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Metallic Macrocycle with a 1,3-Alternate Calix[4]arene Phosphorus Ligand

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The preparation of an 1,3-alternate calix[4]arene phosphorus ligand, 25,27-bis(2-(diphenylphosphino)ethoxy)-26,28-bis(1-propyloxy)calix[4]arene (**3**), is presented. Ligand **3** is obtained in three steps in 64% overall yield. Reaction of **3** with $[Rh(cot)_2]BF_4$ produced the encapsulated rhodium complex $[Rh\{(P,P)\text{-diphen-calix[4]arene}\}]BF_4$ (**4**). As revealed by a single-crystal X-ray diffraction study, the rhodium center has a bent coordination environment with a P–Rh–P angle of 135.66(3)°. Palladation of **3** employing $[Pd(MeCN)_4](BF_4)_2$ yielded the chelate palladium complex **7** in which the palladium center has a slightly bent configuration. Treatment of the ligand with $Pd(cod)Cl_2$ and $[Pd(\eta^3\text{-}C_4H_7)(THF)_2]BF_4$ leads to the isolation of the monometallic complex. Full characterization includes X-ray structural studies of compounds **3**, **4**, and **6**.

Introduction

Calix[4]arenes, which are macrocyclic compounds available in a variety of ring sizes, are of particular interest as inclusion hosts for ions,[1] selective receptors,[2] molecular sensors,[3] and novel sensors for polyanionic species.[4] The recent synthetic development of the functionalization of calix[4]arenes has led to the isolation of cavity-shaped podands displaying highly selective complexation properties toward certain metal ions.[5] The phosphorus functionalization of the calix[4]arene in its cone, patial cone, 1,3-alternate, and 1,2-alternative conformations provides a rather unique set of phosphorus atoms. To date, most studies have focused on calix[4]arenes with phosphorus centers located at the lower rim and some on the upper rim of the macrocycle. Of particular interest, Matt and co-workers[6] prepared conical calix[4]arenes using two anchoring phosphine ligands tethered at distal phenol units. The complexation induced a loop structure through the partial encapsulation of transition metal centers. Their complexation properties seem to be highly dependent on their stereochemical arrangement.

Atwood and co-workers[7] reported the preparation of the tetradentate phosphorus ligand 5,11,17,23-tetrakis(diphenylphosphino)-25,26,27,28-tetramethoxycalix[4]arene. The ligand is shown to exist with multiple conformations, which can be in equilibrium with each other. The introduction of bulky substituents such as propyl and butyl groups at the lower or upper rim is known to inhibit interconversion[8]

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(1) (a) Gutsche, C. D. *Calixarenes*; Royal Society of Chemistry: Cambridge, U.K. (b) Gutsche, C. D. In *Synthesis of Macrocycles: Design of Selective Complexing Agents.* (c) Kim, J. S.; Shon, O. J.; Ko, J. W.; Cho, M. H.; Yu, I. Y.; Vicens, J. *J. Org. Chem.* **2000**, *65*, 2386. (d) Kim, J. S.; Lee, W. K.; No, K.; Asfari, Z.; Vicens, J. *Tetrahedron Lett.* **2000**, *41*, 3345.

(2) (a) Cameron, B. R.; Loeb, S. J. *Chem. Commun.* **1996**, 2003. (b) Kubo, Y.; Maruyana, S.; Ohhara, N.; Nakamura, M.; Tokita, S. *J. Chem. Soc., Chem. Commun.* **1995**, 1727.

(3) (a) Marsella, M. J.; Newland, R. J.; Carroll, P. J.; Swager, T. M. *J. Am. Chem. Soc.* **1995**, *117*, 9842. (b) Kawaguchi, M.; Ikeda, A.; Shinkai, S. *J. Chem. Soc., Perkin Trans. 1* **1998**, 179. (c) Beer, P, D.; Gale, P. A.; Chen, G. Z. *J. Chem. Soc., Dalton Trans.* **1999**, 1897.

(4) (a) Marsella, M. J.; Newland, R. J.; Carroll, P. J.; Swager, T. M. *J. Am. Chem. Soc.* **1995**, *117*, 9842. (b) Beer, P. D. *Chem. Commun.* **1996**, 689. (c) Cameron, B. R.; Loeb, S. J. *Chem. Commun.* **1996**, 2003.

(5) (a) Coolen, H. K. A. C.; van Leeuwen, P. W. N. M.; Nolte, R. J. M. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 905. (b) Cameron, B. R.; Loeb, S. J. *Chem. Commun.* **1996**, 2003. (c) Reetz, M. T.; Rudolph, J. *Tetrahedron Asymmetry* **1993**, *4*, 2405.

(6) (a) Wieser- Jeunesse, C.; Matt, D.; Cian, A. D. *Angew. Chem., Int. Ed.* **1998**, *37*, 2861. (b) Bagatin, I. A.; Matt, D.; Thönnessen, H.; Jones, P. G. *Inorg. Chem.* **1999**, *38*, 1581.

(7) Hamada, F.; Fukugaki, T.; Murai, K.; Orr, G. W.; Atwood, J. L. *J. Inclusion Phenom.* **1991**, *10*, 57.

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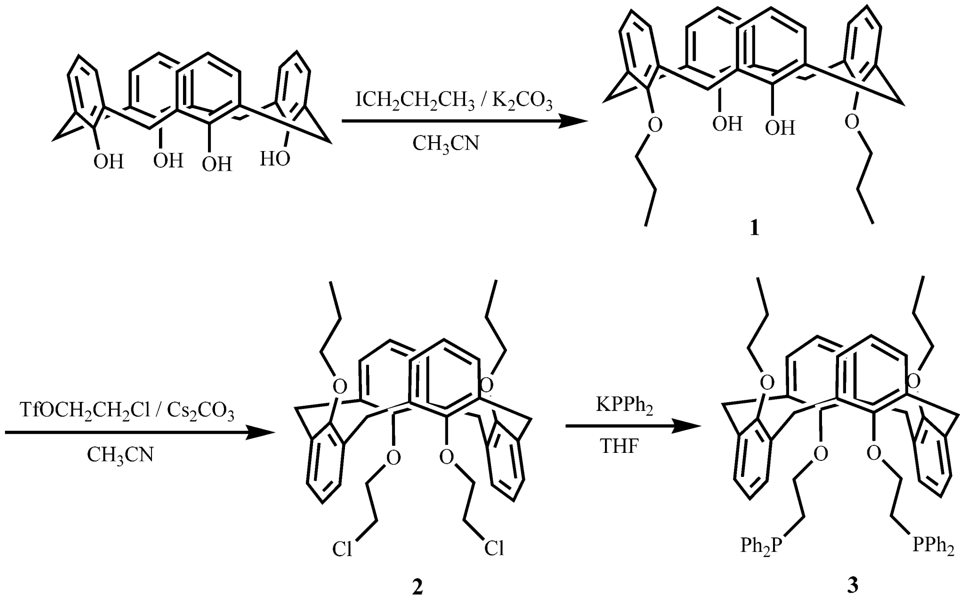
Scheme 1



between the four possible conformations (cone, patial cone, 1,3-alternate, and 1,2-alternate).

