.g. Rh^{I} , Pt^{II} , Pd^{II}), in pursuit of a supramolecular catalyst,¹³ have been investigated to an even lesser extent.^{11a} Early transition metal complexes of calix[4]arenes, in which the transition metal cation coordinates directly to the phenoxide moieties of the calix[4]arene skeleton have been isolated.¹⁰ There are examples in which the calix[4]arene acts as a second sphere ligand for $\text{Ni}^{\text{II}}(\text{OH}_2)_5(\text{NC}_5\text{H}_5)$ and $\text{Cu}^{\text{II}}(\text{OH}_2)_4(\text{NC}_5\text{H}_5)_2$ cations.¹² Tri-substituted calix[4]arene^{11b} (lower rim) and tetrasubstituted calix[4]arene^{11a} (upper rim) ligands have been prepared and have shown a high affinity for transition metal cations; however, no metal complexes have been isolated. Selective alkylation at the 1,3-distal hydroxy groups of the calix[4]arene with 2-(bromomethyl)-6-(hydroxymethyl)pyridine or 6-(bromomethyl)-6'-methylbipyridine¹⁴ afforded bis-functionalized calix[4]arene ligands. The mononuclear Cu^{I} and Cu^{II} complexes of the respective ligands were reported.

The fact that bis-phosphine ligands play an important role in transition metal based catalysis is well known, and more recently chiral monodentate ligands have proven to be good catalysts in hydrosilylation reactions.¹⁵

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Scheme 1

A few reports¹⁶ have appeared on the phosphorylation of calix[4]arenes; however, these pentavalent phosphorus compounds are not sufficient ligands for transition metal cations in low oxidation states. To our knowledge only one example of a phosphine functionalized calix[4]arene (upper rim) has been prepared by Atwood and co-workers.¹⁷ Extraction experiments showed the calix[4]arene to have a high affinity for transition metal cations; however, no complexes were isolated. Floriani *et al.*¹⁸ have prepared a tetraphosphinite calix[4]arene (lower rim) and the polymetallic Cu^I compound where the versatile coordination geometries of the Cu^I ions (diagonal and trigonal) are realized. Other phosphinite calix[4]arenes have been synthesized;¹⁹ however, no coordination properties were investigated. Puddephatt and co-workers²⁰ have designed a tetraphosphonite resorcin[4]arene (upper rim) and prepared the tetra Au^I, tetra Cu^I, and tetra Ag^I metal complexes. In the case of the tetranuclear Cu^I and Ag^I complexes, an unprecedented halide inclusion was recognized, in which a chloride ion is included *via* three bonds to the four Cu^I centers or through four bonds to the four Ag^I centers, respectively.

In the present report we describe the preparation of lower rim 1,3-diphosphinite and 1,3-diphosphino calix[4]arenes. The isolation and coordination properties of the Rh^I, Pt^{II}, and Cu^I transition metal complexes is described.

Results and Discussion

Ligand Synthesis. The syntheses of the calix[4]arene ligands **3** and **5** are depicted in Scheme 1. Previously, the analogous 5,11,17,23-tetra-*tert*-butyl-25,27-bis((diphenylphosphino)oxy)-26,28-dimethoxy calix[4]arene has been prepared and shown to exist in a partial cone conformation when potassium hydride was used as the base.^{19a}

However, when *n*-BuLi was used as the base during the reaction,^{19b} a mixture of the cone (25%) and the 1,2-alternate (60%) conformations was observed. For this reason, we decided to use the dipropoxy precursor, **2**, where the bulkier *n*-propyl groups fix the calix[4]arene skeleton in a specific conformation.^{4b}

