Reactions of a Hydroxy Phosphonite Ligand in the Coordination Sphere of Rhodium(I)

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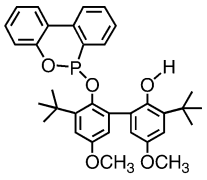
The complexation behavior of 6-(3,3′-di-*tert*-butyl-5,5′-dimethoxy-2-hydroxy-2′-oxybiphenyl)-6*H*-[*c*,*e*]-1,2-oxaphosphorine, which generates an active and *n*-regioselective rhodium(I) catalyst for the isomerizing hydroformylation of internal octenes, was studied. Investigations in the absence of CO/H_2 revealed that coordination of the phenolate moiety of the hydroxy phosphonite on the rhodium center is possible. Interestingly, under conditions related to the hydroformylation (syngas, higher temperature and P:Rh ratios) the ligand suffers two transformations. The first is based on a transesterification reaction involving 2 equiv of the hydroxy phosphonite, giving rise to a substituted biphenol and a symmetric bidentate phosphorus ligand of a heretofore uncertain structure. The second transformation is concerned with a selective Rh(I)-catalyzed P−C bond cleavage of the initial phosphonite structure under the formation of a phosphite. X-ray structural analyses will illustrate the structures of rhodium(I) complexes bearing the original hydroxy phosphonite ligand, a phenoxy phosphonite chelate, and a phosphite formed by selective P−C bond cleavage, respectively.

Introduction

Rhodium(I) complexes bearing trivalent phosphorus compounds as ancillary ligands play a pivotal role as efficient homogeneous catalysts in the hydroformylation of alkenes, representing a process of crucial economic importance.[1−3] Current academic and industrial research is focused on the identification of ligands which allow the highly regioselective production of terminal aldehydes from 1-olefins.[4] As an alternative, the formation of *n*-aldehydes by isomerization/hydroformylation of internal olefins has attracted increasing attention.[5−13] Recently, we reported that phosphonites belonging to a class of trivalent P compounds hitherto fully underestimated as ligands for homogeneous catalysis give very active rhodium catalysts for the hydroformylation of internal octenes under mild conditions.[11] Of particular interest was our finding that the catalyst formed with the hydroxy phosphonite **1** was superior with respect to *n*-regioselectivity in comparison to the methyl ether analogue and other related monodentate phosphonites.



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We speculated that the unique catalytic properties found for the hydroxy ligand could be attributed to the effect of the phenolic OH group: e.g., hemilabile coordination to the metal center.[14] To find rationalizations, the coordination behavior and the stability of **1** were investigated in detail. Herein, we will give proof that

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‡ Carl von Ossietzky Universität.
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(1) Frohning, C. D.; Kohlpaintner, C. W. In *Applied Homogeneous Catalysis with Organometallic Compounds*; Cornils, B., Herrmann, W. A., Eds.; VCH-Wiley: Weinheim, Germany, 1996; Vol. 1, pp 3−25.
(2) Herrmann, W. A.; Cornils, B. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1047.
(3) Beller, M.; Cornils, B.; Frohning, C. D.; Kohlpaintner, C. W. *J. Mol. Catal. A* **1995**, *104*, 17.
(4) van Leeuwen, P. W. N. M., Claver, C., Eds. *Rhodium Catalyzed Hydroformylation*; Kluwer: Dordrecht, The Netherlands, 2000.
(5) van Leeuwen, P. W. N. M.; Roobeek, C. F. Brit. Patent 2,068,377, 1980 (to Shell).
(6) van Leeuwen, P. W. N. M.; Roobeek, C. F. *J. Organomet. Chem.* **1983**, *258*, 343.
(7) Billig, E.; Abatjoglou, A. G.; Bryant, D. R.; Murray, R. E.; Maher, J. M. U.S. Patent 4,717,775, 1988 (to Union Carbide Corporation).
(8) Burke, P. M.; Garner, J. M.; Kreutzer, K. A.; Teunissen, A. J. J. M.; Snuder, C. S.; Hansen, C. B. WO 97/33854, 1997 (to DSM/DuPont).
(9) van der Veen, L. A.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Angew. Chem., Int. Ed.* **1999**, *111*, 336.
(10) van der Veen, L. A.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Organometallics* **1999**, *18*, 4765.
(11) Selent, D.; Röttger, D.; Wiese, K.-D.; Börner, A. *Angew. Chem., Int. Ed.* **2000**, *39*, 1639.
(12) Selent, D.; Hess, D.; Wiese, K.-D.; Röttger, D.; Kunze, C.; Börner, A. *Angew. Chem., Int. Ed.* **2001**, *40*, 1696.
(13) Klein, H.; Jackstell, R.; Wiese, K.-D.; Borgmann, C.; Beller, M. *Angew. Chem., Int. Ed.* **2001**, *40*, 3408.

