Sterically Crowded, Rigid, C_3 Symmetric Phosphites: Synthesis, Structure, and Preparation of Metal Complexes

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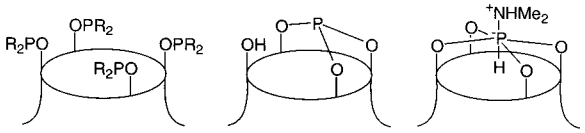
Received June 22, 2000

The sterically congested, rigid, C_3 symmetric phosphites (**2a**−**e**) have been synthesized by reaction of PCl_3 with the corresponding tris(3,5-dialkyl-2-hydroxyphenyl)methanes (3,5-di-*tert*-butyl; 3-*tert*-butyl-5-methyl; 3,5-di-*tert*-pentyl; 3-adamantyl-5-methyl; 3,5-dimethyl) and characterized. The arsenite derivative (**3b**) of tris(3-*tert*-butyl-5-methyl-2-hydroxyphenyl)methane was similarly prepared by reaction with AsI_3. Both the phosphite **2a** and the arsenite derivative **3b** have been examined by single-crystal X-ray analyses. Metal complexes (**4**−**6**) of the phosphites were prepared by reaction of the phosphite with [$PdCl_2$(cod)] (cod = 1,5-cyclooctadiene), [$PdCl(\eta^3$-$C_3H_5)]_2$ and [$Rh(CO)_2$(acac)] (acac = acetylacetonate), respectively, and examples of each are represented by X-ray structure determinations.

Introduction

Over the years, the synthesis and study of bulky phosphorus ligands have attracted considerable interest since these materials can have a profound impact on reaction outcomes; indeed the steric requirements of phosphines and phosphites have been deemed equally important as electronic factors.[1] Recently, there has been a renewed interest in the use of phosphite ligands,[2] both academically and industrially, primarily due to their applications in reactions such as nickel(0)-based hydrocyanation[3] and rhodium(I)-based hydroformylation,[4,5] among others.[6−8] In consideration of the unique steric properties of this macrocycle, a number of groups have begun actively preparing the phosphite derivatives, and subsequent metal complexes thereof, of the calix[*n*]arene systems. Two main types of phosphite derivatives of calix[4]arenes have been synthesized; Floriani has incorporated four phosphite functionalities,[9−11] while Lattman incorporated only a single phosphite moiety.[12,13] The related arsenic derivatives have also been prepared and structurally characterized.[14] Very recently, some platinum group metal and gold derivatives of the Lattman phosphites have been reported,[15] and the rhodium(I) adducts proved to be capable hydroformylation catalysts.[16,17] Finally, diphosphite systems derived from calix[6]arene have also appeared in the literature,[18,19] and a palladium dichloride adduct showed high activity toward the copolymerization of carbon monoxide and ethene.[18]



Floriani phosphite (R = Me, Ph) Lattman phosphites

Given the geometry preference of the phosphorus atom, using a ligand with four or six functional groups is not wholly satisfactory. For example, the remaining hydroxyl group in the Lattman calix[4]arene phosphite is reactive, and although it

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10.1021/ic000683j CCC: $20.00
Published on Web 01/27/2001

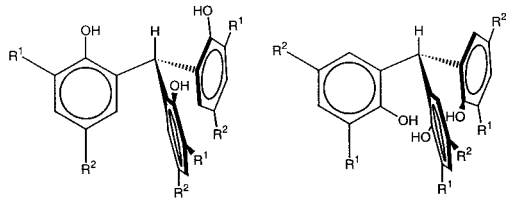
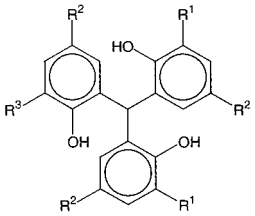


Figure 1. Conformations of tris(3,5-di-*tert*-butyl-2-hydroxyphenyl)-methane (**1**).

could be rendered inert by derivatization, this requires additional step(s).[17] Moreover, the yields of the calixarene phosphites were generally low, due to the ability of the calix[4]arene precursors[20] and the resulting phosphites[17] to adopt multiple configurations in solution. Unfortunately, calix[*n*]arene-like macrocycles with only three oxygen donors are often quite difficult to prepare. Ligands such as hexahomooxacalix[3]arenes and trihydroxy-[3.3.3]metacyclophanes, require longer linkers between the aryloxide ligands and involve several synthetic steps.[21] With the larger cyclic structures, the macrocycles are extremely flexible, complicating the preparation of complexes.

Intent on the preparation of complexes incorporating a bulky, rigid phenolic ligand with only three oxygen donors, we have been exploring the synthesis and reactivity of the C_3 symmetric ligands tris(3,5-dialkyl-2-hydroxyphenyl)methanes (**1a**−**e**),[22] and with these ligands, two extremes of conformation can be envisaged, Types 1 and 2 (Figure 1). Extensive solution and solid-state studies have confirmed that Type 1, with the hydroxide groups aligned with the central methine hydrogen is the preferred conformer,[22−24] even when bulky substituents were introduced at the central carbon linker. Despite much effort, metal complexes of **1** were consistently found to retain the Type 1 configuration, often at the expense of incomplete reaction of one hydroxyl group.[25] Sterically, the inversion of the Type 1 system to Type 2 is not precluded, so the persistence of Type 1 is most likely an electronic effect. Nevertheless, the ligands can be coaxed into the Type 2 configuration to form a robust *tricyclic* chelate with the appropriate metal center. Herein we report the preparation of sterically encumbered phosphite derivatives of **1**, together with work regarding their utility for the preparation of metal complexes.



1a $R^1, R^2, R^3 = t$Bu
1b $R^1, R^3 = t$Bu; R^2 = Me
1c $R^1, R^2, R^3 = t$-pentyl
1d R^1, R^2, R^3 = Me
1e R^1, R^3 = Ad; R^2 = Me
1f R^1 = Ad; R^2 = Me; $R^3 = t$Bu

Experimental Section

Unless otherwise stated, all manipulations were carried out under an inert atmosphere of N_2 on a vacuum line using standard Schlenk techniques. All solvents used were dried and distilled prior to use. NMR spectra were recorded on a Varian VXR 300 MHz spectrometer at 299.95, 75.47, and 121.42 MHz for the proton, carbon, and phosphorus channels, respectively, using $CDCl_3$ solvent. IR spectra were recorded as KBr disks on a Bruker Vector 22 instrument at a resolution of 2 cm^{-1}. Melting points were determined using a capillary melting point apparatus and are uncorrected. Elemental analyses were performed by the University of Florida Spectroscopic services. 2-Adamantyl-4-methylphenol, ethylmagnesium bromide, triethyl orthoformate, phosphorus trichloride, arsenic triiodide, $[PdCl_2(cod)]$ (cod = 1,5-cyclooctadiene), and $[Rh(CO)_2(acac)]$ (acac = acetylacetonate) were obtained from commercial sources and used as received. 3-*tert*-Butyl-5-methyl-4-hydroxybenzaldehyde[26] and $[(\eta^3\text{-}C_3H_5)PdCl]_2$[27] were synthesized following literature procedures. The linked phenoxides ligands tris(3,5-dialkyl-2-hydroxyphenyl)methanes **1a**−**d**[22] were prepared as previously described, although for convenience other acid sources such as thionyl chloride or PCl_3 were often used in place of dry HCl with moderately lower yields.

Synthesis of 1e. To a solution of 2-adamantyl-4-methylphenol (1.00 g, 4.13 mmol) in anhydrous ether (40 mL) was added, dropwise, ethylmagnesium bromide (1.38 mL, 3 M in diethyl ether, 4.14 mmol), and the mixture was refluxed for 1 h. Triethyl orthoformate (0.23 mL, 1.38 mmol) was added, the resulting solution was heated (oil bath 100 °C), and the ether was allowed to evaporate. Toluene was introduced, producing a deep blue solution, and this mixture was refluxed for 12 h, during which time the solution became yellow concomitant with precipitate formation. After cooling, the mixture was transferred to a separating funnel, and dilute hydrochloric acid (60 mL) was added. The aqueous phase was separated, leaving a white suspension of the product in the organic layer, which was isolated by filtration. The solid was washed with methanol and pentane and dried under vacuum to give tris(3-adamantyl-5-methyl-2-hydroxyphenyl)methane (**1e**) as a white powder (0.45 g, 45%). The acid-catalyzed condensation previously reported for the synthesis of **1a**−**d** was found to be less satisfactory in this case, and reaction of 3-adamantyl-5-methyl-4-hydroxybenzaldehyde (0.75 g, 2.77 mmol) with 2-adamantyl-4-methylphenol (1.40 g, 5.78 mmol) gave **1e** in only 18% yield. The compound **1e** was found to have extraordinarily low solubility in common organic solvents and did not dissolve to a perceptible extent in boiling heptane, Et_2O, C_6H_6, toluene, CH_2Cl_2, $CHCl_3$, THF, CH_3CN, MeOH, EtOH, pyridine, DMF, or DMSO. The very low solubility precluded additional purification and acquisition of even a ^1H NMR spectrum. Mp > 310 °C; found C, 84.17; H, 9.13; $C_{52}H_{64}O_3$ requires C, 84.74; H, 8.75; ν_{max}/cm^{-1} (OH region): 3500s v br.

Synthesis of 1f. Powdered 2-adamantyl-4-methylphenol (1.0 g, 4.1 mmol) and 3-*tert*-butyl-5-methyl-4-hydroxybenzaldehyde (0.40 g, 2.1 mmol) were dissolved in methanol (10 mL). The resulting solution was immersed in an ice bath, and $SOCl_2$ (5 mL) was added dropwise. The solution slowly turned red, and a precipitate began to form. The pink mixture was allowed to stir at room-temperature overnight, after which time the precipitate was filtered off, washed with methanol and CH_2Cl_2, and dried under vacuum to give pure bis(3-adamantyl-5-methyl-2-hydroxyphenyl)(3-*tert*-butyl-5-methyl-2-hydroxyphenyl)methane **1f** (0.75 g, 55%) as a white powder. The material had only very poor solubility in common organic solvents, but was somewhat soluble in THF. A weak ^1H NMR could be obtained in $CDCl_3$, however the poor solubility precluded acquisition of ^{13}C NMR data. Mp decomposes without melting (~300 °C); found C, 83.54; H, 9.20; $C_{46}H_{58}O_3$ requires C, 83.84; H, 8.87; ν_{max}/cm^{-1} (OH region): 3505s v br; ^1H NMR: δ 7.08 (d, *J* 2.4 Hz, 1H, *t*Bu ring Ar-*H*), 7.03 (d, *J* 2.4 Hz, 2H, Ad ring Ar-*H*), 6.51 (d, *J* 2.4 Hz, 3H, Ad/*t*Bu ring Ar-*H*), 5.56 (s, 1H, C*H*), 4.79 (s, 1H, *t*Bu ring Ar-O*H*), 4.76 (s, 1H, Ad Ar-O*H*), 2.18 (s, 9H,

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Ad/*t*Bu ring CH_3), 2.07 (s br, 11H, Ad), 2.04 (s br, 5H, Ad), 1.74 (s br, 11H, Ad), 1.54 (s, 3H, Ad), 1.35 (s, 9H, *t*Bu).