Selective alkylation of calix[4]arene **1** with *n*-propyl iodide (K₂CO₃, CH₃CN) results in calix[4]arene **2** in exclusively the cone conformation. Deprotonation of the remaining phenolic oxygens of the cone precursor, **2**, with a strong base (*n*-BuLi) and subsequent reaction with chlorodiphenylphosphine resulted in the formation of the diphosphinite calix[4]arene ligand **3**, which was isolated in 53% yield. NMR spectroscopy proved that the cone conformation is maintained in calix[4]arene **3**. Two doublets in the ¹H NMR spectrum (4.13 and 2.77 ppm, *J* = 12.5 Hz), and one peak at 32.0 ppm in the ¹³C NMR spectrum²¹ for the methylene bridge, are observed. The separation of the *tert*-butyl resonances (1.29 and 0.79 ppm, respectively) and the aryl protons of the calix[4]arene skeleton (6.98 and 6.31 ppm) in the ¹H NMR spectrum indicate a "pinched" cone conformation. The ¹³C NMR spectrum further indicates that the phenyl rings on the phosphorus atoms are not equivalent since 16 resonances are observed in the aromatic region (only 12 would be expected if these phenyl rings were equivalent). This is probably due to restricted rotation of the phenyl rings imposed by steric constraints of the calix[4]arene skeleton. The ³¹P NMR spectrum shows only one peak at 121.62 ppm (relative to 85% H₃PO₄), demonstrating the equivalency of the phosphorus atoms, and also that no oxidation of the phosphinite had occurred. It is noteworthy that oxidation does occur in the mass spectrum (FAB-MS). The molecular ion peak at 1101.4 [M + H]⁺ is present; however, additional, smaller peaks corresponding to the oxidation of the phosphorus atoms are observed.

Calix[4]arene **5** was prepared from the known ditosylate calix[4]arene **4**²² with KPPH₂ in THF in 58% yield after column chromatography. The cone conformation is confirmed by NMR spectroscopy (¹H NMR: two doublets at 4.33 and 3.04 ppm (*J* = 12.5 Hz), for the methylene bridge protons; ¹³C NMR: one peak at 31.33 ppm for the methylene bridge;¹⁹ ³¹P NMR: one peak at -23.93 ppm). In contrast to **3**, calix[4]arene **5** does not exist in such an extreme "pinched" cone conformation, as can be seen

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Chart 1

Chart 2

from the ^1H NMR spectrum (aryl protons at 6.75 and 6.74 ppm, and *tert*-butyl peaks at 1.063 and 1.060 ppm). As in the case of the diphosphinite calix[4]arene **3**, the diphosphine **5** also exhibits a molecular ion peak at 1156.8 in the FAB-MS, as well as additional peaks corresponding to the oxidation of the phosphorus atoms. Both the diphosphinite calix[4]arene **3** and the pendant diphosphine calix[4]arene **5** are stable in the solid state; however, if left in solution they are prone to oxidation of the phosphorus atoms.

Transition Metal Complexes. Reaction of 0.5 mol equiv of $[\text{Rh}(\text{COD})\text{Cl}]_2$ with calix[4]arene **3** resulted in the isolation of two distinct species. These compounds were identified as the bimetallic (**6**) and the monometallic (**7**) Rh^{I} complexes shown in Chart 1. FAB-MS and TLC gave no indication that a third compound, e.g. a monorhodium bis-coordinated species, was present. If 1 mol equiv of the starting Rh^{I} dimer was used during the reaction, then the bimetallic complex was formed exclusively. The structures were determined based on elemental analysis and NMR spectroscopy. The bimetallic complex **6** exhibits two COD molecules per calix[4]arene in the ^1H NMR spectrum, accompanied by the characteristic downfield shift of the olefinic protons *trans* to the phosphinite ligand. Also, the ^{31}P NMR spectrum shows only one resonance (doublet) at 131.13 ppm (~ 10 ppm downfield with respect to the free ligand) with a characteristic coupling constant of $J_{\text{Rh-P}} = 182.5$ Hz.²³ An important structural feature of the bimetallic complex **6** is that the calix[4]arene skeleton dictates that the two metal centers are on the same face of the molecule. This has been shown²⁴ to be a significant aspect in the design of bimetallic catalysts. The monometallic complex shows only one COD molecule per calix[4]arene in the ^1H NMR spectrum. The ^{31}P NMR spectrum has two resonances, one doublet corresponding to the coordinated phosphinite at 131.56 ($J_{\text{Rh-P}} = 182.5$ Hz) and one singlet at 31.59 ppm. This latter resonance is typical of an oxidized phosphinite, which probably occurred during handling of the sample. In both cases the ligand coordinates in a monodentate fashion.