During the course of our studies concerning the multifunctional phosphine calix[4]arene, we found that the 1,3-alternate phosphorus calix[4]arene of the type **3** has not been previously known, and the ligand provides a diphosphine ligand suitable for the encapsulation of metal complexes. Of particular importance is the 1,3-alternate conformation which is capable of having π-metal complexation between an entrapped metal cation and two rotated benzene rings to give a more efficient metal ion complexation.[9] Here we describe the novel synthesis of the 1,3-alternate phosphorus calix[4]arene. The isolation and coordination properties of the Rh(I), Pd(II), and Pt(II) metal complexes are described.

Results and Discussion

1,3-Alternate Diphosphinated Calix[4]arene Ligand. The 1,3-alternate diphosphinated ligand **3** can be prepared in three steps, as shown in Scheme 1. In each step, the reaction proceeds smoothly and the product can be obtained in high yield. In the first step, selective alkylation of calix[4]arene with propyl iodide results in the calix[4]arene **1**. It is well-known that the bulky alkyl substituents such as the propyl or butyl group fix the calix[4]arene skeleton in a specific conformation.[9] Diphosphine **3** was prepared via compound **2** and obtained in high yield by reacting **1** with $TfOCH_2CH_2Cl$. The phosphinylation of **2** was performed using 2 equiv of $KPPh_2$ in THF. A similar preparation of tethering $CH_2CH_2PPh_2$ groups has been reported by the Reinhoudt group[10] for a related calixarene. Ligand **3** is a crystalline solid that is stable in air and even in wet $CDCl_3$. Compound **3** is souble in toluene and THF. The ^{1}H, ^{13}C, and ^{31}P NMR spectra, FAB-MS, and X-ray crystal structure for **3** support the proposed structure. The ^{31}P NMR spectrum of **3** shows a singlet at -20.7 ppm. This value is comparable to that observed for the lower rim 1,3-diphosphino calix[4]arene.[11] ^{1}H and ^{13}C NMR signals ascribable to the $ArCH_2Ar$ moiety were observed at 3.63 and 37.4 ppm, respectively. The 1,3-alternate diphosphine ligand **3** also exhibits a molecular ion peak at m/z 933 in the FAB-MS. The structure of **3** was unambiguously established by single-crystal X-ray analysis and is shown in Figure 1. The crystallographic data and processing parameters are given in Table 1. The molecule of **3** possesses a crystallographic 2-fold axis on which the C(16) and C(16a) atoms lie. The interesting feature of the molecular structure of **3** is that the aryl rings bearing the phosphorus units are splayed outward with the aryl rings moving upward and the aryl rings with the propyl groups are pinched together with the aryl rings moving downward. The phosphorus lone pairs are directed toward the exterior of the cavity. A similar geometric configuration was observed in the 26,28-bis((diphenylphosphino)methoxy)calix[4]arene.[12] The three P−C bond lengths lie in the usual range for P−C single bonds.

Rhodium Chelation with 1,3-Alternate Diphosphine Ligand. Ligand **3** was found to be a good model to test the suitability of specific phosphino ether coordination environments for complexing Rh(I). Ligand **3** cleanly reacts with a Rh(I) source generated via the reaction of $[Rh(cot)_2Cl]_2$ with $AgBF_4$ to form the 18-membered $[Rh\{(P,P)\text{-diphencalix[4]arene}\}]BF_4$ (**4**) as shown in Scheme 2. It is noteworthy that

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(8) (a) Bocci, V.; Foina, D.; Pochini, A.; Ungaro, R.; Andretti, G. D. *Tetrahedron* **1982**, *38*, 373. (b) Gutsche, C. D.; Dhawan, B.; Levine, J. A.; No, K. H.; Bauer, L. J. *Tetrahedron* **1983**, *39*, 409. (c) Vézina, M.; Gagnon, J.; Villeneuve, K.; Drouin, M.; Harvey, P. *Organometallics* **2001**, *20*, 273.

(9) (a) Casnati, A.; Pochini, A.; Ungaro, R.; Ugozzoli, F.; Arnaud-Neu, F.; Fanni, S.; Schwing, M.-J.; Egberink, R. J. M.; de Jong, F.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **1995**, *117*, 2767. (b) Kim, J. S.; Shon, O. J.; Lee, J. K.; Lee, S. H.; Kim, J. Y.; Park, K. M.; Lee, S. S. *J. Org. Chem.* **2002**, *67*, 1372.

(10) Cameron, B. R.; van Veggel, F. C. J. M.; Reinhoudt, D. N. *J. Org. Chem.* **1995**, *60*, 2802.

(11) Jeunesse, C.; Dieleman, C.; Steyer, S.; Matt, D. *J. Chem. Soc., Dalton Trans.* **2001**, 881.

(12) Loeber, C.; Matt, D.; Cian, A. D.; Fischer, J. *J. Organomet. Chem.* **1994**, *475*, 297.

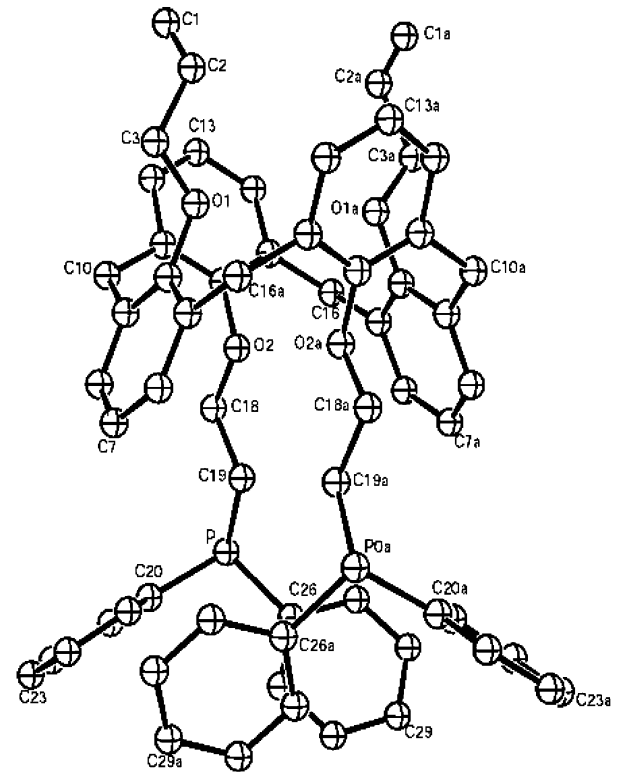

Figure 1. Molecular structure of **3** with 50% probability thermal ellipsoids depicted. Selected bond lengths (Å) and angle (deg): P−C(26) = 1.821(3), P−C(19) = 1.847(3), O(1)−C(3) = 1.368(5), O(2)−C(17) = 1.383(3); C(26)−P−C(20) = 102.44(13), C(18)−C(19)−P = 110.3(2).