Synthesis of Phosphites 2a−f. General Procedure. The appropriate compound **1** (1 equiv) and Et_3N (3 equiv) were mixed in dry, degassed toluene, and phosphorus trichloride (1 equiv) was added to the mixture resulting in precipitate formation. The solution was refluxed for 1 h. After being cooled to room temperature, the precipitate was filtered off without further regard to exclude air. The supernatant was evaporated to dryness under vacuum to leave a white residue of the crude phosphite, and in most instances this material was sufficiently pure for further reactions. A longer reaction time of 17 h was used for the synthesis of **2e**, due to the very poor solubility of the tris-phenol precursor. Compound **2d** was formed only in very low yield and could not be readily separated from the multiple oligomeric products formed in the reaction mixture.

2a. Recrystallized from ether; Yield 94%; Mp 242−245 °C; found C, 77.83; H, 9.39; $C_{43}H_{61}O_3P\cdot{}^1/_2Et_2O$ requires C, 77.87; H, 9.59; ^{31}P NMR: δ 113.1; ^{1}H NMR: δ 7.27 (d, *J* 2.4 Hz, 3H, Ar-*H*), 7.14 (d, *J* 2.4 Hz, 3H, Ar-*H*), 5.32 (s, 1H, C*H*), 1.42 (s, 27H, *t*Bu), 1.30 (s, 27H, *t*Bu); ^{13}C NMR: δ 147.6 (d, $J_{C,P}$ = 13.1 Hz, $C_{Ar}O$), 145.5 (C_{Ar}), 139.9 (d, $J_{C,P}$ = 3.0 Hz, C_{Ar}), 132.0 (d, $J_{C,P}$ = 4.0 Hz, C_{Ar}), 126.5, 123.2 (C_{Ar}), 60.2 (*C*H), 35.0, 34.5 [*C*$(CH_3)_3$], 31.6 [C(*C*$H_3)_3$], 30.5 [d, $J_{C,P}$ = 2.5 Hz, C(*C*$H_3)_3$].

2b. Recrystallized from CH_2Cl_2/pentane diffusion; Yield 98%; Mp > 310 °C; found C, 76.40; H, 8.19; $C_{34}H_{46}O_3P$ requires C, 76.52; H, 8.69; ^{31}P NMR: δ 113.3; ^{1}H NMR: δ 7.03 (d, *J* 2.4 Hz, 3H, Ar-*H*), 6.97 (d, *J* 2.4 Hz, 3H, Ar-*H*), 5.20 (s, 1H, C*H*), 2.26 (s, 9H, CH_3), 1.40 (s, 27H, *t*Bu); ^{13}C NMR: δ 147.5 (d, $J_{C,P}$ = 13.1 Hz, $C_{Ar}O$), 140.5 (d, $J_{C,P}$ = 3.0 Hz, C_{Ar}), 132.6 (C_{Ar}), 132.4 (d, $J_{C,P}$ = 4.5 Hz, C_{Ar}), 130.0, 126.7 (C_{Ar}), 58.6 (*C*H), 34.6 [*C*$(CH_3)_3$], 29.4 [d, $J_{C,P}$ = 2.5 Hz, C(*C*$H_3)_3$], 20.9 (Ar-*C*H_3).

2c. Recrystallized from ether/methanol evaporation; Yield 93%; Mp 132−134 °C; found C, 78.44; H, 10.36; $C_{49}H_{73}O_3P\cdot Et_2O$ requires C, 78.09; H, 10.26; ^{31}P NMR: δ 113.2; ^{1}H NMR: δ 7.16 (d, *J* = 2.4 Hz, 3H, Ar-H), 7.11 (d, *J* = 2.4 Hz, 3H, Ar-H), 5.34 (s, 1H, C*H*), 1.94 (br, 6H, CH_2CH$_3$), 1.62 (q, *J* = 7.3 Hz, 6H, CH_2CH$_3$), 1.40 (s, 21H, CMe$_2$), 1.33 (s, 21H, CMe$_2$), 0.63 (t, *J* = 7.2 Hz, 6H, CH$_2$CH_3), 0.58 (t, *J* = 7.5 Hz, 6H, CH$_2$CH_3); ^{13}C NMR: δ 147.7 (d, $J_{C,P}$ = 12.6 Hz, $C_{Ar}O$), 143.8 (C_{Ar}), 137.8 (d, $J_{C,P}$ = 3.0 Hz, C_{Ar}), 132.4 (d, $J_{C,P}$ = 4.5 Hz, C_{Ar}), 127.2, 125.4 (C_{Ar}), 59.8 (*C*H), 38.9, 37.8 [*C*$(CH_3)_2$], 37.5 (*C*H$_2$-CH$_3$), 34.3 (d, $J_{C,P}$ = 4.5 Hz, *C*H$_2$CH$_3$), 28.9, 28.7 [C(*C*$H_3)_2$], 9.4, 9.1 (CH$_2$*C*H$_3$).

2d. Not isolated, yield by integration of ^{31}P NMR <5%; ^{31}P NMR: δ 110.0; ^{1}H NMR: δ 7.07 (d, *J* 2.4 Hz, 3H, Ar-*H*), 7.02 (d, *J* 2.4 Hz, 3H, Ar-*H*), 5.28 (s, 1H, C*H*), 2.39 (s, 9H, CH_3), 2.35 (s, 9H, CH_3); ^{13}C NMR: δ 147.1 (d, $J_{C,P}$ = 12.6 Hz, $C_{Ar}O$), 133.5 (C_{Ar}), 131.1 (d, $J_{C,P}$ = 4.5 Hz, C_{Ar}), 130.8 (C_{Ar}), 130.1 (d, $J_{C,P}$ = 3.0 Hz, C_{Ar}), 129.5 (C_{Ar}), 57.7 (*C*H), 20.7, 17.3 (Ar-*C*H_3).

2e. Crude material recrystallized from diffusion of pentane into an ether solution; yield 84%, Mp > 310 °C; found C, 81.39; H, 8.24; $C_{52}H_{61}O_3P$ requires C, 81.64; H, 8.04; ^{31}P NMR: δ 113.3; ^{1}H NMR: δ 7.00 (d, *J* 2.4 Hz, 3H, Ar-*H*), 6.97 (d, *J* 2.4 Hz, 3H, Ar-*H*), 5.21 (s, 1H, C*H*), 2.28 (s, 9H, Ar-CH_3), 2.13 (s br, 24H, Ad), 1.74 (s br, 16H, Ad); ^{13}C NMR: δ 147.9 (d, $J_{C,P}$ = 12.6 Hz, $C_{Ar}O$), 140.5 (d, $J_{C,P}$ = 3.5 Hz, C_{Ar}), 132.8 (d, $J_{C,P}$ = 6.0 Hz, Ad ring C_{Ar}), 130.1, 127.0 (C_{Ar}), 58.9 (*C*H), 41.1, 37.3, 37.1, 29.3 (Ad), 21.1 (Ar-*C*H_3).

2f. Crude material thoroughly washed with methanol and used without further purification; Yield 96%; Mp > 310 °C; ^{31}P NMR: δ 113.4; ^{1}H NMR: δ 7.01 (d, *J* 2.4 Hz, 1H, *t*Bu ring Ar-*H*), 6.95 (d, *J* 2.4 Hz, 2H, Ad ring Ar-*H*), 6.94 (d, *J* 2.4 Hz, 3H, Ad/*t*Bu rings Ar-*H*), 5.17 (s, 1H, C*H*), 2.24 (s, 9H, Ar-CH_3), 2.07 (s br, 18H, Ad), 1.74 (s br, 12H, Ad), 1.38 (s, 9H, *t*Bu); ^{13}C NMR: δ 147.8 (d, $J_{C,P}$ = 13.1 Hz, Ad/*t*Bu ring $C_{Ar}O$), 140.6 (d, $J_{C,P}$ = 3.1 Hz, *t*Bu ring C_{Ar}), 140.5 (d, $J_{C,P}$ = 3.7 Hz, Ad ring C_{Ar}), 132.8−132.7 (m, Ad/*t*Bu ring C_{Ar}), 130.2 (*t*Bu ring C_{Ar}), 130.1 (Ad ring C_{Ar}), 127.0 (Ad ring C_{Ar}), 126.8 (*t*Bu ring C_{Ar}), 58.9 (*C*H), 41.1, 37.2, 37.1 (Ad), 34.8 [*C*$(CH_3)_3$], 30.5 [d, $J_{C,P}$ = 2.5 Hz, C(*C*$H_3)_3$], 29.3 (Ad), 21.1 (Ad ring Ar-*C*H_3), 21.0 (*t*Bu ring Ar-*C*H_3).

Synthesis of Arsenite 3b. Compound **1b** (0.25 g, 0.50 mmol) was dissolved in degassed toluene (40 mL) containing Et_3N (0.21 mL, 1.50 mmol), and arsenic triiodide (0.227 g, 0.5 mmol) was added. The mixture was refluxed for 12 h, during which time the solid AsI_3 slowly dissolved. The resulting yellowish solution was filtered, and the toluene was removed under reduced pressure. The residue was crystallized from benzene/pentane diffusion to yield **3b**$\cdot 2C_6H_6$ as thick colorless rods (0.085 g, 26%), that slowly lost solvent. Mp > 310 °C; found C, 71.59; H, 8.22; $C_{34}H_{46}O_3As\cdot{}^1/_2C_6H_6$ requires C, 71.62; H, 8.01; ^{1}H NMR: δ 7.05 (d, *J* 2.4 Hz, 3H, Ar-*H*), 6.98 (d, *J* 2.4 Hz, 3H, Ar-*H*), 5.33 (s, 1H, C*H*), 2.29 (s, 9H, CH_3), 1.44 (s, 27H, *t*Bu); ^{13}C NMR: δ 149.5 ($C_{Ar}O$), 140.4, 133.9, 131.5, 130.2, 126.3 (C_{Ar}), 57.8 (*C*H), 34.7 [*C*$(CH_3)_3$], 30.6 [C(*C*$H_3)_3$], 20.8 (Ar-*C*H_3).