The Cu^{I} complex of calix[4]arene **3** (**8**, Chart 2) has been prepared by reaction of the free ligand with $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$ in THF. The ^1H NMR confirms the "pinched" cone conformation of the ligand since a significant chemical shift difference is observed for the aryl protons and for the *tert*-butyl groups of the calix[4]arene. The ^{31}P NMR shows only one peak at 92.05 ppm, indicating the equivalence of the two phosphorus atoms. The FAB-MS does not show a molecular ion peak $[\text{Cu}^{\text{I}}(\text{3})(\text{CH}_3\text{CN})(\text{PF}_6)]$; however, it does have a peak corresponding to the $\text{Cu}^{\text{I}}(\text{3})$ fragment [1163.8], and a very weak peak at 1179.6, corresponding to the oxidation of one of the phosphorus atoms in this fragment. The FAB-MS showed no evidence of peaks corresponding to two copper atoms per molecule or a 2:1 complex (two calix[4]arene:one copper); thus, combined with the NMR data, a monometallic bidentate coordination complex is likely to be the case. Bidentate coordination of the 1,3-substituted positions of a similar tetraphosphinite calix[4]arene to a Cu^{I} ion has been proven by X-ray crystallography.¹⁸

Interestingly, the elemental analysis shows only one acetonitrile per molecule (coordination to the Cu^{I} ion is confirmed by IR spectroscopy), indicating that either the PF_6^- anion is coordinated to the Cu^{I} ion or that the coordination number of the metal ion is less than four. Either case is known to occur for Cu^{I} coordination compounds and it is impossible to draw a sound conclusion as to the exact coordination environment of the metal ion at this stage of the investigation. The postulated importance of coordinatively unsaturated Cu^{I} complexes in catalytic²⁵ and biological²⁶ systems has increased the interest in the isolation of these complexes.²⁷ The factors governing the stabilization of three-coordinate Cu^{I} complexes are based on steric or electronic effects. Certainly, the steric effects imposed by the calix[4]arene skeleton may stabilize such a coordinatively unsaturated Cu^{I} metal center.

A molecular mechanics simulation, using the UFF in Cerius², has been carried out in order to determine if a tetrahedral coordination of Cu^{I} is possible. For reasons

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Figure 1. Minimized structure of **8** as $\text{Cu(3)(CH}_3\text{CN)(BF}_4\text{)}$, including point charges.

outlined in the experimental section, simulations with and without point charges have been included. The minimized structure of **8** [as $\text{Cu(3)(CH}_3\text{CN)(BF}_4\text{)}$] is shown in Figure 1 and makes clear that a tetrahedral coordination of Cu^{I} is very well possible. A selection of coordination distances and angles is given in the supplementary material, which shows that the differences between including or excluding the electronic contributions is only marginal. It is also noteworthy that the calculated structure is a pinched cone, which is in full agreement with the NMR experiments.

The fact that a bidentate coordination complex is formed with Cu^{I} and monodentate coordination complexes with Rh^{I} may be explained in terms of the preferred coordination geometries of the metal ions and steric restraints imposed by the ligand. Cu^{I} , a d^{10} metal ion, is known to exist in a tetrahedral geometry²⁸ (with coordination number four) or even diagonal and trigonal geometries (with coordination numbers two or three). The most common state for Rh^{I} , a d^8 metal ion, is square planar. CPK models demonstrate that it is much easier to form a tetrahedral bidentate complex (or lower coordination number geometries) than it is to form a square planar bidentate complex.