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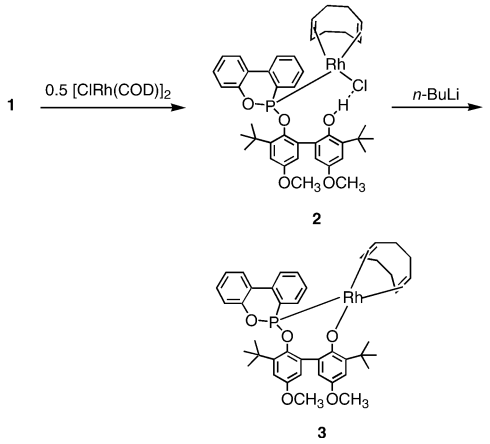
Scheme 1. Coordination and Phenolate Chelate Formation at Rh(I) of Phosphonite 1



the hydroxy phosphonite is not inert as a ligand but subject to two different transformation reactions which take place under conditions related to hydroformylation.

Results and Discussion

Complex Formation of the Hydroxy Phosphonite with Rhodium(I). Since each interpretation of the influence of ligands used in homogeneous catalysis is based on the assumption of ligand stability, first we confirmed that the hydroxy phosphonite **1** showed sufficient thermal stability at the temperature of hydroformylation in the absence of rhodium(I).[15] Thus, compound **1** was treated in a sealed tube in *p*-xylene at 140 °C for several hours. The ^{31}P NMR spectrum showed no tendency to decompose.

Subsequent treatment of 2 equiv of **1** with electronically unsaturated $[ClRh(COD)]_2$ (COD = cyclooctadiene-1.5) in thf at room temperature afforded a yellow solution. In the ^{31}P NMR spectrum resonances of two diastereoisomers at δ 123.1 (d, ^1J(P−Rh) = 230.3 Hz) and δ 131.8 (d, ^1J(P−Rh) = 220.5 Hz) were observed, formed in a 1:5.9 ratio. These diastereomers are due to the hindered rotation of the biphenol unit and the stereogenic phosphorus atom. Obviously small conformational changes of the nearly planar oxaphosphorine are not restricted at room temperature. Therefore, no additional diastereomers were detected in the NMR spectra. An orange solid crystallized, which was identified to be the major complex **2** (Scheme 1). The X-ray structural analysis of this complex showed that the hydroxy phosphonite coordinates in a monodentate fashion (Figure 1; selected bond lengths and angles are given in Table 1). The coordination geometry around the rhodium center is nearly ideally planar, as expected for a 16e Rh(I) complex. Nearly planar geometry is also observed for the dibenzo fused oxaphosphorine ring. Though there is no direct coordination of the OH group at the rhodium center, the crystal structure gives evidence for hydrogen bonding involving the coordinated chloride anion (Cl(1)···H(−O(3)) distance 2.342 Å). The biphenyl unit exhibits a torsion angle of 58.3° due to the steric demand of the bulky ortho-substituted *tert*-butyl substituents. The Rh−P distance is 2.233(2) Å, which is significantly longer compared to the respective distances of 2.156 and 2.174 Å found for the only two other examples of rhodium phosphonite complexes that, to the best of our knowledge, have been characterized structurally so far.[16,17]

To prove the possibility of hemilabile oxygen coordination, we studied the reaction of the lithium phenolate derived from **1** with $[ClRh(COD)]_2$. Interestingly, all attempts to react the free hydroxy phosphonite in the absence of rhodium(I) with butyllithium or KC_7H_7, respectively, in thf at −20 °C did not give the expected