Reaction of 2a and 2b with [PdCl$_2$(cod)]. To a Schlenk flask containing dry degassed toluene were added the respective phosphite **2** (1 equiv) and [PdCl$_2$(cod)] (1 equiv). The resulting yellow suspension was heated to 100 °C for 4 h during which time a clear deep yellow solution developed. The solvent was removed under vacuum, and the residue was dissolved in diethyl ether. The insoluble material was filtered off, and the solvent was removed from the supernatant under reduced pressure. Compound **4a** was purified by recrystallization from a chloroform solution and **4b** by vapor diffusion of pentane into a chloroform solution.

4a. Yield 50%; found C, 61.88; H, 7.18; $C_{86}H_{122}O_6P_2Cl_4Pd_2$ requires C, 61.91; H, 7.37; ^{31}P NMR: δ 50.2; ^{1}H NMR: δ 7.39 (d, *J* 2.4 Hz, 6H, Ar-*H*), 7.05 (d, *J* 2.4 Hz, 6H, Ar-*H*), 5.38 (s, 2H, C*H*), 1.63 (s, 54H, *t*Bu), 1.32 (s, 54H, *t*Bu); ^{13}C NMR: δ 148.1 (d, $J_{C,P}$ = 16.6 Hz, $C_{Ar}O$), 147.8, 140.5, 130.9, 126.5, 125.8 (C_{Ar}), 58.9 (*C*H), 36.1, 34.8 [*C*$(CH_3)_3$], 32.2, 31.7 [C(*C*$H_3)_3$].

4b. Yield 54%; found C, 57.60; H, 6.50; $C_{68}H_{92}O_6P_2Cl_4Pd_2$ requires C, 57.43; H, 6.52; ^{31}P NMR: δ 50.6; ^{1}H NMR: δ 7.17 (d, *J* 2.4 Hz, 6H, Ar-*H*), 6.90 (d, *J* 2.4 Hz, 6H, Ar-*H*), 5.19 (s, 2H, C*H*), 2.26 (s, 18H, CH_3), 1.59 (s, 54H, *t*Bu); ^{13}C NMR: δ 147.9 (d, $J_{C,P}$ = 16.1 Hz, $C_{Ar}O$), 140.9, 134.6, 130.8, 130.1, 129.0 (C_{Ar}), 57.3 (*C*H), 35.6 [*C*$(CH_3)_3$], 31.8 [C(*C*$H_3)_3$], 20.7 (Ar-*C*H_3).

Reaction of 2a−c, 2e, and 2f with [(η^3-C$_3$H$_5$)PdCl]$_2$. Compound **2** (2 equiv) and [(η^3-C$_3$H$_5$)PdCl]$_2$ (1 equiv) were added to CH_2Cl_2 (15 mL), and the resulting solution was stirred at room temperature for 2 h. The solvent was removed under vacuum, and the yellow residues were recrystallized to yield the corresponding complexes **5**. The reactions proceeded essentially quantitatively by NMR analyses and where no yield is given the product was not further isolated.

5a. ^{31}P NMR: δ 109.8; ^{1}H NMR: δ = 7.32 (d, *J* = 2.4 Hz, 3H, Ar-H), 7.09 (d, *J* = 2.4 Hz, 3H, Ar-H), 5.57 (br m, 1H, allyl C*H*), 5.36 (s, 1H, C*H*), 4.82 (br m, 1H, allyl CH_2), 4.44 (br s, 1H allyl CH_2), 3.83 (t, *J* = 15.6 Hz, 1H, allyl CH_2), 3.06 (d, 1H, *J* = 12.3 Hz, allyl CH_2), 1.47 (s, 27H, *t*Bu), 1.31 (s, 27H, *t*Bu); ^{13}C NMR: δ = 147.5 (d, $J_{C,P}$ = 16.6 Hz, $C_{Ar}O$), 146.9 (C_{Ar}), 139.8 (d, $J_{C,P}$ = 5.5 Hz, C_{Ar}), 131.2 (d, $J_{C,P}$ = 4.5 Hz, C_{Ar}), 126.6, 124.5 (C_{Ar}), 118.3 (d, $J_{C,P}$ = 9.1 Hz, allyl *C*H$_2$), 80.7 (d, $J_{C,P}$ = 50.4 Hz, allyl *C*H), 61.7 (allyl *C*H$_2$), 59.7 (*C*H), 35.5, 34.6 [*C*$(CH_3)_3$], 31.6, 31.2 [C(*C*$H_3)_3$].

5b. Recrystallized by slow evaporation of a heptane/ether/CH_2Cl_2 solution. Yield 89%; found C, 62.13; H, 7.48; $C_{37}H_{51}O_3PPdCl$ requires C, 62.01; H, 7.17; ^{31}P NMR: δ 110.3; ^{1}H NMR: δ 7.11 (d, *J* 2.4 Hz, 3H, Ar-*H*), 6.97 (d, *J* 2.4 Hz, 3H, Ar-*H*), 5.54 (sept, *J* = 6.6 Hz, 1H, allyl C*H*), 5.24 (s, 1H, C*H*), 4.84 (dd, *J* = 12.3, 7.2 Hz, 1H, allyl CH_2), 4.43 (d, *J* = 5.4 Hz, 1H allyl CH_2), 3.83 (dd, *J* = 17.4, 14.1 Hz, 1H, allyl CH_2), 3.06 (d, 1H, *J* = 12.3 Hz, allyl CH_2), 2.26 (s, 9H, CH_3), 1.48 (s, 27H, *t*Bu); ^{13}C NMR: δ 147.6 (d, $J_{C,P}$ = 16.6 Hz, $C_{Ar}O$), 140.5 (d, $J_{C,P}$ = 5.5 Hz, C_{Ar}), 133.9 (C_{Ar}), 131.4 (d, $J_{C,P}$ = 4.1 Hz, C_{Ar}), 130.4, 128.0 (C_{Ar}), 118.3 (d, $J_{C,P}$ = 10.1 Hz, allyl *C*H$_2$), 80.5 (d, $J_{C,P}$ = 53.4 Hz, allyl *C*H), 61.5 (d, $J_{C,P}$ = 4.5 Hz, allyl *C*H$_2$), 58.3 (*C*H), 35.2 [*C*$(CH_3)_3$], 31.2 [d, $J_{C,P}$ = 2.5 Hz, C(*C*$H_3)_3$], 20.8 (Ar-*C*H_3).

5c. ^{31}P NMR: δ 110.0; ^{1}H NMR: δ = 7.13 (d, *J* = 2.4 Hz, 3H, Ar-H), 6.98 (d, *J* = 2.4 Hz, 3H, Ar-H), 5.54 (br m, 1H, allyl C*H*), 5.31 (s, 1H, C*H*), 4.79 (dd, *J* = 12.3, 7.5 Hz, 1H, allyl CH_2), 4.37 (br s, 1H allyl CH_2), 3.80 (t, *J* = 16.2 Hz, 1H, allyl CH_2), 3.01 (d, 1H, *J* = 11.7 Hz, allyl CH_2), 1.88 (br q, *J* = 7.8 Hz, 6H, CH_2CH$_3$), 1.55 (q, *J* = 7.4 Hz, 6H, CH_2CH$_3$), 1.40 (s, 21H, CMe$_2$), 1.23 (s, 21H, CMe$_2$), 0.56 (t, *J* = 7.3 Hz, 6H, CH$_2$CH_3), 0.40 (t, *J* = 7.2 Hz, 6H, CH$_2$CH_3); ^{13}C NMR: δ = 147.6 (d, $J_{C,P}$ = 16.4 Hz, $C_{Ar}O$), 144.9 (C_{Ar}), 137.9 (d, $J_{C,P}$ = 5.4 Hz, C_{Ar}), 131.4 (d, $J_{C,P}$ = 4.2 Hz, C_{Ar}), 127.3, 126.1 (C_{Ar}), 118.3 (d, $J_{C,P}$ = 10.8 Hz, allyl *C*H$_2$), 80.7 (d, $J_{C,P}$ = 54.7 Hz, allyl

*C*H), 61.1 (allyl *C*H$_2$), 59.4 (*C*H), 39.1, 37.7 [*C*(CH$_3$)$_2$], 37.2, 34.8 (*C*H$_2$-CH$_3$), 29.2, 28.5 [C(*C*H$_3$)$_2$], 9.3, 9.0 (CH$_2$*C*H$_3$).

5e. ^{31}P NMR: δ 110.6; ^{1}H NMR: δ 7.03 (d, *J* 2.4 Hz, 3H, Ar-*H*), 6.88 (d, *J* 2.4 Hz, 3H, Ar-*H*), 5.52 (m, 1H, allyl C*H*), 5.20 (s, 1H, C*H*), 4.82 (dd, *J* = 12.9, 7.8 Hz, 1H, allyl C*H*$_2$), 4.35 (m, 1H allyl C*H*$_2$), 3.76 (dd, *J* = 16.2, 14.4 Hz, 1H, allyl C*H*$_2$), 2.99 (d, 1H, *J* = 11.7 Hz, allyl C*H*$_2$), 2.24 (s, 9H, Ar-C*H*$_3$), 2.14 (s br, 24H, Ad), 1.72 (s br, 16H, Ad); ^{13}C NMR: δ 147.8 (d, $J_{C,P}$ = 16.1 Hz, C_{Ar}O), 140.5 (d, $J_{C,P}$ = 5.6 Hz, C_{Ar}), 133.8 (C_{Ar}), 132.0 (d, $J_{C,P}$ = 4.5 Hz, C_{Ar}), 130.1, 128.2 (C_{Ar}), 117.9 (d, $J_{C,P}$ = 9.6 Hz, allyl *C*H$_2$), 81.4 (d, $J_{C,P}$ = 50.8 Hz, allyl *C*H), 63.1 (allyl *C*H$_2$), 58.7 (*C*H), 41.9, 37.7, 37.0, 29.3 (Ad), 21.0 (Ar-*C*H$_3$).