The Cu^{I} complex of the diphosphino calix[4]arene **5** (**9**, Chart 2) was prepared using $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$. Coordination of the Cu^{I} ion results in a more extreme "pinched" cone conformation of the calix[4]arene skeleton than the free ligand as exemplified in the ^1H NMR spectrum. The ^{31}P NMR spectrum has a single peak at -19.30 ppm, also supporting a bidentate monometallic complex. Similarly to complex **8**, a molecular ion peak $[\text{Cu}^{\text{I}}(\text{5})(\text{CH}_3\text{CN})(\text{PF}_6)]$ is not observed in the positive FAB-MS; however, a peak is present for the $\text{Cu}^{\text{I}}(\text{5})$ fragment [1219.5]. Small peaks corresponding to the oxidation of the phosphorus atoms are observed, but peaks corresponding to higher aggregates are not observed. Elemental analysis shows only one acetonitrile per molecule (coordination to the Cu^{I} ion confirmed by IR spectroscopy), again indicating either coordination of the PF_6^- anion to the metal center or a lower coordination number than four for the Cu^{I} metal ion. The molecular mechanics simulation on **9** [as $\text{Cu(5)(CH}_3\text{CN)(BF}_4\text{)}$] also shows that

a tetrahedral coordination of Cu^{I} is possible (see supplementary material) with the calix[4]arene skeleton in a pinched cone.

The Pt^{II} complex of calix[4]arene **5** (**10**, Chart 2) was prepared from the commercially available *cis*-bis(acetonitrile) platinum(II) chloride, or from *trans*-bis(benzonitrile) platinum(II) chloride.²⁹ In both instances the same product was isolated from the crude mixture. As in the case of complex **9**, complex **10** also exists in a "pinched" cone conformation, as confirmed by spectroscopy. The ^1H NMR has only two doublets (4.13 and 3.08 ppm, $J = 12.5$ Hz) for the methylene bridge protons. The aryl protons of the calix[4]arene backbone are separated by approximately 0.7 ppm, and the *tert*-butyl resonances are separated by approximately 0.6 ppm. The FAB-MS has a molecular ion peak at 1423.5 $[\text{M} + \text{H}]^+$, and also peaks corresponding to the loss of one Cl^- ion (1387.5), and to the loss of two Cl^- ions (1349.8). The most common state for a four coordinate Pt^{II} (d^8) metal complex is square planar. The ^{31}P NMR indicates that the coordination geometry about the Pt^{II} metal ion center is *cis*, as determined from the large coupling constant ($J_{\text{Pt-P}} = 3460$ Hz).²³

Conclusions

Lower rim 1,3-diphosphinite and 1,3-diphosphino calix[4]arene ligands were prepared. The bimetallic Rh^{I} and monometallic Rh^{I} complexes of the 1,3-diphosphinite calix[4]arene exhibit monodentate coordination of the calix[4]arene ligand, whereas in the case of the Cu^{I} complex a bidentate coordination is observed. The Cu^{I} and Pt^{II} complexes of the 1,3-diphosphino calix[4]arene exhibit a bidentate coordination of the ligand, in which a coordinatively unsaturated environment for the Cu^{I} may be realized. A *cis* coordination geometry of ligand **5** with Pt^{II} is observed. Future investigations will involve the analysis of these systems in catalytic reactions, such as hydrogenation and hydroformylation reactions. Present work also includes the selective functionalization of calix[4]arene at the upper rim to obtain suitable ligand systems for the coordination of transition metal cations.