Table 1. Crystal and Structure Refinement Data for **3**, **4**, and **6**

	3	**4**	**6**
empirical formula	$C_{62}H_{62}O_4P_2$	$C_{62}H_{62}BF_4O_4P_2Rh$	$C_{62}H_{62}Cl_2O_4P_2Pt$
fw	933.06	1122.78	1199.10
cryst dimens (mm)	0.15 × 0.20 × 0.30	0.30 × 0.30 × 0.40	0.25 × 0.18 × 0.13
cryst syst	monoclinic	monoclinic	monoclinic
space group	*C*2/*c*	*P*2$_1$/*n*	*C*2/*c*
a (Å)	20.0299(18)	14.6562(8)	19.434(5)
b (Å)	16.2113(15)	13.8847(7)	27.224(5)
c (Å)	18.4857(16)	25.5461(14)	13.074(5)
β (deg)	120.196(2)	100.6690(10)	103.435(5)
V (Å^3)	5188.0(8)	5508.6(5)	6728(3)
Z value	4	4	4
D_{calc} (g/cm^3)	1.195	1.354	1.442
F(000)	1984	2328	2968
μ(Mo Kα) (mm^{-1})	0.131	0.429	2.419
temp (K)	298	298	173
2θ range (deg)	1.75−28.32	2.94−56.68	3.00−57.06
no. of reflcns measd	16 900	35 635	20 642
no. of observns ($I > 2\sigma(I)$)	6256	13 407	8023
R	0.0623	0.0532	0.0572
R_w	0.1478	0.1086	0.1116
goodness-of-fit	0.985	0.944	0.992

the calix[4]arene-derived diphosphines bearing auxiliary groups control the degree of encapsulation of the chelated metal atom.[13] A recent report by Matt and co-workers[14] revealed that the reaction of the diphosphane calix[4]arene with $[Rh(1,5\text{-cod})Cl]_2$ or $[Rh(nbd)Cl]_2$ in the presence of $AgBF_4$ afforded the complex with the Rh(cod) or Rh(nbd) fragment.

The characterization of **4** was spectroscopically done using ^{1}H, ^{13}C, and ^{31}P NMR, and the elemental analysis was in excellent agreement with its formulation. The monomeric nature of **4** established by the FAB-MS *m*/*z* 1036. NMR spectroscopy proved that a slight cone conformation is maintained in **4**. Two doublets in the ^{1}H NMR spectrum (3.66 and 3.51 ppm, $J = 15.2$ Hz), and one peak at 31.5 ppm in the ^{13}C NMR spectrum for the methylene bridge, are observed. The ^{31}P NMR spectrum shows only one peak at −10.4 ppm (∼10 ppm downfield with respect to the free ligand) with a characteristic coupling constant of $J_{Rh-P} = 532.2$ Hz. The upfield resonance of **4** resembles the values reported for the $[Rh(cod)(Ph_2PCH_2CH_2OCH_3)_2]$[15] and *cis*-$[RhCl(CO)Ph_2PCH_2P(O)Ph_2]$.[16]

The solid-state crystal structure of **4** (Figure 2) confirmed the results in solution derived from the NMR data. The crystallographic data and processing parameters are given in Table 1. The view from the side, Figure 2a, shows an abbreviated numbering scheme where the hydrogens were omitted for clarity. The view from the top, Figure 2b, indicates that the rhodium atom is located in the middle of the cavity. The shape of the calix[4]arene may be viewed as a pinched cone; the dihedral angle between the aryl rings bearing the phosphorus units is 18.4(2)°, whereas that between the aryl rings substituted by the propyloxy group is 93.8(1)°. Complex **4** has a bent geometry with the bond angle of P(1)−Rh−P(2) being 135.66(3)°. In particular, the angle is such that the rhodium atom is pushed into the cavity. Presumably, the phosphorus arms cause steric strain at the rhodium center, resulting in the slightly distorted configuration of the rhodium atom coordinating to other atoms in the cavity. The long bond distances of Rh−O(3) (3.261(3) Å) and Rh−O(4) (3.386(2) Å) indicates that the oxygen atoms are actually not coordinated to the rhodium center. However, the solid-state structure shows that two of the carbon atoms [C(4), 3.0552(4) Å; C(16), 3.05614(4) Å] lie sufficiently close to the rhodium so as to undergo a substantial interaction.

The agostic C−H··Rh interaction is supported by spectroscopic data. The ^{1}H NMR spectrum of **4** shows the high-field shift of the proton giving rise to a doublet of triplet at 6.50 ppm. The small value of the J_{Rh-H} coupling constant of 1.8 Hz suggests the slight interaction between the rhodium and C−H. In the ^{13}C NMR spectrum of **4**, the quaternary carbon resonance appears at 122.8 ppm. The signal is shifted to slightly high field as a consequence of weak bond encountered between C−H and Rh. Such an interaction was observed in the complex $[Rh(PPh_3)_3]^+$ in which a fairly close side-on one *ortho* C−H bond on one of the phenyl rings is achieved[17] and in the pincer complexes of rhodium.[18]

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(13) (a) Wieser, C.; Matt, D.; Toupet, L.; Bourgeois, H.; Kintzinger, J.-P. *J. Chem. Soc., Dalton trans*. **1996**, 4041. (b) Wieser, C.; Matt, D.; Fischer, J.; Harriman, A. *J. Chem. Soc., Dalton Trans*. **1997**, 2391.