5f. ^{31}P NMR: δ 110.0; ^{1}H NMR: δ 7.07 (d, *J* 2.4 Hz, 3H, Ad/*t*Bu ring Ar-*H*), 6.94 (d, *J* 2.4 Hz, 2H, Ad ring Ar-*H*), 6.91 (d, *J* 2.4 Hz, 1H, *t*Bu rings Ar-*H*), 5.55 (sept, *J* 6.5 Hz, 1H, allyl C*H*), 5.26 (s, 1H, C*H*), 4.75 (dd, *J* = 13.2, 7.2 Hz, 1H, allyl C*H*$_2$), 4.44 (d, *J* 6.6 Hz, 1H allyl C*H*$_2$), 3.76 (dd, *J* = 18.0, 14.1 Hz, 1H, allyl C*H*$_2$), 3.08 (d, *J* 12.6 Hz, allyl C*H*$_2$), 2.261 (s, 3H, Ad ring Ar-C*H*$_3$), 2.252 (s, 3H, Ad ring Ar-C*H*$_3$), 2.242 (s, 3H, *t*Bu ring Ar-C*H*$_3$), 2.15 (s br, 12H, Ad), 2.00 (s br, 6H, Ad), 1.80 (s br, 6H, Ad), 1.69 (s br, 6H, Ad), 1.43 (s, 9H, *t*Bu); ^{13}C NMR: δ 147.8 (d, $J_{C,P}$ = 13.1 Hz, Ad/*t*Bu ring C_{Ar}O), 140.6 (d, $J_{C,P}$ = 3.1 Hz, *t*Bu ring C_{Ar}), 140.5 (d, $J_{C,P}$ = 3.7 Hz, Ad ring C_{Ar}), 132.8−132.7 (m, Ad/*t*Bu ring C_{Ar}), 130.2 (*t*Bu ring C_{Ar}), 130.1 (Ad ring C_{Ar}), 127.0 (Ad ring C_{Ar}), 126.8 (*t*Bu ring C_{Ar}), 58.9 (*C*H), 41.1, 37.2, 37.1 (Ad), 34.8 [*C*(CH$_3$)$_3$], 30.5 [d, $J_{C,P}$ = 2.5 Hz, C(*C*H$_3$)$_3$], 29.3 (Ad), 21.1 (Ad ring Ar-*C*H$_3$), 21.0 (*t*Bu ring Ar-*C*H$_3$).

Reaction of 2a−c, 2e, and 2f with [Rh(CO)$_2$(acac)]. Compound **2** (1 equiv) and [Rh(CO)$_2$(acac)] (1.1 equiv) were dissolved in CH_2Cl_2 (15 mL), and the resulting mixture was stirred for 2 h. The dark yellow solution was filtered and the solvent removed under reduced pressure to leave a yellow residue of the phosphite adducts **6**. NMR analyses of the crude material indicated no significant impurities were present and where no yield is given the product was not further isolated.

6a. Yield 93%; found C, 68.24; H, 8.35; $C_{49}H_{68}O_4PRh$ requires H, 8.02 C, 68.84; ν_{max}/cm^{-1} (CO region): 2009vs, 1990vs; ^{31}P NMR: δ 107.7 (d, $J_{P,Rh}$ = 312.8 Hz); ^{1}H NMR: δ 7.32 (d, *J* = 2.4 Hz, 3H, Ar-H), 7.11 (d, *J* = 2.4 Hz, 3H, Ar-H), 5.50 (s, 1H, acac-H), 5.35 (s, 1H, C*H*), 1.85 (s, 3H, acac C*H*$_3$), 1.52 (s, 27H, *t*Bu), 1.44 (s, 3H, acac C*H*$_3$), 1.33 (s, 27H, *t*Bu); ^{13}C NMR: δ 186.5 (d, $J_{C,Rh}$ = 98.9 Hz), 147.9 (d, $J_{C,P}$ = 16.2 Hz, C_{Ar}O), 146.6 (C_{Ar}), 140.3 (d, $J_{C,P}$ = 5.8 Hz, C_{Ar}), 131.4 (d, $J_{C,P}$ = 3.9 Hz, C_{Ar}), 126.7, 124.2 (C_{Ar}), 101.2 (CO*C*HCO), 59.9 (*C*H), 35.6, 34.7 [*C*(CH$_3$)$_3$], 31.7, 31.4 [C(*C*H$_3$)$_3$], 30.6 (d, $J_{C,Rh}$ = 2.7 Hz, acac *C*H$_3$), 27.4 (acac *C*H$_3$).

6b. Yield 74%; found C, 62.85; H, 6.78; $C_{40}H_{53}O_6PRh$ requires C, 62.91; H, 6.99; ν_{max}/cm^{-1} (CO region): 1998vs; ^{31}P NMR: δ 108.3 (d, $J_{P,Rh}$ = 313.5 Hz); ^{1}H NMR: δ 7.08 (d, *J* = 2.4 Hz, 3H, Ar-H), 6.95 (d, *J* = 2.4 Hz, 3 H, Ar-H), 5.49 (s, 1H, acac-H), 5.25 (s, 1 H, C*H*), 2.26 (s, 3H, Ar-C*H*$_3$), 2.10 (s, 3H, acac C*H*$_3$), 1.85 (s, 3 H, acac C*H*$_3$), 1.49 (s, 27H, *t*Bu); ^{13}C NMR: δ 186.5 (d, $J_{C,Rh}$ = 101.7 Hz), 148.0 (d, $J_{C,P}$ = 16.2 Hz, C_{Ar}O), 141.0 (d, $J_{C,P}$ = 5.8 Hz, C_{Ar}), 133.7 (C_{Ar}), 131.7 (d, $J_{C,P}$ = 3.9 Hz, C_{Ar}), 130.4, 127.8 (C_{Ar}), 101.2 (CO*C*HCO), 58.5 (*C*H), 35.3 [*C*(CH$_3$)$_3$], 31.4 [C(*C*H$_3$)$_3$], 27.5 (br, 2x acac *C*H$_3$), 21.0 (Ar-*C*H$_3$).

6c. ν_{max}/cm^{-1} (CO region): 2007vs, 1995s; ^{31}P NMR: δ 108.1 (d, $J_{P,Rh}$ = 312.9 Hz); ^{1}H NMR: δ 7.17 (d, *J* = 2.4 Hz, 3H, Ar-H), 7.03 (d, *J* = 2.4 Hz, 3H, Ar-H), 5.48 (s, 1H, acac-H), 5.27 (s, 1H, C*H*), 2.10 (s, 3H, acac C*H*$_3$), 2.04 (q, *J* = 7.0 Hz, 6H, C*H*$_2$CH$_3$), 1.84 (s, 3H, acac C*H*$_3$), 1.55 (q, *J* = 7.2 Hz, 6H, C*H*$_2$CH$_3$), 1.40 (s, 21H, CMe$_2$), 1.24 (s, 21H, CMe$_2$), 0.56 (t, *J* = 7.2 Hz, 6H, CH$_2$C*H*$_3$), 0.38 (t, *J* = 7.5 Hz, 6H, CH$_2$C*H*$_3$); ^{13}C NMR: δ 186.5 (d, $J_{C,Rh}$ = 99.8 Hz), 148.0 (d, $J_{C,P}$ = 15.6 Hz, C_{Ar}O), 144.5 (C_{Ar}), 138.1 (d, $J_{C,P}$ = 5.5 Hz, C_{Ar}), 131.6 (d, $J_{C,P}$ = 3.6 Hz, C_{Ar}), 127.2, 125.9 (C_{Ar}), 101.2 (CO*C*HCO), 59.4 (*C*H), 39.2, 37.8 [*C*(CH$_3$)$_2$], 37.4, 35.0 (*C*H$_2$CH$_3$), 29.4, 28.6 [C(*C*H$_3$)$_2$], 27.6 (d, $J_{C,Rh}$ = 9.1 Hz, acac *C*H$_3$), 27.3 (acac *C*H$_3$), 9.3, 9.1 (CH$_2$*C*H$_3$).

6e. ν_{max}/cm^{-1} (CO region): 2006vs; ^{31}P NMR: δ 107.2 (d, $J_{P,Rh}$ = 309.1 Hz); ^{1}H NMR: δ 7.02 (d, *J* 2.4 Hz, 3H, Ar-*H*), 6.92 (d, *J* 2.4 Hz, 3H, Ar-*H*), 5.46 (s, 1H, acac-H), 5.20 (s, 1H, C*H*), 2.25 (s, 9H, Ar-C*H*$_3$), 2.19 (s br, 16H, Ad), 2.09 (s, 3H, acac C*H*$_3$), 2.00 (s br, 10H, Ad), 1.80 (s br, 2H, Ad), 1.79 (s, 3H, acac C*H*$_3$), 1.76 (s br, 4H, Ad), 1.69 (s br, 4H, Ad), 1.65 (s br, 2H, Ad), 1.56 (s br, 6H, Ad); ^{13}C NMR: δ 186.6 (d, $J_{C,Rh}$ = 107.9 Hz), 148.2 (d, $J_{C,P}$ = 16.1 Hz, C_{Ar}O), 140.0 (d, $J_{C,P}$ = 6.0 Hz, C_{Ar}), 133.6 (C_{Ar}), 131.7 (d, $J_{C,P}$ = 3.8 Hz, C_{Ar}), 130.3, 127.9 (C_{Ar}), 101.1 (CO*C*HCO), 59.1 (*C*H), 41.8, 37.8, 37.1, 29.5 (Ad), 27.5 (d, $J_{C,Rh}$ = 9.9 Hz, acac *C*H$_3$), 27.0 (acac *C*H$_3$), 21.0 (Ar-*C*H$_3$).