Experimental Section

^1H and ^{13}C NMR spectra were recorded in CDCl_3 relative to TMS (internal standard) unless otherwise stated. ^{31}P NMR spectra were recorded in CDCl_3 relative to 85% H_3PO_4 (external standard). Fast atom bombardment (FAB) mass spectra were obtained using *m*-nitrobenzyl alcohol as a matrix. $[\text{Rh}(\text{COD})\text{Cl}]_2$ and $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$ were bought from Aldrich and used without further treatment. Chlorodiphenylphosphine was distilled immediately prior to use and all other chemicals were analytically pure and used without further purification. Solvent molecules present in the elemental analysis were confirmed by NMR spectroscopy or by Karl Fischer titration. Compounds **1**,³⁰ **2**,^{4b} **4**,²² and $\text{Pt}(\text{PhCN})_2\text{Cl}_2$ ²⁹ were prepared according to literature procedures. All reactions were performed under an argon atmosphere, and in the preparations of **3** and **5**, standard Schlenk techniques were used.

5,11,17,23-Tetra-*tert*-butyl-25,27-bis((diphenylphosphino)oxy)-26,28-dipropoxycalix[4]arene, 3. Compound **2** (1.00 g, 1.36 mmol) was dissolved in dry THF (14 mL) and kept under an argon atmosphere. The solution was cooled to -78°C , and *n*-BuLi (3.41 mL, 5.46 mmol, 1.60 M solution in hexane) was added. The reaction mixture was warmed to room temperature and stirred for approximately 10 min, after

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which the solution was cooled again to $-78\text{ }^{\circ}\text{C}$. ClPPH_2 (0.98 mL, 5.46 mmol) was added in one portion to the reaction mixture. The solution was warmed to room temperature and eventually refluxed for 2 h. The solvent was removed under vacuum and the residue dissolved in toluene (15 mL). After filtration of the LiCl , the volume of the toluene solution was reduced to approximately 1/3 of the original volume, and the product was precipitated as a white solid from solution by the addition of CH_3CN ($\sim 5\text{ mL}$): yield 53%; mp $265\text{--}268\text{ }^{\circ}\text{C}$; ^1H NMR δ 7.72–7.66 (m, 8H), 7.42–7.39 (m, 12H), 6.98 (s, 4H), 6.31 (s, 4H), 4.13 and 2.77 (AB quartet, 8H, $J = 12.5\text{ Hz}$), 3.88 (t, 4H, $J = 7.5\text{ Hz}$), 1.78–1.68 (m, 4H), 1.29 (s, 18H), 0.79 (s, 18H), 0.67 (t, 6H, $J = 7.5\text{ Hz}$); ^{13}C NMR δ 153.5, 149.5, 144.5, 143.9, 140.8, 140.4, 135.8 (s), 132.3, 132.0 (d), 131.1, 131.0 (s), 129.8, 128.2, 128.0, 125.6, 124.6 (d), 75.6 (t), 34.0 (s), 33.6 (s), 32.0 (t), 31.7 (q), 31.1 (q), 22.6 (t), 9.7 (q); ^{31}P NMR δ 121.62; FAB-MS, m/e 1101.4 $[\text{M}^+]$. Anal. Calcd for $\text{C}_{74}\text{H}_{86}\text{O}_4\text{P}_2\cdot\text{H}_2\text{O}$: C, 79.39; H, 7.92. Found: C, 79.11; H, 7.77. Karl Fischer titration calcd for one water per molecule: 1.61. Found: 1.69.