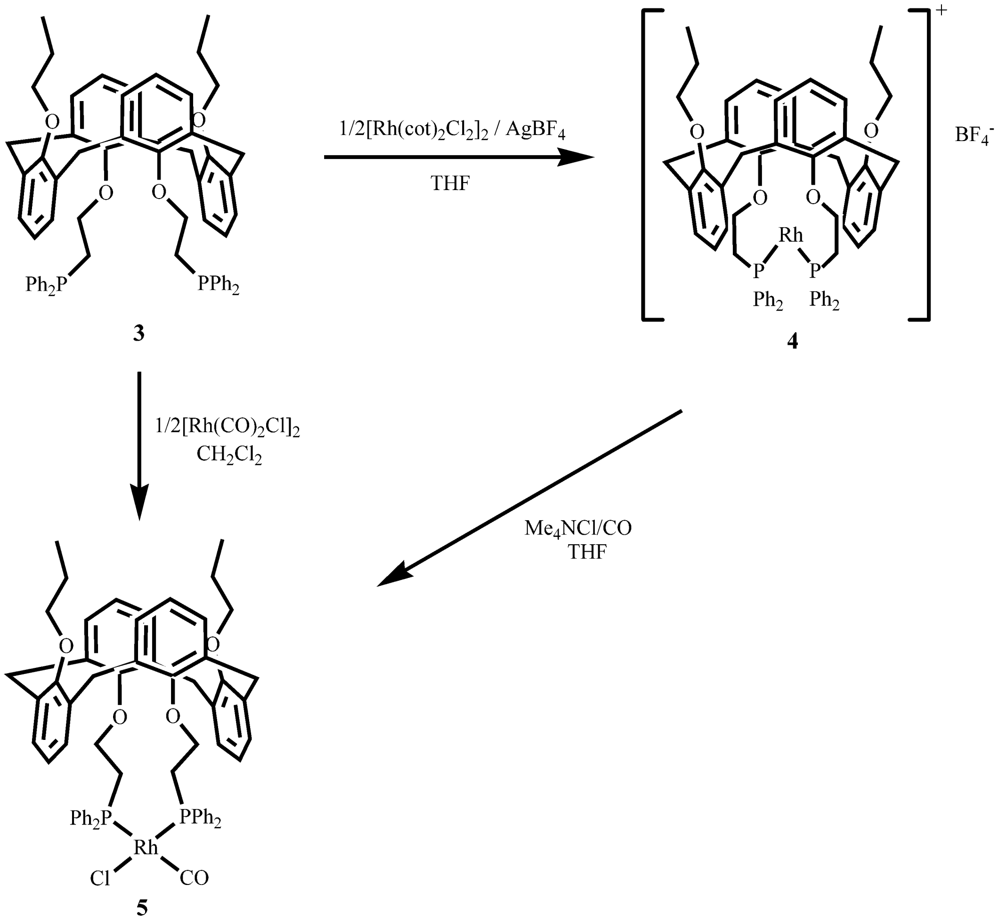
(14) Loeber, C.; Matt, D.; Briard, P.; Grandjean, D. *J. Chem. Soc., Dalton Trans.* **1996**, 513.

(15) Lindner, E.; Norz, H. *Chem. Ber*. **1990**, *123*, 459.

(16) Wegman, R. W.; Abatjoglou, A. G.; Harrison, A. M. *J. Chem. Soc., Chem. Commun*. **1987**, 1891.

(17) Yared, Y. W.; Miles, S. L.; Bau, R.; Reed, C. A. *J. Am. Chem. Soc.* **1977**, *99*, 7076.

Scheme 2



The 1,3-alternate phosphine ligand **3** readily reacted with $[Rh(CO)_2Cl]_2$ in CH_2Cl_2 and yielded the chelate complex **5** which was characterized by ^1H,^{13}C, and ^{31}P NMR, FAB-MS, and IR spectroscopies. The ^{31}P NMR spectrum of **5** exhibited one resonance at 13.1 ppm ($J_{Rh-P} = 122.3$ Hz, $J_{P-P} = 26.6$ Hz) arising from the nonequivalent phosphorus atoms. The J_{Rh-P} coupling constant of 122.3 Hz indicates a cis arrangement.[19] Such a cis configuration was observed in the complex reported by Matt and co-workers.[10] In the ^{13}C NMR spectrum, all the bridging methylene carbon of **5** are equivalent, giving a singlet at 28.8 ppm. The IR spectrum of **5** exhibits one strong $\nu(C{\equiv}O)$ absorption band at 1969 cm^{-1}. All these results clearly indicate that **5** has a cis configuration. We have also carried out the reaction of **4** with Me_4NCl/CO in THF at room temperature in an alternate synthesis of complex **5**, which was isolated as yellow crystals in 90% yield (Scheme 2).

Dichloro Pt(II) Complex [PtCl$_2${(*P*,*P*)-diphencalix[4]-arene}] (6). The reaction of $Pt(cod)Cl_2$ with **3** in CH_2Cl_2 yielded the dichloro platinum complex **6** in 80% yield (Scheme 3). The NMR and FAB-MS spectroscopies and elemental analysis provided the identification of **6**. The intial indication of the mononuclear formulation for **6** stemmed from the observation of a parent peak at *m*/*z* 1199 in the FAB-MS spectrum. The ^{31}P NMR spectrum of **6** shows a typical pattern for the proposed cis formulation. The large coupling constant ($J_{Pt-P} = 3625$ Hz) value indicates the cis coordination of the phosphine ligand about the platinum atom.[20]

The structure of **6** was unequivocally confirmed by X-ray diffraction. Figure 3 shows the molecular structure of **6** with the selected bond distances and angles. The complex has a crystallographic 2-fold symmetry, running through the two oxygens O(1) and O(2) of the propyloxy groups and platinum(1) atom. The geometry of the palladium is approximately square planar in which both phosphorus atoms in **6** are cis with the P(1)−Pt(1)−P(1)* angle of 106.63(8)°.

The bond distances to Pt for both Cl(1) (2.3430(16) Å) and P(1) (2.2751(16) Å) are comparable to those reported for *cis*-$Pt(PEt_2Ph)(EtNC)Cl_2$.[21]

Palladium Chelation with 1,3-Alternate Diphosphine Ligand. The palladation of **3** employing $[Pd(MeCN)_4](BF_4)_2$ in acetone yielded the chelate palladium complex **7** in 67% yield. The resulting yellow complex **7** was isolated as an

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(18) (a) Crabtree, R. H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 789. (b) Vigalok, A.; Uzan, O.; Shimon, L. J. W.; Ben-David, Y.; Martin, J. M. L.; Milstein, D. *J. Am. Chem. Soc.* **1998**, *120*, 12539.

(19) Loeber, C.; Wieser, C.; Matt, D.; Cian, A. D.; Fischer, J.; Toupet, L. *Bull. Soc. Chim. Fr.* **1995**, *132*, 166.

(20) (a) Takenaka, K.; Obora, Y.; Jiang, L. H.; Tsuji, Y. *Organometallics* **2002**, *21*, 1158. (b) Favez, R.; Roulet, R.; Pinkerton, A. A.; Schwarzenbach, D. *Inorg. Chem.* **1980**, *19*, 1356. (c) Pregosin, P. S.; Kunz, R. W. *^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes*; Springer-Verlag: Berlin, 1976; Vol. 16.

(21) Jovanovic, B.; Manojlovi'c-Muir, L. *J. Chem. Soc., Dalton Trans.* **1972**, 1176.