6f. Yield 71%; found C, 67.92; H, 7.29; $C_{52}H_{62}O_6PRh$ requires C, 68.11; H, 6.82; ν_{max}/cm^{-1} (CO region): 2012vs; ^{31}P NMR: δ 108.2 (d, $J_{P,Rh}$ = 312.0 Hz); ^{1}H NMR: δ 7.05 (d, *J* 2.4 Hz, 1H, *t*Bu ring Ar-*H*), 7.02 (d, *J* 2.4 Hz, 2H, Ad ring Ar-*H*), 6.96 (d, *J* 2.4 Hz, 2H, Ad ring Ar-*H*), 6.88 (d, *J* 2.4 Hz, 1H, *t*Bu ring Ar-*H*), 5.46 (s, 1H, acac-H), 5.23 (s, 1H, C*H*), 2.29 (s br, 2H, Ad), 2.27 (s, 6H, Ad ring Ar-C*H*$_3$), 2.25 (s br, 4H Ad), 2.23 (s, 3H, *t*Bu ring Ar-C*H*$_3$), 2.18 (s br, 4H Ad), 2.14 (s br, 2H Ad), 2.08 (s, 3H, acac C*H*$_3$), 1.98 (s br, 6H, Ad), 1.81 (s br, 4H Ad), 1.80 (s, 3H, acac C*H*$_3$), 1.78 (s br, 2H Ad), 1.68 (s br, 4H, Ad), 1.64 (s br, 2H, Ad), 1.56 (s br, 6H, Ad), 1.42 (s, 9H, *t*Bu); ^{13}C NMR: δ 186.4 (d, $J_{C,Rh}$ = 104.8 Hz), 148.6 (d, $J_{C,P}$ = 16.1 Hz, *t*Bu ring C_{Ar}O), 147.9 (d, $J_{C,P}$ = 16.1 Hz, Ad ring C_{Ar}O), 141.3 (d, $J_{C,P}$ = 6.0 Hz, *t*Bu ring C_{Ar}), 140.9 (d, $J_{C,P}$ = 6.0 Hz, Ad ring C_{Ar}), 134.1 (*t*Bu ring C_{Ar}), 133.5 (Ad ring C_{Ar}), 132.2 (d, $J_{C,P}$ = 4.0 Hz, *t*Bu ring C_{Ar}), 131.3 (d, $J_{C,P}$ = 4.0 Hz, Ad ring C_{Ar}), 131.1 (*t*Bu ring C_{Ar}), 130.1, 127.8 (Ad ring C_{Ar}), 127.7 (*t*Bu ring C_{Ar}), 101.1 (CO*C*HCO), 58.9 (*C*H), 41.8, 37.7, 37.1 (Ad), 35.3 [*C*(CH$_3$)$_3$], 31.0 [C(*C*H$_3$)$_3$], 29.5 (Ad), 27.6 (d, $J_{C,Rh}$ = 9.6 Hz, acac *C*H$_3$), 27.2 (d, $J_{C,Rh}$ = 4.2 Hz, acac *C*H$_3$), 21.1 (Ad ring Ar-*C*H$_3$), 20.9 (*t*Bu ring Ar-*C*H$_3$).

X-ray Crystallography. Unit cell dimensions and intensity data for all the structures were obtained on a Siemens CCD SMART diffractometer at −100 °C. The data collections nominally covered over a hemisphere of reciprocal space, by a combination of three sets of exposures; each set had a different ϕ angle for the crystal, and each exposure covered 0.3° in ω. The crystal to detector distance was 5.0 cm. The data sets were corrected empirically for absorption using SADABS.[28] All the structures were solved using the Bruker SHELXTL software package for the PC, using the direct methods option of SHELXS. The space groups for all of the structures were determined from an examination of the systematic absences in the data and the successful solution and refinement of the structures confirmed these assignments. All hydrogen atoms were assigned idealized locations and were given a thermal parameter equivalent to 1.2 or 1.5 times the thermal parameter of the carbon atom to which it was attached. For the methyl groups, where the location of the hydrogen atoms was uncertain, the AFIX 137 card was used to allow the hydrogen atoms to rotate to the maximum area of residual density, while fixing their geometry.

The structures of **4a** and **5b** contain two independent molecules in the asymmetric unit. For the structures of **3b**, **4a**, and **6a** severely disordered solvates were removed ("squeezed") from the data by the Platon for Windows software program.[29] The electron density removed corresponded to two benzene solvates in the case of **3b**, 6^1/$_2$ chloroform molecules in the asymmetric unit for **4a**, and two toluene molecules for **6a**.

Results and Discussion

Synthesis and Properties. Addition of phosphorus trichloride to a toluene solution of tris(3,5-di-*tert*-butyl-2-hydroxyphenyl)-methane (**1a**) and triethylamine, produced, after workup, a white material soluble in nonpolar organic solvents. Complete conversion of **1a** to the Type 2 (Figure 1, a) C_3 symmetric phosphite (**2a**) was observed in the ^{1}H and ^{31}P NMR spectra of the material, which had formed with no detectable side reactions. The 3-*tert*-butyl-5-methyl (**2b**), 3,5-di-*tert*-pentyl (**2c**), and 3-adamantyl-5-methyl (**2e**) derivatives could be similarly prepared, together with that derived from the non-C_3 symmetric bis(3-adamantyl-5-methyl-2-hydroxyphenyl)(3-*tert*-butyl-5-methyl-2-hydroxyphenyl)methane **1f**. The 3,5-dimethyl compound (**2d**), however, was formed in only very low yields (∼5% by ^{31}P

(28) Blessing, R. H. *Acta Crystallogr., Sect. A* **1995**, *51*, 33−38.
(29) Spek, A. L. *Acta Crystallogr., Sect. A* **1990**, *46*, C-34.

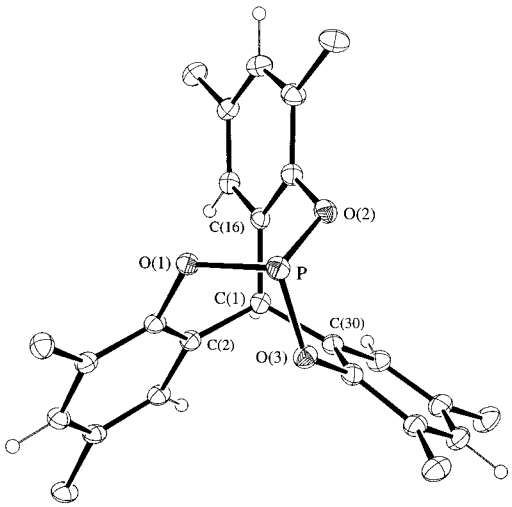


Figure 2. Structure of **2a** (30% probability ellipsoids). The *tert*-butyl methyl groups have been omitted, for clarity. The complete numbering scheme is given in the Supporting Information. Selected bond lengths (Å) and angles (deg): P−O(1) 1.623(1), P−O(2) 1.625(1), P−O(3) 1.628(1), C(1)···P 3.275(3). O(1)−P−O(2) 100.69(7), O(1)−P−O(3) 102.69(7), O(2)−P−O(3) 101.72(7).

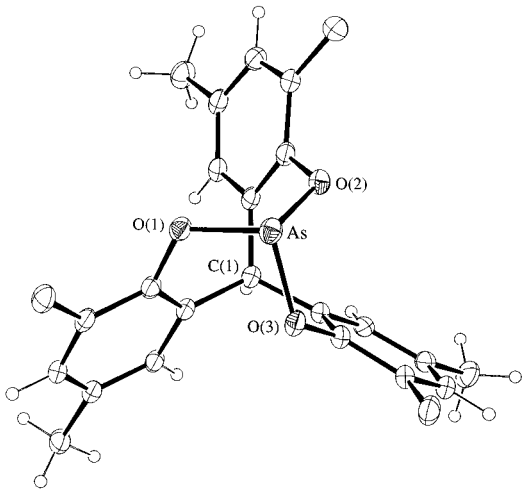


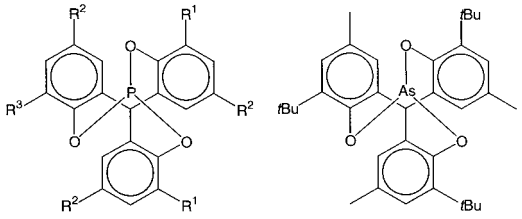
Figure 3. Structure of **3b**·$2C_6H_6$ (30% probability ellipsoids). The *tert*-butyl methyl groups have been omitted, for clarity. The complete numbering scheme is given in the Supporting Information. Selected bond lengths (Å) and angles (deg): As−O(1) 1.776(1), As−O(2) 1.785-(1), As−O(3) 1.772(1), C(1)···As 3.337(2). O(1)−As−O(2) 100.50-(6), O(1)−As−O(3) 98.18(6), O(2)−As−O(3) 100.00(6).

NMR), with unidentified oligomeric products predominating in this case. The reason for the poor yields of **2d**, especially in light of the essentially quantitative conversions observed for the other phosphites, is possibly attributable to the loss of the favorable steric congestion *ortho* to the hydroxyl groups, which for **1d** might allow the phosphorus to bridge adjacent molecules.

As reported for the calix[4]arene derived monophosphites,[15] the isolated phosphites were found to be remarkably stable with respect to oxidation, and even after refluxing in toluene or acetone/water in the presence of air for 24 h, no decomposition could be detected. The stability of these compounds is in sharp contrast to triphenyl phosphite, which undergoes complete decomposition in air after refluxing in acetone/water for 3 h.[15] The formation of the oxide of **2** was also attempted by reactions of **1** with phosphorus oxychloride, but in these cases only starting materials could be detected in the NMR spectra of the reaction mixtures. The stability of **2** with respect to hydrolysis was also substantial. When **2b**, dissolved in chloroform, was thoroughly mixed with either 1.2 M HCl or 1 M NaOH for 1 h, examination of the ^{1}H and ^{31}P NMR spectra revealed that no detectible decomposition had occurred. Even after 24 h, only the acid solution had induced some decomposition (<20%), evidenced by a new signal in the ^{31}P NMR spectra at 1.6 ppm. Given that phosphites are generally fairly easy to hydrolyze, the very high stability of **2** may be of utility if hydrolyzing reaction conditions are needed.