5,11,17,23-Tetra-*tert*-butyl-25,27-bis((diphenylphosphino)ethoxy)-26,28-dipropoxycalix[4]arene, 5. Compound 4 (1.00 g, 0.89 mmol) was dissolved in dry THF (10 mL) after which the solution was degassed by the freeze/thaw method. KPPH_2 (4.46 mL, 2.23 mmol, 0.50 M solution in THF) was added to the resulting solution, and the reaction mixture was refluxed for 1 h. After cooling to room temperature, the solvent was removed to leave a yellow foam which was purified by column chromatography (SiO_2 , CH_2Cl_2) yielding a white foam: yield 58%; ^1H NMR δ 7.46–7.31 (m, 20H), 6.75 (s, 4H), 6.74 (s, 4H), 4.33 and 3.04 (AB quartet, 8H, $J = 12.5\text{ Hz}$), 4.10–3.99 (m, 4H), 3.77 (t, 4H, $J = 7.5\text{ Hz}$), 2.75 (t, 4H, $J = 10.0\text{ Hz}$), 1.063 (s, 18H), 1.06 (s, 18H), 0.87 (t, 6H, $J = 7.5\text{ Hz}$); ^{13}C NMR δ 153.6, 152.7, 144.5, 144.3, 138.6, 138.4 (s), 134.0, 133.7 (d), 132.8 (s), 132.5, 128.5, 124.9 (d), 78.1, 71.5, 71.0 (t), 33.8, 33.8 (s), 31.4 (q), 31.3 (t), 23.4 (t), 10.3 (q); ^{31}P NMR δ -23.93 ; FAB-MS, m/e 1156.8 $[\text{M}^+]$. Anal. Calcd for $\text{C}_{78}\text{H}_{94}\text{O}_4\text{P}_2$: C, 80.93; H, 8.19. Found: C, 80.68; H, 8.14.

$\text{Rh}_2(\mathbf{3})(\text{COD})_2\text{Cl}_2$ (**6**) and $\text{Rh}(\mathbf{3}(\text{P}=\text{O}))(\text{COD})\text{Cl}$ (**7**). Compound **3** (0.10 g, 0.09 mmol) was dissolved in degassed CH_2Cl_2 (5 mL), and subsequently $[\text{Rh}(\text{COD})\text{Cl}]_2$ (0.022 g, 0.045 mmol) was added to the solution, followed by stirring for approximately 1 h at room temperature. The solvent was removed under reduced pressure to yield a yellow solid which was subsequently purified by column chromatography (SiO_2 , CH_2Cl_2). Compound **6** was isolated as the first band ($R_f = 0.4$) and **7** as the second band ($R_f = 0.2$).

$\text{Rh}_2(\mathbf{3})(\text{COD})_2\text{Cl}_2$ (**6**): yield 62%; mp $188\text{--}190\text{ }^{\circ}\text{C}$ dec; ^1H NMR δ 7.75–7.68 (m, 8H), 7.47–7.29 (m, 12H), 6.78 (s, 4H), 6.07 (s, 4H), 5.57 (bs, 4H), 4.28 (bs, 4H), 4.00–3.89 (m, 8H), 2.70–2.48 (m, 10H), 2.18–2.08 (m, 10H), 1.98–1.92 (m, 4H), 1.26 (s, 18H), 0.97 (t, 6H, $J = 7.5\text{ Hz}$), 0.77 (s, 18H); ^{31}P NMR δ 131.13 (d, $J_{\text{Rh-P}} = 182.5\text{ Hz}$); FAB-MS, m/e 1486.2 $[\text{M} - \text{COD}]^+$, 1346.1 $[\text{M} - 2\text{COD} - \text{Cl} + 3\text{H}]^+$, 1238.8 $[\text{M} - 2\text{COD} - \text{Cl} - \text{Rh}]^+$. Anal. Calcd for $\text{C}_{90}\text{H}_{110}\text{O}_4\text{P}_2\text{Rh}_2\text{Cl}_2\cdot\text{H}_2\text{O}$: C, 67.03; H, 7.00. Found: C, 67.20; H, 6.87.