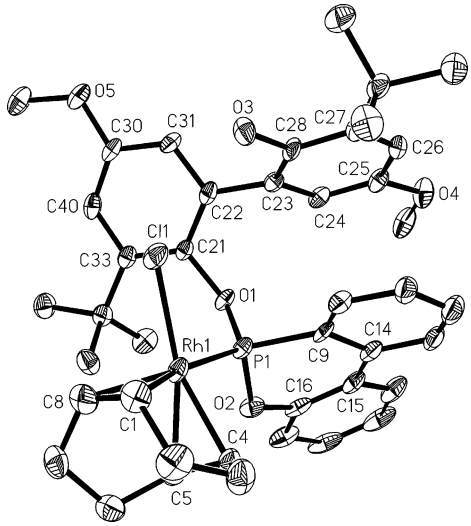


Figure 1. Crystal structure of **2**. Hydrogen atoms are omitted for clarity. The thermal ellipsoids correspond to 30% probability. The torsion angle between phenylic planes defined by C21, C22, C31, C30, C40, C33 (mean deviation from the best plane 0.0161 Å) and C23, C24, C25, C26, C27, C28 (mean deviation from the best plane 0.0086 Å) is 58.3°. The mean deviation from the best plane defined by X1a, X1b, Rh1, P1, Cl1 is 0.0687 Å (X1a, X1b: midpoints of cyclooctadiene double bonds). Selected bond lengths and angles are given in Table 1. For details of the X-ray structural analysis see Table 4.

Table 1. Selected Bond Lengths and Angles in 2

Bond Lengths (Å)			
Rh(1)−P(1)	2.233(2)	P(1)−O(2)	1.630(4)
Rh(1)−Cl(1)	2.371(2)	O(2)−C(16)	1.409(7)
Rh(1)−C(1)	2.289(6)	P(1)−C(9)	1.792(7)
Rh(1)−C(8)	2.264(6)	C(9)−C(14)	1.437(8)
Rh(1)−C(4)	2.120(7)	C(14)−C(15)	1.453(10)
Rh(1)−C(5)	2.165(7)	C(15)−C(16)	1.374(9)
C(1)−C(8)	1.365(10)	O(1)−C(21)	1.412(7)
C(4)−C(5)	1.379(10)	C(22)−C(23)	1.491(9)
P(1)−O(1)	1.619(4)	C(30)−O(5)	1.390(8)

Bond Angles (deg)			
O(1)−P(1)−O(2)	97.2(2)	C(9)−P(1)−Rh(1)	114.1(2)
O(1)−P(1)−C(9)	106.0(3)	C(4)−Rh(1)−C(5)	37.5(3)
O(2)−P(1)−C(9)	99.9(3)	C(8)−Rh(1)−C(1)	34.9(3)
O(1)−P(1)−Rh(1)	123.3(2)	P(1)−Rh(1)−Cl(1)	93.47(7)
O(2)−P(1)−Rh(1)	112.7(2)	C(21)−O(1)−P(1)	130.9(3)

(14) The hemilabile behavior of phosphino ethers has been found to be valuable for transition-metal-catalyzed carbonylation reactions: Bader, A.; Lindner, E. *Coord. Chem. Rev.* **1991**, *108*, 27. Remote hydroxy groups present in rhodium catalysts used for asymmetric hydrogenation of prochiral olefins are used for the control of the reactivity of the metal: Börner, A. *Eur. J. Inorg. Chem.* **2001**, 327.

(15) A 0.1 M solution of hydroxy phosphonite **1** was used for this experiment.

(16) Bondoux, D.; Tkatchenko, I.; Houalla, D.; Wolf, R.; Pradat, C.; Riess, J. G.; Mentzen, B. F. *J. Chem. Soc., Chem. Commun.* **1978**, 1022.

(17) Kumar, R.; Puddephatt, R. J.; Fronczek, F. R. *Inorg. Chem.* **1990**, *29*, 4850.

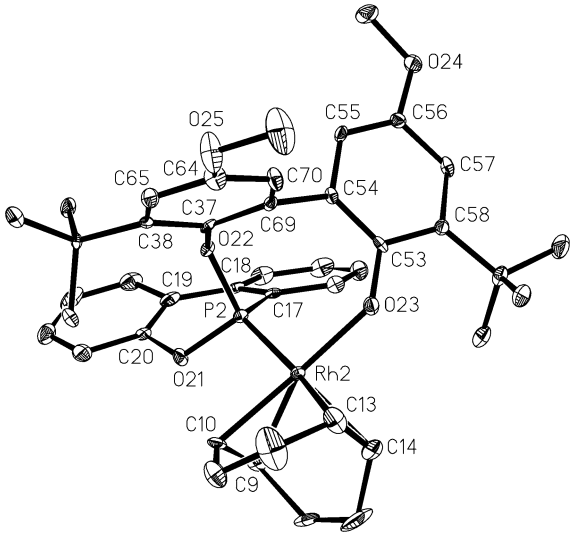


Figure 2. Crystal structure of one of the two symmetry-independent molecules of **3**. Hydrogen atoms are omitted for clarity. The thermal ellipsoids correspond to 30% probability. The torsion angle between phenylic rings defined by C53, C54, C55, C56, C57, C58 (mean deviation from the best plane 0.0151 Å) and C37, C38, C65, C64, C70, C69 (mean deviation from the best plane 0.0162 Å) is 91.2°. The mean deviation from the best plane defined by X1a, X1b, Rh2, P2, O23 is 0.0303 Å (X1a, X1b: midpoints of cyclooctadiene double bonds). Selected bond lengths and angles are given in Table 2. For details of the X-ray structural analysis see Table 4.