The ^{31}P NMR spectra exhibit a single resonance at 113 ppm for **2a**−**c**, **2e**, and **2f**, and 110 ppm for **2d**; these values compare with one of 129.1 ppm for triphenyl phosphite. Our experience has shown that generally the most diagnostic signal in the ^{1}H NMR spectra of materials derived from **1** is the central methine, which undergoes significant changes in chemical shift upon derivatization of the triarylmethane hydroxyl groups.[22−24] In the compound **2a**, the methine proton resonates at 5.32, slightly shifted upfield relative to the value of 5.64 ppm for the starting material **1a**. Inexplicably, while **2b** shows a similar difference, the di-*tert*-pentyl (**2c**) and dimethyl (**2d**) substituted materials show *downfield* shifts of 0.33 and 0.56 ppm, respectively. The ^{13}C NMR spectra proved more diagnostic, and significant downfield shifts from ∼40 ppm in the starting materials **1** to ∼60 ppm in the corresponding phosphites **2** were measured. These ^{13}C NMR chemical shift differences have been the largest seen for derivatives of **1** and are apparently indicative of inversion of the conformation from Type 1 to Type 2 (Figure 1). The closely related cage phosphine compound, phosphatriptycene, with the phosphorus directly bound to the aromatic rings has also been reported, for which the central methine showed very similar chemical shift values of 5.62 and 59.5 ppm for the ^{1}H and ^{13}C NMR spectra, respectively.[30]

To examine the ability of the tris-phenol ligands to accommodate larger atoms, the arsenic analogue of **2b** was explored by reaction of **1b** with AsI_3 in refluxing toluene. As expected, the arsenite derivative **3b** formed, although only in low yield. Unsurprisingly, the ^{1}H and ^{13}C NMR spectra closely resemble that of **2b**.



2a $R^1, R^2, R^3 = t$Bu
2b $R^1, R^3 = t$Bu; R^2 = Me
2c $R^1, R^2, R^3 = t$-pentyl
2d R^1, R^2, R^3 = Me
2e R^1, R^3 = Ad; R^2 = Me
2f R^1 = Ad; R^2 = Me; $R^3 = t$Bu

3b

Structural Analyses. Single crystals of **2a** were grown by the slow evaporation of an acetonitrile/ether solution, while large colorless rods of **3b** could be obtained after the slow diffusion of pentane into a saturated benzene solution. Figures 2 and 3 depict and ORTEP representations of the structures of **2a** and **3b**, respectively, together with selected bond lengths and angles. Collection parameters for both structures are given in Table 1.

The orientation of the three phenolate rings in **2a** have indeed "flipped" and now adopt a Type 2 structure, and these compounds represent the first examples of this conformation for systems derived from **1a**. Space-filling models clearly show

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Table 1. X-ray Data[a] for All Crystallographically Characterized Complexes

	2a	**3b**·$2C_6H_6$	**4a**·$7^3/_4CHCl_3$	**5b**	**6a**·2PhMe	**6f**
chemical formula	$C_{43}H_{61}O_3P$	$C_{46}H_{55}O_3As$	$C_{93.75}H_{129.75}O_6P_2Cl_{27.25}Pd_2$	$C_{37}H_{48}O_3PClPd$	$C_{63}H_{84}O_6PRh$	$C_{52}H_{62}O_6PRh$
formula weight	656.89	730.82	2593.48	713.57	1071.18	916.90
space group	$P2_1/n$	$R\bar{3}$	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P2_1/n$
μ(Mo−Kα) (mm^{-1})	0.103	0.947	0.946	0.689	0.382	0.460
a (Å)	10.5332(9)	26.4932(14)	18.206(2)	17.477(1)	13.909(1)	18.0013(9)
b (Å)	19.641(2)	-	25.301(2)	21.485(1)	26.103(2)	11.7064(6)
c (Å)	20.020(2)	27.759(2)	29.814(3)	18.748(1)	15.497(1)	21.7780(11)
α (deg)	-	-	70.109(2)	-	-	-
β (deg)	101.499(2)	-	74.658(2)	97.980(1)	90.943(2)	97.882(1)
γ (deg)	-	-	81.012(2)	-	-	-
V_c (Å^3)	4058.7(6)	16873.6(18)	12420.6(19)	6971.3(8)	5625.4(8)	4545.9(4)
Z	4	18	4	8	4	4
$R1$[b]	0.0596	0.0449	0.0892	0.0484	0.0509	0.0379
$wR2$[c]	0.1673	0.1229	0.2623	0.1356	0.1256	0.1027

[a] Obtained with monochromatic Mo Kα radiation (λ = 0.71073 Å). [b] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (XP)^2 + YP]$ where $P = (F_o^2 + 2F_c^2)/3\}$.

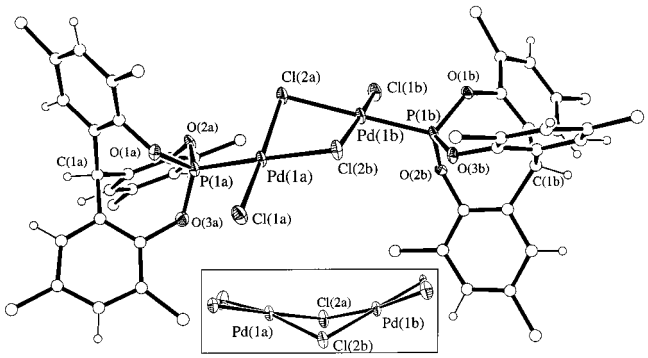


Figure 4. Structure of molecule 1 of **4a**·$7^3/_4CHCl_3$ (30% probability ellipsoids). The *tert*-butyl methyl groups and chloroform solvates have been omitted, for clarity. The inset illustrates the bent metal core. The complete numbering scheme is given in the Supporting Information. Selected bond lengths (Å) and angles (°): Pd(1a)−P(1a) 2.211(2), Pd(1b)−P(1b) 2.206(2), Pd(1a)−Cl(1a) 2.263(3), Pd(1a)−Cl(2a) 2.314(3), Pd(1a)−Cl(2b) 2.404(2), P(1a)−O(1) 1.575(6), P(1a)−O(2a) 1.575(6), P(1a)−O(3a) 1.580(7), C(1a)···P(1a) 3.14(1). P(1a)−Pd(1a)−Cl(1a) 87.44(9), Cl(2a)−Pd(1a)−Cl(2b) 84.34(8), Pd(1a)−Cl(2a)−Pd(1b) 89.47(9), Pd(1a)−Cl(2b)−Pd(1b) 89.01(8), O(1a)−P(1a)−O(2a) 108.0(3), O(1a)−P(1a)−O(3a) 106.9(4), O(2a)−P(1a)−O(3a) 103.9(3).

the phosphorus atom occupies an extremely sterically congested environment and, from the crystal data, the Tolman cone-angle for this ligand was estimated to be greater than 180° using a metal-phosphorus distance of 2.28 Å.[1]

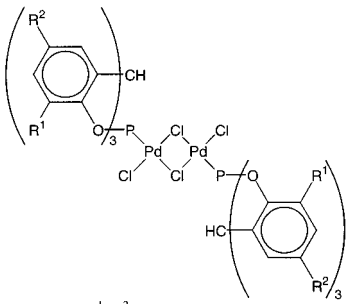
The aromatic rings are canted in a propeller-like fashion with angles relative to the C(1), C(16), C(30) plane being 66.28(6)−68.56(7)°. Although the ligand constrains the geometry of the phosphorus environment, it is nonetheless a good match for an atom adopting a tetrahedral coordination sphere. This favorable geometry is evidenced by the typical P−O bond lengths and O−P−O bond angles, which average 1.625(3) Å and 102(1)°, respectively, indicative of little to no strain.

A closely related species, the phosphorus(III) adduct of 2,2′,2″-nitrilotriphenol, has been reported.[31] This material was characterized crystallographically and shows P−O bond distances averaging 1.63 Å and O−P−O angles of 102.7°, statistically identical to those measured for **2a**. The nitrogen in the nitrilotriphenol phosphorus derivative was found to not interact with the phosphorus atom and is only marginally closer (3.14 Å) than the carbon linker in **2a** [3.275(3) Å].

The crystal structure of the arsenic derivative **3b** was also elucidated and demonstrates that a compound analogous to **2a** had formed. The ligand has sufficient flexibility to accommodate the binding desires of the larger arsenic atom and typical As−O (1.778 Å) and O−As−O (99.6°) bond lengths and angles were measured. As expected, the rings are canted, relative to the C(1), C(13), C(24) plane, to a marginally greater degree than measured for **2a**, with an average tilt angle of 64.9°.

Reaction of 2 with Metal Complexes. To ascertain the predilection of the prepared phosphites to form metal complexes, compounds **2** were reacted with two palladium materials and one rhodium system, since these metal phosphite derivatives have attracted particular interest in the past.[4,5,7,16,17]

[$PdCl_2$(cod)] (cod = 1,5-cyclooctadiene). An excess of the phosphites **2a** and **2b** were reacted with [$PdCl_2$(cod)] in toluene at 100 °C, since no reaction was observed at room temperature. The ^{31}P NMR spectrum of the reaction product revealed, atypically, that only a single equivalent of phosphite reacted with the palladium precursor, and a large upfield shift of 63 ppm was observed. Single crystals of **4a** were grown from chloroform. Figure 4 depicts the structure, while data collection details are shown in Table 1.



4a $R^1, R^2 = t$Bu
4b $R^1 = t$Bu; R^2 = Me

The structure of **4a** confirms the 1:1 stoichometry of Pd to phosphite observed in the ^{31}P NMR spectrum. Apparently the steric constraints of **2a** preclude the formation of a monomeric diphosphite adduct. Rather, a dimeric chloride bridged material forms, with the two phosphites mutually trans to one another. The Pd−P bond distance, averaging 2.203(7) Å for the palladium centers, is virtually indistinguishable from the value of 2.187(3) Å measured for [Pd_2Cl_4{$P(OPh)_3$}$_2$].[32] The Pd−Cl distances are similarly typical and compare favorably with those measured for the triphenyl phosphite adduct. The average P−Pd−Cl bite angle of 86(1)° is also congruent with the value

(31) Müller, E.; Bürgi, H.-B. *Helv. Chim. Acta* **1987**, *70*, 1063−1069.

(32) Grigsby, W. J.; Nicholson, B. K. *Acta Crystallogr. Sect. C* **1992**, *48*, 362−364.