$\text{Rh}(\mathbf{3}(\text{P}=\text{O}))(\text{COD})\text{Cl}$ (**7**): yield 24%; ^1H NMR δ 7.82–7.71 (m, 8H), 7.59–7.51 (m, 2H), 7.48–7.29 (m, 10H), 6.98 (s, 1H), 6.95 (s, 1H), 6.80 (s, 1H), 6.79 (s, 1H), 6.34 (s, 2H), 5.98 (s, 2H), 5.55 (bs, 2H), 4.35 (bs, 2H), 4.28 and 2.72 (AB quartet, 4H, $J = 12.5\text{ Hz}$), 3.95–3.83 (m, 6H), 2.61–2.39 (m, 4H), 2.21–2.05 (m, 6H), 1.98–1.79 (m, 4H), 1.28 (s, 18H), 0.84 (s, 9H), 0.75 (t, 6H, $J = 7.5\text{ Hz}$), 0.70 (s, 9H); ^{31}P NMR δ 131.56 (d, $J_{\text{Rh-P}} = 182.5\text{ Hz}$), 31.59 (s); FAB-MS, m/e 1327.7 $[\text{M} - \text{Cl}]^+$, 1219.3 $[\text{M} - \text{Cl} - \text{COD}]^+$. Anal. Calcd for $\text{C}_{82}\text{H}_{98}\text{O}_5\text{P}_2\text{RhCl}\cdot 2\text{H}_2\text{O}\cdot\text{CH}_2\text{Cl}_2$: C, 67.13; H, 7.06. Found: C, 67.11; H, 6.87.

$\text{Cu}(\mathbf{3})(\text{CH}_3\text{CN})\text{PF}_6$ (**8**). Compound **3** (0.130 g, 0.120 mmol) was dissolved in dry THF (5 mL) and $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$ (0.037 g, 0.120 mmol) was added to the ligand solution. The reaction mixture was stirred at room temperature for approximately one hour. On reduction of the solution volume to approximately 1/3 of the original volume a white solid precipitated from the solution. Yield: 75%; ^1H NMR δ 8.01–7.98 (m, 8H), 7.51–7.40 (m, 12H), 7.09 (s, 4H), 6.26 (s, 4H), 3.80, 2.65 (AB quartet, 8H, $J = 12.5\text{ Hz}$), 3.24 (t, 4H, $J = 7.5\text{ Hz}$), 1.39 (s, 18H), 0.89–0.81 (m, 4H), 0.74 (s, 18H), 0.49 (t, 6H, $J = 7.5\text{ Hz}$); ^{31}P NMR δ 92.05; IR 2279 cm^{-1} (CN); FAB-MS, m/e

1163.5 $[\text{M} - \text{CH}_3\text{CN} - \text{PF}_6]^+$. Anal. Calcd. for $\text{C}_{76}\text{H}_{89}\text{O}_4\text{P}_3\text{NF}_6\text{-Cu}$: C, 67.56; H, 6.64; N, 1.03. Found: C, 67.52; H, 6.93; N, 0.68.

$\text{Cu}(\mathbf{5})(\text{CH}_3\text{CN})(\text{PF}_6)$ (**9**). Compound **5** (0.100 g, 0.087 mmol) was dissolved in dry THF (5 mL), and $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$ (0.032 g, 0.087 mmol) was added to the ligand solution. The solvent was removed to leave a white solid which was purified by column chromatography (SiO_2 , CH_2Cl_2). The product was further purified by recrystallization from a mixture of $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}/\text{CH}_3\text{OH}$: yield 59%; ^1H NMR δ 7.75–7.65 (m, 8H), 7.31–7.28 (m, 12H), 7.01 (s, 4H), 6.37 (s, 4H), 4.39 (t, 4H, $J = 7.5\text{ Hz}$), 4.28 and 3.10 (AB quartet, 8H, $J = 12.5\text{ Hz}$), 3.60 (t, 4H, $J = 10.0\text{ Hz}$), 3.36 (m, 4H), 1.58 (m, 4H), 1.33 (s, 18H), 0.79 (s and t, 24H, $J = 7.5\text{ Hz}$); ^{31}P NMR δ -19.30 ; IR 2272 cm^{-1} (CN); FAB-MS, m/e 1219.5 $[\text{M} - \text{CH}_3\text{CN} - \text{PF}_6]^+$, 1235.9 $[\text{M} - \text{CH}_3\text{CN} - \text{PF}_6 + \text{O}]^+$, 1251.6 $[\text{M} - \text{CH}_3\text{CN} - \text{PF}_6 + 2\text{O}]^+$. Anal. Calcd for $\text{C}_{80}\text{H}_{97}\text{O}_4\text{P}_3\text{NF}_6\text{Cu}\cdot\text{CH}_3\text{OH}$: C, 67.60; H, 7.07; N, 0.97. Found: C, 67.83; H, 6.95; N, 0.83.