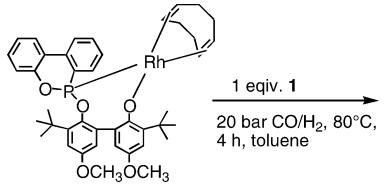
phenolate salt but led to immediate unselective formation of a mixture of phosphorus-containing products. In contrast, a clean reaction took place when a base such as *n*-butyllithium was added to the Rh-coordinated phosphonite. Under these conditions elimination of HCl occurred and a single diastereomer of the phenolate−phosphonite chelate complex **3** crystallized in 60% yield (Scheme 1).[18] The new complex was characterized in ^{31}P NMR spectroscopy by a resonance at δ 135.9 ($^{1}J(^{31}\mathrm{P}-^{103}\mathrm{Rh}) = 241.4$ Hz).

An X-ray structure analysis was performed showing two symmetry-independent molecules in the asymmetric unit. The structure analysis confirmed the formation of a mononuclear eight-membered rhodacyclic complex (see Figure 2; selected bond lengths and angles are given in Table 2). The chelate-like coordination at the rhodium center is facilitated after a pronounced rotation around the biphenyl axis. Torsion angles of 91.2 and 82.1°, respectively, were determined. These features give evidence that there is no hindrance which prevents the aryloxy group from coordinating; therefore, the sterically demanding phosphonite phenolate ligand can achieve a relatively stable chelate coordination at rhodium, similar to the case for *o*-phosphino phenolates.[19]

Table 2. Selected Bond Lengths and Angles in 3 (for One of the Symmetry-Independent Molecules)

Bond Lengths (Å)			
Rh(2)−P(2)	2.240(1)	P(2)−O(21)	1.630(3)
Rh(2)−O(23)	2.013(3)	P(2)−O(22)	1.617(3)
Rh(2)−C(9)	2.136(5)	P(2)−C(17)	1.799(5)
Rh(2)−C(10)	2.141(5)	O(21)−C(20)	1.415(5)
Rh(2)−C(13)	2.266(5)	O(22)−C(37)	1.423(5)
Rh(2)−C(14)	2.289(5)	O(23)−C(53)	1.337(5)
C(9)−C(10)	1.375(7)	O(24)−C(56)	1.390(6)
C(13)−C(14)	1.373(8)	C(54)−C(69)	1.495(7)
Bond Angles (deg)			
P(2)−Rh(2)−O(23)	98.6(1)	Rh(2)−O(23)−C(53)	132.8(3)
Rh(2)−P(2)−O(21)	111.0(1)	C(9)−Rh(2)−C(10)	37.5(2)
Rh(2)−P(2)−O(22)	116.5(1)	C(13)−Rh(2)−C(14)	35.1(2)
Rh(2)−P(2)−C(17)	123.1(2)	O(21)−P(2)−C(17)	98.7(2)

Scheme 2. Proposed Result of Catalyst Preformation with [Rh]/1



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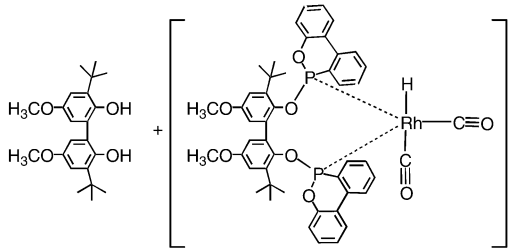


Transformation of Hydroxy Phosphonite 1 under CO/H$_2$. Subsequently, hydroxy phosphonite **1** was added to complex **3** under syngas in toluene, corresponding to a P/Rh ratio of 2 (Scheme 2).[20] The mixture was heated to 80 °C for 4 h at 20 bar and then cooled and depressurized to give a light brown solution. ^{1}H NMR spectra of the solution revealed the formation of a mixture of several hydrido rhodium complexes, which were characterized by a set of overlapping hydride shifts at approximately δ −10.1. The ^{31}P{^{1}H} NMR spectrum showed doublet resonances between δ 171.3 and 172.4, all exhibiting coupling constants ^{1}J(P−Rh) in the range of 197−205 Hz. The unusually large ligand ^{31}P downfield shift of approximately 35 ppm relative to the free phosphonite matches the complexation shift usually observed for diphosphite ligands coordinated to a hydrido rhodium core.[21] A ^{1}H,^{31}P HMQC NMR spectrum verified that all phosphorus resonances give correlation signals to the hydride part of the proton spectrum. Coupling constants J(H−P) between 13.5 and 15.4 Hz were measured. The signals observed clearly correspond to a set of complexes with a $HRhP_2$ core possessing chemically equivalent phosphorus atoms. Storage of the reaction solution at low temperature afforded the crys-