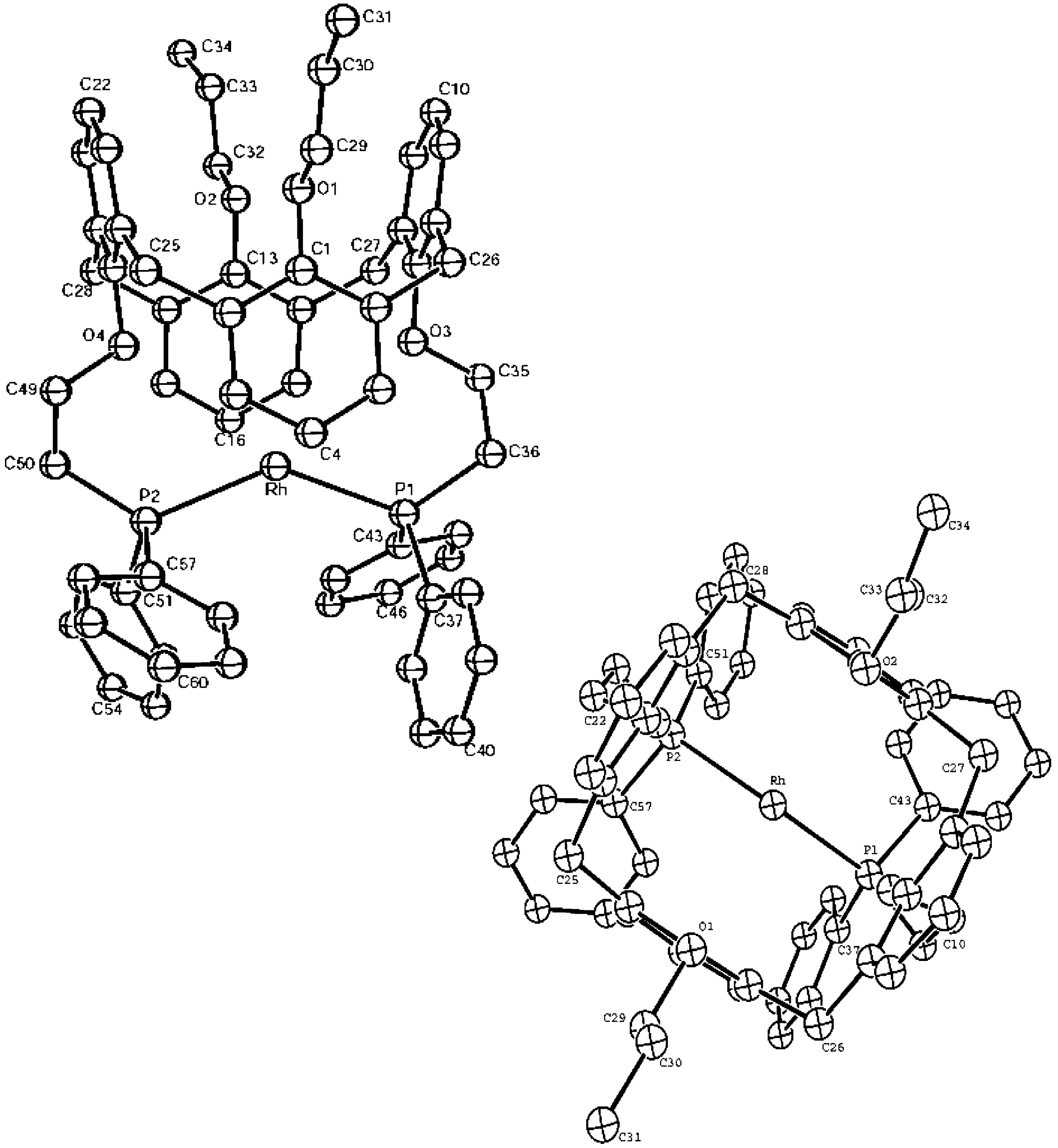
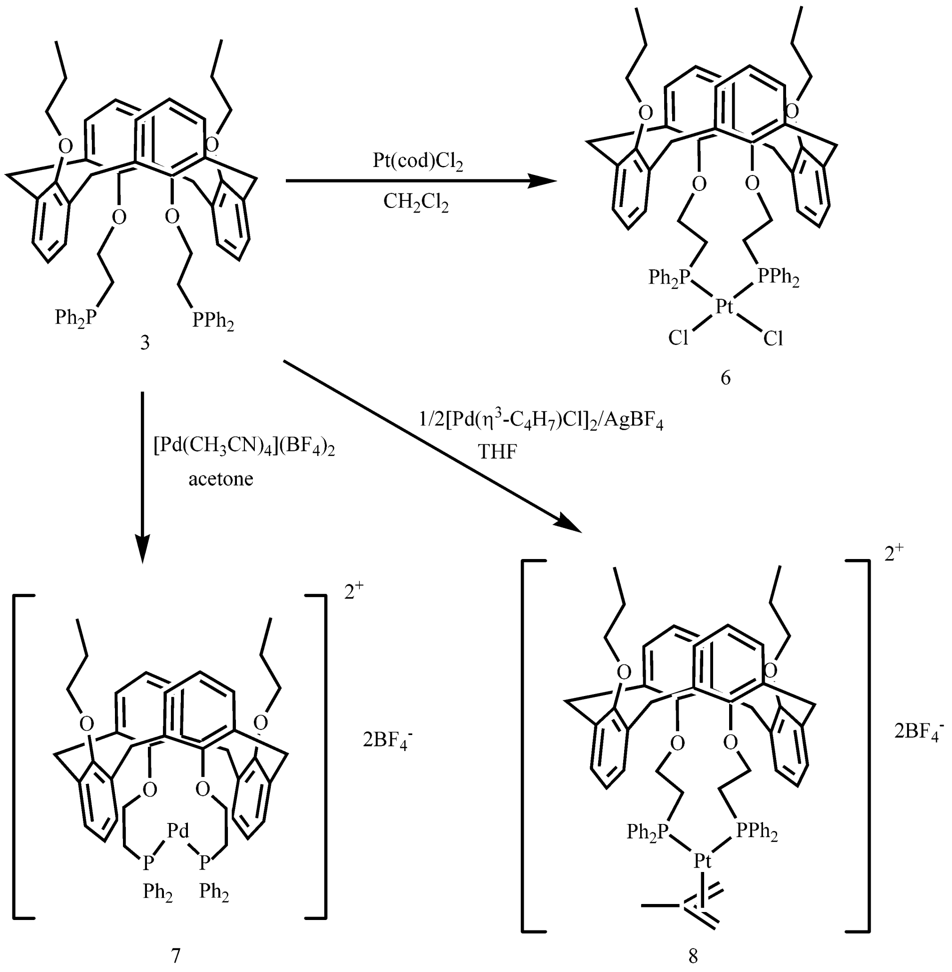


Figure 2. ORTEP representation of **4** with 50% probability thermal ellipsoids depicted: (a) view from the side; (b) view from the above. Selected bond lengths (Å) and angle (deg): Rh−P(1) = 2.4276(9), Rh−P(2) = 2.4275(9), Rh−O(3) = 3.261(3), Rh−O(4) = 3.386(2), Rh−C(4) = 3.0553(4), Rh−C(16) = 3.056(4); O(3)−Rh−O(4) = 97.73(5), P(1)−Rh−P(2) = 135.66(3).

air-sensitive solid. The structure was determined on the basis of an elemental analysis and FAB-MS and NMR spectroscopies. The ^{1}H and ^{13}C NMR spectrum show one resonance at 3.16 and 36.7 ppm, respectively, due to the hydrogen atoms of the ArCH_2Ar groups. The ^{31}P NMR shows only one peak at 17.39 ppm, indicating the equivalence of the two phosphorus atoms. The FAB-MS spectrum of **7** exhibits a peak at *m*/*z* 1039 displaying the expected isotopic profile of the $[M - 2BF_4]^+$ cation. The elemental analysis shows the proposed formulation, indicating that CH_3CN is not coordinated to the Pd(II) center. It is noteworthy that the Cu(I) complex of the calix[4]arene prepared by the reaction of the 1,3-diphosphino calix[4]arene with $[Cu(CH_3CN)_4]PF_6$ has a tetrahedral coordination of Cu(I) coordinated by CH_3CN and PF_6.[10] On the basis of the spectroscopic data, we can tentatively assign that the palladium atom has a slightly bent configuration, as with the rhodium complex **4**.