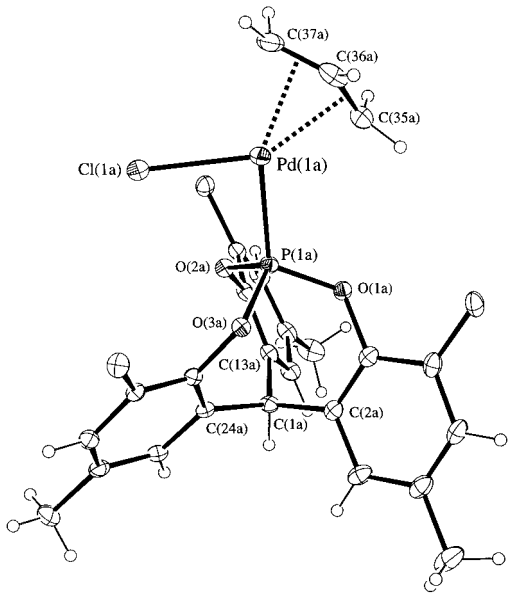


Figure 5. Structure of Molecule 1 of **5b** (30% probability ellipsoids). The *tert*-butyl methyl groups have been omitted, for clarity. The complete numbering scheme is given in the Supporting Information. Selected bond lengths (Å) and angles (deg): Pd(1a)−P(1a) 2.268(1), Pd(1a)−Cl(1a) 2.367(1), Pd(1a)−C(35a) 2.141(5), Pd(1a)−C(36a) 2.175(5), Pd(1a)−C(37a) 2.215(4), P(1a)−O(1) 1.599(3), P(1a)−O(2a) 1.598(3), P(1a)−O(3a) 1.602(3), P(1a)···C(1a) 3.208(6), C(35a)−C(36a) 1.396(7), C(36a)−C(37a) 1.363(7). P(1a)−Pd(1a)−Cl(1a) 88.89(4), C(35a)−C(36a)−C(37a) 120.3(5), O(1a)−P(1a)−O(2a) 104.1(1), O(1a)−P(1a)−O(3a) 102.6(1), O(2a)−P(1a)−O(3a) 106.3(1).

of 86.5(1)° found in $[Pd_2Cl_4\{P(OPh)_3\}_2]$. The most striking aspect of the structure is the unusual nonplanarity observed between the two palladium planes at the vector joining the two chlorine bridges (Figure 4 inset). To the best of our knowledge, this motif is unprecedented for the $M_2Cl_4P_2$ system (M = Ni, Pd, Pt; P = phosphorus moiety) and has been observed only twice previously; for $Pd_2Cl_4L_2$ [L_2 = (*R*,*R*)-1,5-bis{*o*-(*p*-toluenesulfinyl)phenoxy}-3-oxapentane[33] and L = 1,3-di-*tert*-butyl-2,2-dimethyl-1,3-diaza-2-sila-cyclopentene].[34] The coordination environment of the palladiums are square planar, with no atom deviating from a least squares plane drawn through Pd(1), P(1), Cl(1), Cl(2a), and Cl(2b) by more than 0.119(1) and 0.091(1) Å for the A and B palladiums (Figure 4). The butterfly angle formed between these two planes is 38.06(6)°. The reason for the observed bending is not entirely clear, but is in all likelihood a weak solid-state effect.

Despite the significant change in the ^{31}P NMR spectrum upon coordination of the phosphite, changes in the ^{1}H and ^{13}C NMR spectra were only slight to negligible. Indeed, the central methine signal in the ^{1}H NMR spectrum does not shift to an appreciable extent. In the ^{13}C NMR spectrum the central carbon resonance shifts 1.3 ppm upfield for both **4a** and **4b**. The remainder of the signals are essentially unaffected by the coordination of the phosphorus to the palladium center.

$[PdCl(\eta^3\text{-}C_3H_5)]_2$. The phosphite derivatives of $[PdCl(\eta^3\text{-}C_3H_5)]_2$ have been shown to be superior hydrosilation catalysts,[7] so the reactivity of **2** toward $[PdCl(\eta^3\text{-}C_3H_5)]_2$ was examined. Unlike the reactions of **2** with $[PdCl_2(cod)]$, ^{31}P NMR showed the reaction of **2** with $[PdCl(\eta^3\text{-}C_3H_5)]_2$ rapidly gave the corresponding monophosphite adducts **5**. To unambiguously establish the geometry and absolute connectivity of **5**, a single-crystal structure determination was carried out. Crystals of **5b** suitable for analyses were grown by the slow evaporation of a ether/CH_2Cl_2/heptane solution. An ORTEP representation of the structure is shown in Figure 5 with data collection parameters given in Table 1.

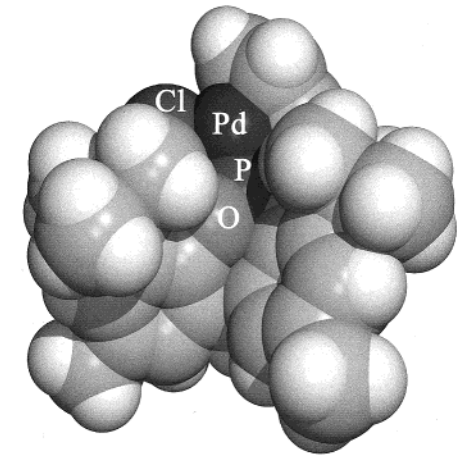
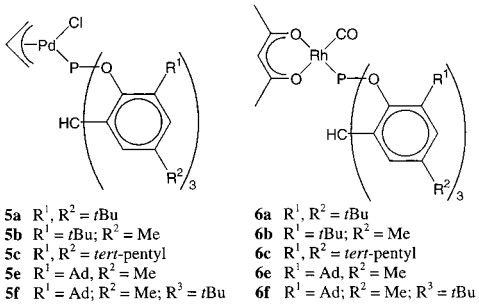


Figure 6. CPK representation of molecule 1 of **5b**.



5a R^1, R^2 = *t*Bu
5b R^1 = *t*Bu; R^2 = Me
5c R^1, R^2 = *tert*-pentyl
5e R^1 = Ad, R^2 = Me
5f R^1 = Ad; R^2 = Me; R^3 = *t*Bu

6a R^1, R^2 = *t*Bu
6b R^1 = *t*Bu; R^2 = Me
6c R^1, R^2 = *tert*-pentyl
6e R^1 = Ad, R^2 = Me
6f R^1 = Ad; R^2 = Me; R^3 = *t*Bu

The structure, surprisingly, is the first example of a phosphite derivative of an allyl palladium chloride, although a number of phosphine derivatives have been reported. The Pd−C and Pd−Cl bond lengths in **5b** are consistent with those of $[PdCl(\eta^3\text{-}C_3H_5)(PPh_3)]$[35,36] and $[PdCl(\eta^3\text{-}2\text{-}Me\text{-}C_3H_4)(PPh_3)]$.[36] Since the phosphite ligand is a better π-acceptor than phosphine, the Pd−P distance in **5b** is slightly shorter (∼0.04 Å) than those in the phosphine counterparts. The allyl group is fully delocalized, in agreement with the results previously measured for the room-temperature structures of $[PdCl(\eta^3\text{-}C_3H_5)(PPh_3)]$ and $[PdCl(\eta^3\text{-}2\text{-}Me\text{-}C_3H_4)(PPh_3)]$,[36] but contradictory to the low-temperature structure of $[PdCl(\eta^3\text{-}C_3H_5)(PPh_3)]$ which reportedly showed localized single and double bonds.[35] Like **4a**, no substantial deformation of the phosphite molecule relative to **2a** is observed upon coordination to the metal. The P(1a)−C(1a) distance of 3.208(6) Å in **5b** is only slightly shorter than in **4a** [3.275(3) Å], and the propeller angles of the aromatic rings relative to the C(2), C(13) and C(24) planes are 64.3(2)−69.4(1)° and 64.7(1)−67.7(2)° for the independent molecules 1 and 2, respectively; quite similar to those measured for the free phosphite **4a**. The CPK representation (Figure 6) of the structure allows for an accurate estimation of the cone-angle and, accordingly, a Tolman cone angle of ∼190 ° was measured for **2b**. From the CPK depiction, it is also evident that the chlorine atom is snugly nestled between two of the *ortho*-*tert*-butyl groups. It

(33) Hambley, T. W.; Raguse, B.; Ridly, D. D. *Aust. J. Chem.* **1985**, *38*, 1455−1460.
(34) Zettlitzer, M.; tom Dieck, H.; Stamp, L. *Z. Naturforsch., Teil B* **1986**, *41*, 1230−1238.
(35) Smith, A. E. *Acta Crystallogr. Sect. A* **1969**, *25*, S161.
(36) Faller, W.; Blankenship, C.; Whitmore, B.; Sena, S. *Inorg. Chem.* **1985**, *24*, 4483−4490.

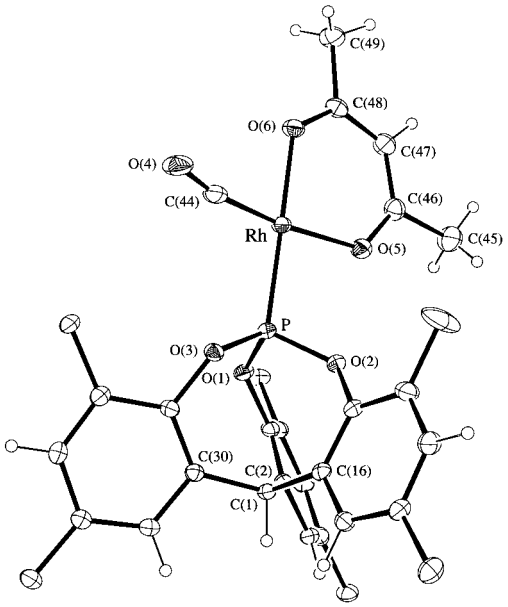


Figure 7. Structure of **6a**·2PhMe (30% probability ellipsoids). The *tert*-butyl methyl groups have been omitted, for clarity. The complete numbering scheme is given in the Supporting Information. Selected bond lengths (Å) and angles (deg): Rh−P 2.2072(8), Rh−C(44) 1.805(4), Rh−O(5) 2.044(2), Rh−O(6) 2.059(2), P−O(1) 1.601(2), P−O(2) 1.602(2), P−O(3) 1.598(2), P···C(1) 3.276(5), C(44)−O(4) 1.147(4), O(5)−C(46) 1.278(4), O(6)−C(48) 1.278(4), C(47)−C(46) 1.387(4), C(47)−C(48) 1.381(4). P−Rh−C(44) 95.4(1), P−Rh−O(5) 89.71(6), O(5)−Rh-O(6) 89.70(8), C(44)−Rh−O(6) 85.4(1), Rh−C(44)−O(4) 169.7(3), O(1)−P−O(2) 104.5(1), O(1)−P−O(3) 102.5(1), O(2)−P-O(3) 105.6(1).

would seem unlikely that phosphite complexes using [PdCl(η^3-C_3H_5)]$_2$ could form if significantly bulkier substituents were placed at the *ortho*-position of the phosphite ligand.