(18) Complex **3** gave a powerful hydroformylation catalyst for a mixture of internal octenes, provided an excess of **1** was present (conditions: 140 °C/20 bar of CO/H$_2$ (1:1), toluene, [**3**] = 0.1078 M, olefin:Rh ratio of 15 700). Catalysis in the presence of 9 equiv of the hydroxy phosphonite resulted in 50% yield of aldehyde with a linearity of ca. 48%. Obviously the same catalyst is generated from **3** as it is from the acetyl acetonate precursor.[11]

(19) Kadyrov, R.; Heinicke, J.; Kindermann, M. K.; Heller, D.; Fischer, C.; Selke, R.; Fischer, A. K.; Jones, P. G. *Chem. Ber./Recl.* **1997**, *130*, 1663. Trzeciak, A. M.; Ziólkowski, J. J.; Lis, T.; Choukroun, R. *J. Organomet. Chem.* **1999**, *575*, 87.

(20) As was proved by ^{31}P NMR spectroscopy, the mixture of phenolate rhodium complex **3** and ligand **1a** in toluene did behave inertly at room temperature, as long as an argon atmosphere was present.

(21) van Rooy, A.; Kamer, P. C. J.; van Leeuwen, P. W. N. M.; Goubitz, K.; Fraanje, J.; Veldman, N.; Spek, A. L. *Organometallics* **1996**, *15*, 835.

tallization of colorless needles, which were identified to be 3,3′-di-*tert*-butyl-5,5′-dimethoxybiphenyl-2,2′-diol.[22] Workup of the filtrate gave a brown residue, showing fragments in FAB MS at *m/e* 915 (M^+, 10%) and 859 ($M^+ - 2CO$, 62%). Obviously, in the presence of rhodium and syngas 2 equiv of **1** reacts under transesterification, thus forming the parent dihydroxy biphenyl and diastereomeric $HRhP_2(CO)_2$ type complexes. The coordinated bidentate ligand is likely a symmetric diphosphonite with a 3,3′-di-*tert*-butyl-5,5′-dimethoxybiphenyl-2,2′-diolate backbone, phosphorylated with two of the oxaphosphorine moieties as present in **1**.[23]

P−C Bond Activation of 1. Next, complex **3** was treated in toluene under ambient temperature with an excess of the ligand (overall ratio Rh:P = 1:20). Then the temperature was raised while the syngas pressure was maintained constant at 20 bar. After cooling and depressurization, ^{31}P and ^1H NMR spectra were recorded for every batch. Spectra recorded after an initial treatment at 80 °C/30 min showed signals identical with those of the hydride complexes described above together with resonances of the free ligand at δ 134.8 and 135.2. Integration verified a ratio of coordinated to uncoordinated phosphorus of 1:9; therefore, further evidence was provided that 2 equiv of **1** are consumed for complex formation. Heating of the reaction mixture under 20 bar of CO/H_2 to 100 °C/4 h led to the appearance of a new singlet at δ 139.2. This signal gained 11% of the relative intensity of the uncoordinated ligand part of the ^{31}P NMR spectrum when the solution was kept at 120 °C for 4 h; simultaneously, the signals of **1** lost intensity. At 140 °C the reaction was more pronounced, giving a 67% fraction of the new compound within 4 h and resulting in the complete transformation of the free hydroxy phosphonite after 8 h. The ^1H NMR spectrum indicated the formation of a compound with chemically equivalent *tert*-butyl and methoxy substituents, respectively, characterized by singlets at δ 1.34 and 3.83. No crystallization of the new compound was achieved; therefore, the reaction solution was treated with an appropriate amount of $[ClRh(COD)]_2$ at room temperature. As a result, the phosphite rhodium complex [ClRh(COD)(**4**)] (**5**) was obtained in analytically pure form after workup and recrystallization from toluene/hexane (Scheme 3, Figure 3; selected bond lengths and angles are given in Table 3). Complex **5** crystallized as fine, needlelike yellow crystals which could be handled in air for a short time. Structural features of the complex such as Rh−P and Rh−Cl bond lengths as well as the distances from the rhodium center to the vinylic carbon atoms of coordinated cyclooctadiene do not markedly differ from those obtained for the chloro phosphonite complex **2**.