$\text{Pt}(\mathbf{5})\text{Cl}_2$ (**10**). Compound **5** (0.34 g, 0.30 mmol) was dissolved in degassed CH_2Cl_2 (10 mL). Solid *trans*- $\text{Pt}(\text{PhCN})_2\text{Cl}_2$ (0.14 g, 0.30 mmol) or *cis*- $\text{Pt}(\text{CH}_3\text{CN})_2\text{Cl}_2$ was added to the ligand solution, and the reaction mixture was stirred at room temperature for approximately 1 h. After solvent removal, the crude product was purified by column chromatography (SiO_2 , CH_2Cl_2): yield 41%; ^1H NMR δ 7.95–7.85 (m, 8H), 7.50–7.43 (m, 12H), 7.06 (s, 4H), 6.35 (s, 4H), 4.13 and 3.08 (AB quartet, 8H, $J = 12.5\text{ Hz}$), 3.94 (m, 4H), 3.71–3.64 (m, 8H), 1.74–1.66 (m, 4H), 1.30 (s, 18H), 0.92 (t, 6H, $J = 7.5\text{ Hz}$), 0.77 (s, 18H); ^{31}P NMR δ 0.13 ($J_{\text{Pt-P}} = 3460\text{ Hz}$); FAB-MS, m/e 1423.5 $[\text{M} + \text{H}]^+$, 1387.5 $[\text{M} + \text{H} - \text{Cl}]^+$, 1349.8 $[\text{M} - 2\text{Cl}]^+$. Anal. Calcd for $\text{C}_{78}\text{H}_{94}\text{O}_4\text{P}_2\text{PtCl}_2\cdot 5\text{H}_2\text{O}$: C, 61.89; H, 6.93. Found: C, 61.64; H, 6.71.

Molecular Mechanics. Calculations were carried out with the universal force field in Cerius², Version 1.5.³¹ Since the provided charge equilibration method³² to calculate point charges on the atoms is conformation dependent, the following approach was used. Initially no coulomb interactions were included until a chemically reasonable structure was obtained. Atom typing was performed automatically, except for the phosphorus and the boron atoms. A BF_4^- ion was used instead of a PF_6^- ion since no atom type for this phosphorus atom was available. Although the PF_6^- ion is somewhat larger than the BF_4^- ion we do not expect a significant difference (see Results and Discussion). For the phosphorus atom a P-3+q atom type was used, as recommended in ref 33, and for the boron atom a B-3 atom type was used. Minimization was performed with a Fletcher–Powell algorithm until the RMS of the energy gradient was $\leq 0.01\text{ kcal mol}^{-1}\text{ \AA}^{-1}$, with no cutoff on the nonbonded interactions. A dielectric constant of 1 was used. The charge equilibration method applied to the complex as a whole led to unrealistically high charges on the copper atom ($> +2.5$). Therefore, the various constituents were treated independently. The formal charge of +1.0 was placed on the copper atom. The molecule of acetonitrile and the ligands **3** and **5** were independently calculated with an overall charge of 0.0. The counteranion was also calculated separately with an overall charge of -1.0 . The resulting structure was minimized including the Coulomb interaction, without a cutoff, until the RMS of the energy gradient was $\leq 0.01\text{ kcal mol}^{-1}\text{ \AA}^{-1}$. The minimization was repeated until after recalculation of the point charges the RMS on the energy gradient was $\leq 0.01\text{ kcal mol}^{-1}\text{ \AA}^{-1}$ without minimization.

Supplementary Material Available: Table with selected distances ($\text{\AA}$) and angles (degrees) of the minimized structures of **8** and **9** (2 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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