In contrast to the spectra recorded for **4a** and **4b**, the ^{31}P NMR spectra of the complexes **5** show only very small (∼3 ppm) upfield shifts relative to the corresponding phosphite precursors **2**. With the exception of **5e** and **5f**, the ^{1}H and ^{13}C NMR spectra of the phosphite ligands are also virtually unchanged, with retention of C_3 symmetry. For the complexes **5e** and **5f**, however, symmetry has been lost, solely evidenced by the splitting of the adamantyl resonances and, for **5f**, three separate Ar-CH_3 signals were observed. In all examples of **5**, resonances associated with the allyl group were also diagnostic with the five protons and three carbons rendered inequivalent. Thus, in contrast to the three signals witnessed in the ^{1}H NMR spectrum of [PdCl(η^3-C_3H_5)]$_2$, the allyl group in **5** exhibits five distinct signals distributed almost evenly over a 3 ppm range. The ^{13}C NMR resonances are similarly split from two for [PdCl(η^3-C_3H_5)]$_2$ (111.4 and 63.2 ppm) into three signals for **5**, at ∼118, 80, and 60 ppm.

[Rh(CO)$_2$(acac)] (acac = acetylacetonate). As already mentioned, bulky phosphite derivatives of rhodium(I) have been shown to be the among the best catalysts for the hydroformylation reaction,[5b] with sterically congested diphosphites proving to produce more selective hydroformylation catalysts.[5a] Since the phosphites **2** are extremely sterically crowded, we reasoned that they may produce interesting Rh complexes. Thus, the compounds **2** were reacted with [Rh(CO)$_2$(acac)] in CH_2Cl_2 solvent, producing the corresponding monophosphite adducts **6**. As observed for the complexes **4**, the complexes **6** failed to react with an additional equivalent of phosphite. Single crystals of **6a** and **6f** suitable for X-ray diffraction were obtained and both were subjected to an X-ray crystallographic study. Figures

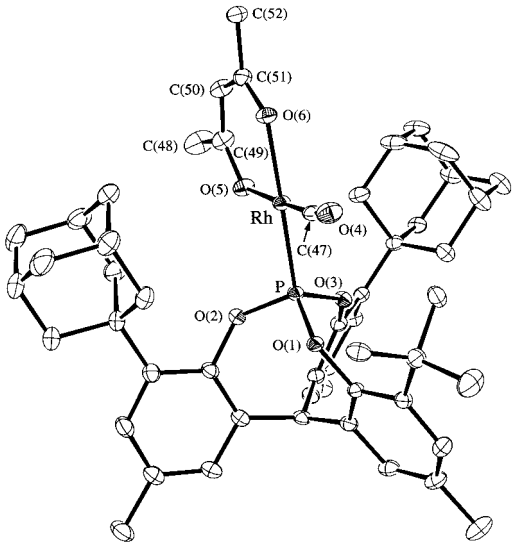


Figure 8. Structure of **6f** (30% probability ellipsoids). All hydrogen atoms have been omitted, for clarity. The complete numbering scheme is given in the Supporting Information. Selected bond lengths (Å) and angles (deg): Rh−P 2.2007(6), Rh−C(47) 1.822(3), Rh−O(5) 2.036(2), Rh−O(6) 2.066(2), P−O(1) 1.600(2), P−O(2) 1.599(2), P−O(3) 1.605(2), P···C(1) 3.265(5), C(47)−O(4) 1.144(3), O(5)−C(49) 1.277(3), O(6)−C(51) 1.266(3), C(50)−C(49) 1.387(4), C(50)−C(51) 1.396(4). P−Rh−C(47) 95.78(7), P−Rh−O(5) 88.45(5), O(5)−Rh−O(6) 90.01(7), C(47)−Rh−O(6) 85.75(9), Rh−C(47)−O(4) 171.5(2), O(1)−P−O(2) 104.11(9), O(1)−P−O(3) 102.01(9), O(2)−P−O(3) 105.21(9).

7 and 8 depict ORTEP representations of **6a** and **6f**, respectively, while the collection and refinement data are given in Table 1.

The overall structures of **6a** and **6f** bear quite strong resemblances to that of **5b**. The rhodium adopts the typical square-planar arrangement with the maximum deviations from the least-squares planes drawn through Rh, P, C, O(5), and O(6) being 0.104(1) Å for Rh in **6a** and 0.032(1) Å for C in **6f**. Comparing these structures with other phosphite complexes derived from [Rh(CO)$_2$(acac)] reveals most of the bond lengths and angles are consistent. The Rh−P distances in **6a** at 2.2072(8) Å and 2.2007(6) Å in **6f** are slightly longer than that measured for [Rh(CO)(DBM)P] (DBM = PhCOCHCOPh; P = 4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane phosphite ligand) [2.169(1) Å],[37] and also the calix[4]arene phosphite derived material [Rh(CO)(acac*)P] (acac* = tBuCOCHCOtBu; P = monophosphite derived from calix[4]arene) [2.184(1) Å].[16] The slight lengthening of the Rh−P bonds may be attributable to the increased steric requirements of the phosphite ligands in **6**. Further evidence of the steric bulk of **2** can be observed in the P−Rh−C bite angles of 95.4(1) and 95.78(7)° in **6a** and **6f**, respectively, these being significantly wider than in [Rh(CO)(DBM)P] [87.8(2)°] and also marginally wider than in the calix[4]arene phosphite derivative, where an angle of 93.1(2) was reported. This wider bite angle is concomitant with a perceptible bending of the carbonyl ligand with Rh−C−O angles of 169.7(3) and 171.5(2)° for **6a** and **6f**, respectively. For comparison, the analogous angle in [Rh(CO)(DBM)P] is 179.4(5)°, while more obtuse angles of 172.7(4) and 173.4(5)° were observed for the two independent molecules in the structure of the [Rh(CO)(acac*)P] complex. Examination of the space-filling models of **6a** and **6f** (Figure 9), reveals the wider P−Rh−C bite angle, and the bent carbonyl could be a result of

(37) Erasmus, J. J. C.; Lamprecht, G. J.; Kohzuma, T.; Nakano, Y. *Acta Crystallogr. Sect. C* **1998**, *54*, 1085−1087.

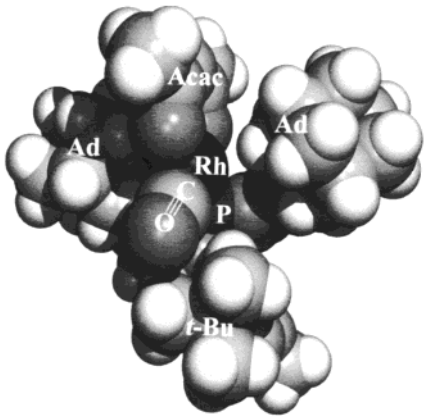


Figure 9. CPK representation of the X-ray structure of **6f**.

the acetylacetonate ligand, which is forced to squeeze between two of the aromatic rings (and its 3-substituents) of the absolutely rigid phosphite platform. To maintain a square-planar geometry about the rhodium center, the carbonyl moiety is forced to orient directly toward the third aromatic ring and its 2-*tert*-butyl group and, to avoid this unfavorable interaction, the carbonyl ligand angles away from the phosphite ligand. As mentioned for **5b**, any significant increase of the steric bulk at the 3-position in **2** would almost undoubtedly render the resulting phosphite inert with regard to reaction with $[Rh(CO)_2(acac)]$. As predicted by trans-influences,[38] the Rh−O distances are inequivalent with Rh−O(5) being shorter than Rh−O(6), the latter being trans to the higher trans-influence phosphite ligand. The Rh−CO bond distances of 1.805(4) and 1.822(3) Å for **6a** and **6f** are typical and compare with lengths of 1.803(5) and 1.817(5) Å reported for [Rh(CO)(DBM)P][37] and [Rh(CO)(acac*)P],[16] respectively.

In the ^{31}P NMR spectra of the rhodium compounds **6** the phosphorus resonances are found at ∼108 ppm with a $^{31}P-^{103}Rh$ coupling constants of ∼313 Hz, similar to the values of 109.8 ppm and 309 Hz reported for [Rh(CO)(acac*)P].[16] The most intriguing aspect of the ^1H and ^{13}C NMR spectra of **6a**−**c** is the observation that, like complexes **4** and **5a**−**c**, the C_3 symmetry of the phosphine has been retained, evidenced by only one unique aromatic ring and its substituents appearing in the spectra. The persistence of C_3 symmetry is contradictory to the solid-state structure of **6a** which would predict, at most, only mirror symmetry for the ligand. Clearly, free rotation of the phosphite about the Rh−P bond takes place in solution at room temperature for **6a**−**c**. As was found for **5e**, however, the C_3 symmetry has apparently been lost in complex **6e**. In this species the adamantyl resonances, which in the free phosphite show only two signals in the ^1H NMR spectrum, are now split into seven peaks. Similarly, the non-C_3 symmetric phosphite **2f**, which shows mirror symmetry in its NMR spectra, was found to have the adamantyl groups split into multiple distinct resonances upon coordination to the metal center. The remainder of the peaks in the ^1H and ^{13}C NMR spectra are otherwise unextraordinary and show only insignificant shifts with respect to the corresponding free phosphites **2**.

(38) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335−422.

Conclusions

The phosphite derivatives of the tripodal-linked phenolic compounds **1** were successfully prepared, together with the arsenite derivative of **1b**. The materials **2a**−**e** were found to be C_3 symmetric, rigid, and bulky, and also showed remarkable stability with respect to hydrolysis and oxidation, presumably due to the stability afforded by the *three* eight-membered rings formed by the ligand wrapping around the phosphorus center. Several different types of metal complexes of the phosphites could be readily prepared, and structural studies revealed the Tolman cone angles in these compounds to be in excess of 180°. Since the steric environment around the metal centers can be readily tuned by the judicious choice of substituents in the 3-position of the corresponding starting materials **1**, the new phosphites may find applicability where bulky phosphite ligands are required. The reactivity of metal derivatives of **2** in various catalytic processes is currently being investigated.

Acknowledgment. We thank the University of Florida, the National Science Foundation (CAREER Award 9874966), and the donors of the American Chemical Society Petroleum Research Fund for funding this research. Support from the Research Corporation is also gratefully acknowledged. We would also like to express our gratitude to Dr. Khalil Abboud at the University of Florida for granting access to X-ray instrumentation.

Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC000683J