Obviously, the hydroxy phosphonite when used in excess suffers selective P−C bond activation, giving a phosphite. It should be noted that no phosphite was found when the hydroxy phosphonite was heated in the absence of rhodium. This means that a catalytic reaction of the coordinated ligand must take place which presumably involves nucleophilic attack of the phenolic hydroxy group at phosphorus.[24] Formally, the P−C bond breakage observed can be considered as the reverse reaction of Lewis-acid-catalyzed formation of 6-chloro-(6*H*)-dibenzo-(*c*,*e*)(1,2)-oxaphosphorine, which was used

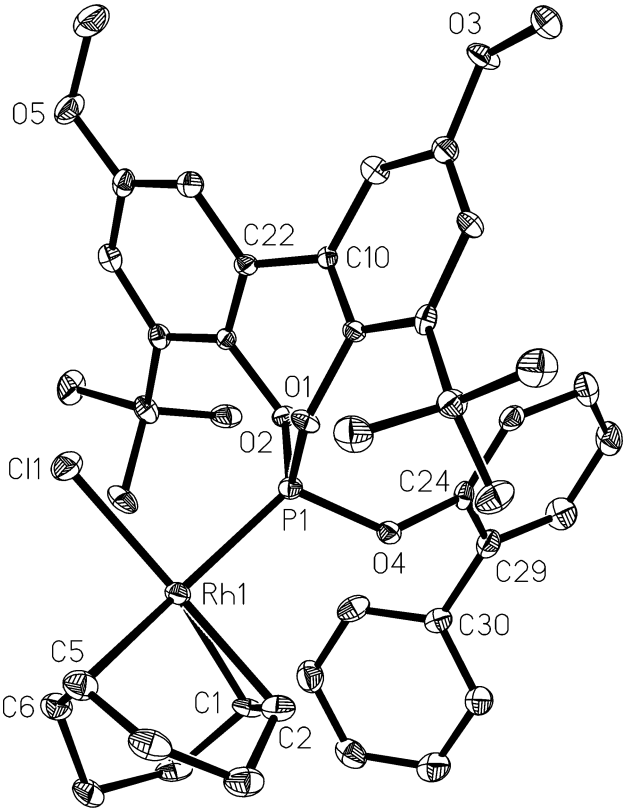
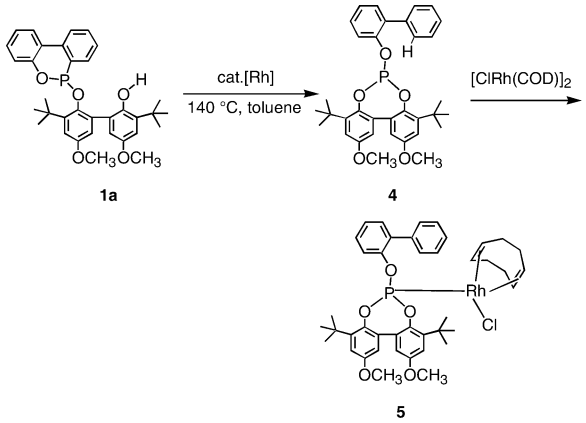


Figure 3. Crystal structure of **5**. Hydrogen atoms are omitted for clarity. The thermal ellipsoids correspond to 30% probability. The mean deviation from the best plane defined by X1a, X1b, Rh1, P1, Cl1 is 0.0881 Å (X1a, X1b: midpoints of cyclooctadiene double bonds). Selected bond lengths and angles are given in Table 3. For details of the X-ray structural analysis see Table 4.

Scheme 3. Hydroxy Phosphonite to Phosphite Transformation and Product Trapping



(22) The bis(phenol) was identified by comparison with an sample synthesized independently by the procedure described in: Moasser, B.; Gross, C.; Gladfelter, W. L. *J. Organomet. Chem.* **1994**, *471*, 201.

(23) Unfortunately, all attempts failed to synthesize this compound according to a protocol described by: Maas, H.; Paciello, R.; Röper, M.; Fischer, J.; Siegel, W. German Pat. DE 198 10 794 A 1, 1998 (to BASF AG). These attempts failed even after variation of the reaction temperature between −40 and 60 °C or by application of *n*-butyllithium or potassium benzyl in thf/hexane mixtures as well as with a large excess of triethylamine as a base in toluene.