The allylpalladium complex **8** was prepared in high yield by the reaction of $[pd(\eta^3\text{-}C_4H_7)(THF)_2]BF_4$ with **3**. The ^{1}H, ^{13}C, and ^{31}P NMR spectra, FAB-MS, and elemental analysis of compound **8** are consistent with the proposed structure. The ^{1}H NMR spectrum of **8** showed the H_{anti} and H_{syn} protons of the allylic part at 3.28 and 3.96 ppm, respectively. Two distinct resonances indicate that the allyl rotation is slow on the NMR time. Upon lowering of the temperature (−40 °C), the two singnals did not change. No dynamics of the metallocyclic unit were observed. A similar observation has

Scheme 3



been seen for the cationic palladium complex.[20] This is in contrast to other Pd η^3-allyl complexes which show a fluxional behavior.[22] The ^{31}P NMR spectrum of **8** showed a single peak at 10.8 ppm. The FAB-MS of **8** showed an intense peak at m/z 1094 corresponding to the $[M - BF_4]^+$ ion.

In summary, a novel 1,3-alternate calix[4]arene phosphorus ligand was prepared. The ligand was an effective reactant in the formation of metal complexes. The monometallic Rh(I) complex of the 1,3-alternate diphosphino calix[4]arene exhibits a chelate coordination of the phosphorus ligands with the rhodium atom having a bent structure, whereas, in the reaction of $[Rh(CO)_2Cl]_2$, a bidentate coordination was observed. The Pt(II) complexes of the 1,3-alternate diphosphino calix[4]arene exhibit a bidentate coordination of the ligand. The cis coordination geometry of ligand **3** with three Pt(II) complexes is observed. Future studies will involve the synthesis of a 1,3-alternate tetraphosphino calix[4]arene and its metal complexes.

Experimental Section

All experiments were performed under a nitrogen atmosphere in a Vacuum Atmospheres drybox or by standard Schlenk techniques. THF, toluene, and ether were distilled from sodium benzophenone. *n*-Hexane, CH$_2$Cl$_2$, and pentane were dried and distilled from CaH$_2$. The ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Varian Gemini 300 spectrometer operating at 300.00, 75.44, and 121.44 MHz, respectively. Chemical shifts were referenced relative to TMS. The IR spectra were recorded on a Biorad FTS-165 spectrometer. Mass spectra were recorded on a JEOL JMS-SX102A instrument. Elemental analyses were performed with a Carlo Erba Instruments CHNS-O EA 1108 analyzer. Calixarene,[23] $[Rh(cot)_2Cl]_2$,[24] $[Rh(CO)_2Cl]_2$,[25] $[Pd(CH_3CN)_4](BF_4)_2$,[26] and $[Pd(\eta^3\text{-}C_4H_7)Cl]_2$[27] were synthesized according to procedures reported in the literature.

26,28-Bis(1-propyloxy)calix[4]arene (1). To a suspension of calix[4]arene (3.27 g, 7.70 mmol) in 150 mL of acetonitrile were added 1-iodopropane (2.90 g, 16.2 mmol) and K$_2$CO$_3$ (1.06 g, 7.70 mmol), and the reaction mixture was refluxed for 24 h under nitrogen atmosphere. The solvents was removed in vacuo, and 50 mL of 10% aqueous HCl solution and 50 mL of CH$_2$Cl$_2$ were added. The organic layer was separated and washed with water (2 × 50 mL). The organic phase was dried over anhydrous MgSO$_4$, and the solvent was removed in vacuo to give a colorless oil which can be easily recrystallized from 100 mL of cosolvents (diethyl ether−hexane: 7:3). Pure product was obtained in 90% yield. Mp: 138 °C. ^{1}H NMR(CDCl$_3$): δ 7.82 (s, 2H, ArO*H*), 7.20−6.48 (m,

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(22) Dieleman, C.; Steyer, S.; Jeunesse, C.; Matt, D. *J. Chem. Soc., Dalton Trans.* **2001**, 2508.
(23) Tashiro, M.; Fukata. G.; Mataka, S.; Oe, K. *Org. Prep. Proced. Int.* **1975**, *7*, 231.
(24) Van der ENT, A.; Onderdelinden, A. L. *Inorg. Synth.* **1990**, *28*, 90.
(25) McCleverty, J. A.; Wilkinson, G. *Inorg. Synth.* **1990**, *28*, 84.
(26) Thomas, Richard R.; Sen, Ayusman. *Inorg. Synth.* **1990**, *28*, 63.
(27) Dent, W. D.; Long, R.; Wilkinson, A. J. *J. Chem. Soc.* **1964**, 1585.

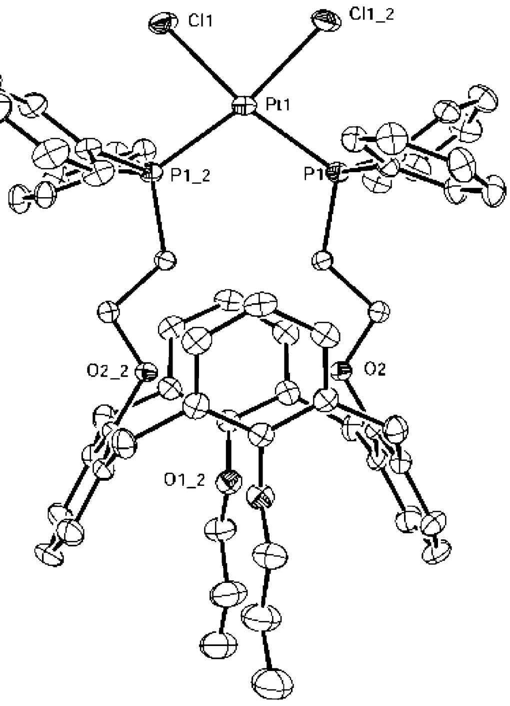

Figure 3. Molecular structure of **6** with 50% probaty thermal ellipsoids depected. Selected bond lengths (Å) and angle (deg): Pt(1)−P(1) = 2.2751(16), Pt(1)−Cl(1) = 2.3430(16); P(1)−Pt(1)−P(1)* = 106.63(8), Cl(1)−Pt(1)−Cl(1)* = 87.72(9).