(24) The outcome of the reaction observed matches earlier results on transition-metal-mediated P−C bond cleavage by nucleophilic attack of alkoxide ligands; see, for example: van Leeuwen, P. W. N. M.; Roobeek, C. F.; Orpen, A. G. *Organometallics* **1990**, *9*, 2179 and references therein.

Table 3. Selected Bond Lengths and Angles in 5

Bond Lengths (Å)			
Rh(1)−P(1)	2.223(1)	P(1)−O(1)	1.605(3)
Rh(1)−Cl(1)	2.358(1)	P(1)−O(2)	1.608(4)
Rh(1)−C(1)	2.120(5)	P(1)−O(4)	1.602(4)
Rh(1)−C(2)	2.144(5)	O(1)−C(9)	1.406(5)
Rh(1)−C(5)	2.247(6)	O(2)−C(17)	1.422(6)
Rh(1)−C(6)	2.291(5)	O(4)−C(24)	1.428(6)
C(1)−C(2)	1.390(7)	C(29)−C(30)	1.496(8)
C(5)−C(6)	1.358(8)	C(10)−C(22)	1.500(7)
Bond Angles (deg)			
P(1)−Rh(1)−Cl(1)	89.45(5)	O(1)−P(1)−O(4)	108.5(2)
Rh(1)−P(1)−O(1)	105.2(1)	O(2)−P(1)−O(4)	96.9(2)
Rh(1)−P(1)−O(2)	125.6(1)	C(1)−Rh(1)−C(2)	38.1(2)
Rh(1)−P(1)−O(4)	115.0(1)	C(5)−Rh(1)−C(6)	34.8(2)
O(1)−P(1)−O(2)	104.6(2)	P(1)−O(4)−C(24)	131.8(3)

as a starting material for **1a** synthesis,[11] from *o*-phenylphenol and phosphorus trichloride.[25]

To confirm the structure of **4** by an independent synthetic pathway, 3,3′-di-*tert*-butyl-5,5′-dimethoxy-1,1′-biphenyl-2,2′-diylphosphorochloridite[26] was reacted with *o*-phenylphenol in the presence of triethylamine to give the desired 6,6′-di-*tert*-butyl-4,4′-dimethoxy-2,2′-bisphenoxyphosphinooxy(2-phenyl)phenyl. This phosphite is a new member of a series of compounds which belong to the parent 2,2′-bisphenoxyphosphinooxyphenyl.[27] Upon coordination to rhodium(I) the relevant ^{31}P NMR spectrum was characterized by a remarkable upfield shift of 19 ppm, leading to a resonance at δ 119.1. The complex prepared from such a phosphite sample with $[ClRh(COD)]_2$ showed the same analytical properties as **5**.

Conclusions

The results may be summarized as follows: the observed coordination modes of **1** found in complexes **2** and **3** in the absence of syngas at room temperature may be important only at early stages of the catalyst formation. Under conditions more related to hydroformylation the reactive phenolic OH group present in **1** is responsible for two modes of ligand transformation. In addition to transesterification, also P−C bond activation and cleavage take place. As a result, new trivalent P compounds arise with the ability to coordinate on the metal. Catalytic investigations are in progress to assess the individual contribution of each newly formed organometallic compound to the overall result of the isomerizing hydroformylation of internal olefins.[28]

Experimental Section

General Considerations. All reactions were carried out using standard Schlenk techniques under an atmosphere of argon (Linde AG). Solvents were distilled from sodium/benzophenone prior to use. Chemicals were purchased from Aldrich Chemical Co. Phosphonite **1a** was prepared according to the literature procedure.[11] NMR spectra were obtained on a Bruker ARX 400 spectrometer (400.1 MHz for ^{1}H NMR, 100.6 MHz for ^{13}C NMR, and 162.0 MHz for ^{31}P NMR at a magnetic field strength of 9.4 T); all shifts are given relative to TMS (^{1}H, ^{13}C) or 85% H_3PO_4 (^{31}P). Mass spectra were measured on a Intectra AMD 402/3 instrument. Elemental analysis data were measured on a Leco CHNS-932 apparatus. IR spectra were recorded on a Nicolet Magna-IR 550 spectrometer.

Pressure Reactions. A 200 mL Buddeberg autoclave equipped with a gas stirrer, a thermocouple, a storage vessel allowing the addition of reactants under pressure applied, a sampling device, a Bronkhorst Hitec pressure controller, and a Bronkhorst gas flow meter was used. The autoclave allowed us to add and remove any media and reagents with the strict exclusion of air. A high-grade pure syngas (99.997%; CO/H_2 1:1) was purchased from Linde AG. The hydroformylation experiments of internal octenes using complex **3** as a catalyst precursor were carried out by using the methodology and substrate described in detail in ref 11.