12H, Ar-*H*), 3.92 (s, 8H, ArC*H₂*Ar), 3.48 (t, 4H, *J* = 7.5 Hz, OC*H₂*), 1.52 (m, 4H, $CH_2CH_2CH_3$) 0.98(t, 6H, *J* = 7.8 Hz, CH_2CH_3).

25,27-Bis(2-chloroethoxy)-26,28-bis(1-propyloxy)calix[4]arene (2), **1,3-Alternate Conformation.** Under nitrogen, a solution of 1,3-bis(propyloxy)calix[4]arene (**1**) (1.07 g, 1.03 mmol), tosylate of 2-(2-chloroethoxy)ethanol (1.84 g, 3.62 mmol), and Cs_2CO_3 (1.2 g, 3.62 mmol) in dry MeCN (50 mL) was refluxed for 24 h. The MeCN was then evaporated in vacuo. The residue was acidified with dilute HCl, and the mixture was extracted with CH_2Cl_2. The combined CH_2Cl_2 extracts were washed with water, dried over $MgSO_4$, and evaporated in vacuo. The pure product was isolated by column chromatography of the residue obtained by evaporation of filtrate on silica gel with EtOAc−hexane (1:3) as eluent. Mp: 145−148 °C. IR (KBr pellet, cm^{-1}): 1382, 1192. ^1H NMR ($CDCl_3$): δ 7.18−6.42 (m, 12H, Ar-*H*), 3.82 (s, 8H, ArC*H₂*Ar), 3.74−3.42 (m, 12H, OC*H₂*−, $ClCH_2CH_2$), 1.75−1.47 (m, 4H, $OCH_2CH_2CH_3$), 1.12−0.98 (t, 6H, $OCH_2CH_2CH_3$).

25,27-Bis(2-(diphenylphosphino)ethoxy)-26,28-bis(1-propyloxy)calix[4]arene, (*P*,*P*)-diphencalix[4]arene (3**).** To a stirred THF solution (15 mL) of **2** (100 mg, 0.16 mmol) was added $KPPh_2$ (0.34 mmol) at 0 °C. The temperature was warmed to room temperature and stirred for 15 h at that temperature. The solvent was removed in vacuo. Column chromatography on silica gel with ethyl acetate−hexane (1:3) as an eluent ($R_f = 0.9$) gave a white solid which could be recrystallized using toluene−hexane to give **3** in 80% yield. Mp: 208 °C. ^1H NMR ($CDCl_3$): δ 7.45−7.33 (m, 20H, P*Ph*), 6.95 (d, 4H, *J* = 7.2 Hz), 6.75 (m, 6H), 6.60 (t, 2H, *J* = 7.2 Hz), 3.63 (S, 8H, ArC*H₂*Ar), 3.56 (t, 4H, *J* = 14.7 Hz), 3.36 (t, 4H, *J* = 6.9 Hz, OC*H₂*), 2.13 (t, 4H, *J* = 7.8 Hz, PC*H₂*), 1.37 (m, 4H, $OCH_2CH_2CH_3$), 0.72 (t, 6H, *J* = 7.2 Hz, CH_2CH_3). $^{13}C\{^1H\}$ NMR($CDCl_3$): δ 157.4, 156.2, 138.1, 134.0, 133.9, 133.0, 132.7, 129.6, 128.8, 128.7, 128.6, 122.4(d), 72.8, 67.2, 37.4, 28.4(d), 23.2, 10.4. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −20.7. Anal. Calcd for $C_{62}H_{62}O_4P_2$: C, 79.81; H, 6.69. Found: C, 79.34; H, 6.54.

[Rh{(*P*,*P*)-diphencalix[4]arene}]BF₄ (**4**)**.** To a stirred THF solution (60 mL) of $[Rh(cot)_2Cl_2]_2$ (35 mg, 0.048 mmol) and $AgBF_4$ (20 mg, 0.107 mmol) was added **3** (90 mg, 0.097 mmol) dissolved in THF (20 mL). The solution was stirred for 20 h at room temperature and filtered. The solution was evaporated and washed with ether and toluene. Recrystallization using CH_2Cl_2/Et_2O gave **4** as reddish-yellow crystals in 64% yield. Mp: 198 °C (dec). ^1H NMR (CD_2Cl_2): δ 7.58−7.26 (m, 20H, P*Ph*), 7.04 (d, 4H, *J* = 7.2 Hz), 6.82−6.75 (m, 6H), 6.50 (dt, 2H, *J* = 7.2 and 1.8 Hz), 4.11−4.02 (m, 4H, OC*H₂*), 3.66 and 3.51 (AB quartet, 8H, *J* = 15.2 Hz PhC*H₂*Ph), 3.46 (t, 4H, *J* = 7.8 Hz, OC*H₂*), 2.94 (m, 4H, PC*H₂*), 1.46 (m, 4H, $CH_2CH_2CH_3$), 0.77 (t, 6H, *J* = 7.5 Hz, CH_2CH_3). $^{13}C\{^1H\}$ NMR($CDCl_3$): δ 158.2, 157.3, 135.3, 133.3, 132.9, 132.5, 132.3, 131.6, 130.5, 129.8, 129.3, 129.0, 122.8, 72.2, 66.2, 37.7, 31.5, 22.6, 9.7. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −10.4 (d, $J_{Rh-P} = 532.2$ Hz). FAB-MS: *m/z* 1036 $[(M - BF_4)^+]$. Anal. Calcd for $C_{62}H_{62}BF_4O_4P_2Rh$: C, 66.32; H, 5.56. Found: C, 65.96; H, 5.42.

[Rh(CO)Cl{(*P*,*P*)-diphencalix[4]arene}] (5). To a stirred CH_2Cl_2 solution (10 mL) of **3** (50 mg, 0.054 mmol) was added $[Rh(CO)_2Cl]_2$ (10 mg, 0.027 mmol) dissolved in CH_2Cl_2 (10 mL). The solution was stirred for 12 h at room temperature. The solution was evaporated and washed with ether. Recrystallization using $CH_2Cl_2-Et_2O$ gave **5** as pale yellow crystals in 67% yield. Mp: 194 °C. ^1H NMR (CD_2Cl_2): δ 7.69−7.22 (m, 20H, P*Ph*), 6.90 (d, 4H, *J* = 7.5 Hz), 6.80−6.60 (m, 6H), 6.52 (t, 2H, *J* = 7.5 Hz), 3.96 (m, 4H, OC*H2*), 3.49 (s, 8H, PhC*H₂*Ph), 3.24 (t, 4H, *J* = 7.5 Hz, OC*H₂*), 2.68 (m, 4H, PC*H₂*), 1.48 (m, 4H, $CH_2CH_2CH_3$), 0.67 (t, 6H, *J* = 7.5 Hz, CH_2CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 167.6, 158.4, 157.2, 145.8, 135.6, 135.2, 134.2, 133.2, 132.4, 131.2, 130.6, 129.6, 128.7, 128.4, 68.0, 56.0, 38.7, 28.8, 22.9, 10.8. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 13.1 (dd, $J_{Rh-P} = 122.3$ Hz, $J_{P-P} = 26.6$ Hz). FAB-MS: *m/e* 1099 $[M^+]$. IR (KBr pellet, cm^{-1}): 1969 (ν_{CO}). Anal. Calcd for $C_{63}H_{62}ClO_5P_2Rh$: C, 68.82; H, 5.67. Found: C, 69.96; H, 5.82.

[PtCl₂{(*P*,*P*)-diphencalix[4]arene}] (**6**)**.** To a stirred CH_2Cl_2 solution (20 mL) of $Pt(cod)Cl_2$ (0.05 g, 0.13 mmol) was added **3** (0.12 g, 0.13 mmol) dissolved in CH_2Cl_2 (10 mL). The solution was stirred for 12 h at room temperature. The solution was evaporated and washed with hexane (2 × 10 mL). Recrystallization using CH_2Cl_2−toluene gave **6** as pale yellow crystals in 81% yield. Mp: 236 °C. ^1H NMR (CD_2Cl_2): δ 7.46−7.12 (m, 20H, P*Ph*), 6.88−6.46 (m, 12H, Ar-*H*). 3.64 (m, 4H, OC*H₂*), 3.43 (s, 8H, Ar*CH₂*Ar), 3.27 (t, 4H, *J* = 7.8 Hz, OC*H₂*). 2.60 (m, 4H, PC*H₂*), 1.43 (m, 4H, $CH_2CH_2CH_3$), 0.76 (t, 6H, *J* = 7.5 Hz, CH_2CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 158.2, 156.8, 137.7, 134.2, 133.6, 131.9, 131.2, 130.0, 129.1, 127.7, 126.8, 126.2, 123.1, 70.8, 65.7, 36.2, 30.2, 22.9, 9.9. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −4.0 (dd, $J_{Pt-P} = 3625$ Hz, $J_{P-P} = 62$ Hz). FAB-MS: *m/e* 1199 $[M^+]$. Anal. Calcd for $C_{62}H_{62}Cl_2O_4P_2Pt$: C, 62.05; H, 5.21. Found: C, 61.84; H, 5.04.

[Pd{(*P*,*P*)-diphencalix[4]arene}](BF₄)₂ (7). To a stirred CH_2Cl_2 solution (15 mL) of **3** (0.095 g, 0.10 mmol) was added $[Pd(CH_3CN)_4](BF_4)_2$ (0.045 g, 0.10 mmol) dissolved in acetone (15 mL). The solution was stirred for 20 h. After filtration, the solvent was removed by rotary evaporation and washed with Et_2O (2 × 10 mL). The product was purified by crystallization from CH_2Cl_2−hexane. Yield: 67%. Mp: 172 °C. ^1H NMR (CD_2Cl_2): δ 7.75−7.18 (m, 20H, P*Ph*), 6.75 (d, 4H, *J* = 7.8 Hz), 6.63 (m, 6H), 6.43 (t, 2H, *J* = 7.8 Hz), 3.55 (m, 4H, OC*H₂*), 3.16 (s, 8H, PhC*H₂*CH₃), 3.06 (t, 4H, *J* = 7.5 Hz, OC*H₂*), 2.08 (m, 4H, PC*H₂*), 1.18 (m, 4H, $CH_2CH_2CH_3$), 0.86 (t, 6H, *J* = 7.5 Hz, CH_2CH_3). $^{31}P\{^1H\}$ NMR(CD_2Cl_2): δ 17.39. FAB-MS: *m/z* 1039 $[(M - 2BF_4)^+]$. Anal. Calcd for $C_{62}H_{62}B_2F_8O_4P_2Pd$: C, 61.38; H, 5.14. Found: C, 61.02; H, 5.02.

[Pd(η^3-2-methylallyl){(*P*,*P*)-diphencalix[4]arene}] (8). To a stirred CH_2Cl_2 of [Pd(η^3-C_4H_7)(THF)$_2$]BF_4 prepared from the reaction of $AgBF_4$ (0.031 g, 0.16 mmol) and [Pd(η^3-C_4H_7)Cl]$_2$ (0.032 g, 0.08 mmol) in THF (2 mL) was added **3** (0.15 g, 0.16 mmol) dissolved in CH_2Cl_2 (10 mL). The solution was stirred for 4 h. The solution was evaporated and washed with hexane (2 × 15 mL). Recrystallization from CH_2Cl_2−Et_2O gave **8** as colorless crystals in 84% yield. Mp: 194 °C (dec). ^1H NMR (CD_2Cl_2): δ 7.54−7.22 (m, 20H, P*Ph*), 7.08 (d, 4H, $J = 7.5$ Hz), 6.80−6.72 (m, 6H), 6.42 (t, 2H, $J = 7.5$ Hz), 4.08 (m, 4H, OC*H2*), 3.96 (m, 2H, CH_{syn} of allyl), 3.54 (s, 8H, PhCH_2Ph), 3.42 (t, 4H, $J = 7.5$ Hz, OCH_2), 3.28 (m, 2H, CH_{anti} of allyl), 2.86 (m, 4H, PCH_2), 1.73 (s, 3H, CH_3C), 1.42 (m, 4H, CH_2CH$_3$), 0.78 (t, 4H, $J = 7.5$ Hz, CH$_2$CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 156.2−123.4, 73.4, 71.2, 67.6, 36.1, 30.8, 20.9, 9.9. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 10.8. FAB-MS: *m*/*z* 1094 [(M − BF_4)$^+$]. Anal. Calcd for $C_{66}H_{69}BF_4O_4P_2Pd$: C, 67.10; H, 5.88. Found: C, 69.84; H, 5.72.

X-ray Crystallography. Details of the crystal data and a summary of intensity data collection parameters for **3**, **4**, and **6** are given in Table 1. Crystals of **3**, **4**, and **6** were grown from ethyl acetate−hexane, CH_2Cl_2−Et_2O, and CH_2Cl_2−toluene, respectively. Crystals of **3**, **4**, and **6** were mounted in thin-walled glass capillaries and sealed under argon. The data sets for **3**, **4**, and **6** were collected on a Siemens P4 diffractometer. Mo Kα radiation ($\lambda = 0.7107$ Å) was used for all structures. Each structure was solved by the application of direct methods using the SHELX-96 program and least-squares refinement using SHELXL-97. All non-hydrogen atoms in compounds **3**, **4**, and **6** were refined anisotropically. All other hydrogen atoms were included in the calculated positions.

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Supporting Information Available: Tables listing crystallographic information, atomic coordinates and *U*(eq) values, and intramolecular bond distances and angles and crystallographic data in CIF format for **3**, **4**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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