X-ray Structural Analyses. Suitable crystals of compounds **2**, **3**, and **5** were obtained from toluene/hexane solutions. X-ray data were collected on a STOE-IPDS diffractometer using graphite-monochromated Mo Kα radiation. The structures were solved by direct methods (SHELXS-86)[29] and refined by full-matrix least-squares techniques against F^2 (SHELXL-93).[30] XP (Siemens Analytical X-ray Instruments, Inc.) was used for structure representations. Crystallographic data are given in Table 4.

Table 4. Crystallographic Data for 2, 3, and 5

	2	**3**	**5**
formula	$C_{42}H_{49}ClO_5PRh$	$C_{42}H_{48}O_5PRh$	$C_{42}H_{49}ClO_5PRh$
fw	803.14	766.68	803.14
temp, K	180	200	200
wavelength, Å	0.710 73	0.710 73	0.710 73
cryst syst	monoclinic	triclinic	tetragonal
space group	$P2_1/n$	$P\bar{1}$	$P4_1$
a, Å	14.023(3)	12.562(2)	10.831(2)
b, Å	12.684(3)	17.480(3)	10.831(2)
c, Å	22.639(5)	18.107(3)	31.904(6)
α, deg	90	68.860(10)	90
β, deg	104.63(3)	82.430(10)	90
γ, deg	90	89.39(2)	90
V, Å^3	3896.2(15)	3673.2(11)	3742.7(12)
Z	4	4	4
d_{calcd}, g cm^{-3}	1.369	1.386	1.452
μ, mm^{-1}	0.591	0.553	0.615
F(000)	1672	1600	1672
cryst dimens, mm	0.3 × 0.3 × 0.2	1.0 × 0.3 × 0.1	0.3 × 0.2 × 0.1
θ range, deg	1.86−24.29	1.90−24.22	1.88−20.96
no. of rflns collected	11 182	10 923	8011
no. of indep rflns	6116	10 923	3930
no. of obsd rflns ($I > 2\sigma(I)$)	3309	6080	3630
no. of params	452	883	451
R1 ($I > 2\sigma(I)$)	0.060	0.039	0.029
wR2 (all data)	0.143	0.071	0.064

Preparation of [ClRh(COD-1.5)(1)] (2). A solution of $[ClRh(COD\text{-}1.5)]_2$ (0.862 g, 1.75 mmol) in thf (60 mL) was treated dropwise with a 0.0915 M stock solution of **1a** in thf (38.2 mL, 3.5 mmol) at room temperature. After it was stirred for an additional 2 h, the solution was concentrated to 15 mL in vacuo and stored at 5 °C for 3 days. The orange crystals that formed were filtered off, washed with cold hexane (2 × 5 mL), and dried in vacuo.

(25) Kleiner, H.-J. EP 0582957 A1, 1994 (to BASF AG).

(26) Arena, C. G.; Nicolo, F.; Drommi, D.; Bruno, G.; Faraone, F. *J. Chem. Soc., Dalton Trans.* **1996**, *23*, 4357.

(27) Arbuzov, B. A.; Kadyrov, R. A.; Arshinova, R. P.; Mukmeneva, N. A. *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.)* **1981**, *30*, 567.

(28) To prove the properties of pure phosphite **4** as a catalyst modifier, hydroformylation of internal octenes was carried out at 140 °C/20 bar ($CO:H_2$ = 1:1). With different Rh:P ratios applied (1:10, 1:20), relatively low regioselectivities of 34.8 and 34.4% were obtained. Aldehyde yields were 83.1 and 89.4%, respectively. These results match the data earlier obtained with the ether phosphonite **1b**. In our opinion it is reasonable to suggest that the newly formed phosphite **4** supports the isomerization activity and stability of the catalyst, respectively, rather than regioselective olefin hydroformylation.

(29) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467.

(30) Sheldrick, G. M. SHELXL-93; University of Göttingen, Göttingen, Germany, 1993.

A second crop of crystals was obtained after concentration of the mother liquor to 5 mL. Overall yield: 2.585 g (92%). Anal. Calcd for $C_{42}H_{49}O_5PClRh$: C, 62.81; H, 6.15; P, 3.86; Rh, 12.81. Found: C, 62.79; H, 6.13; P, 3.61; Rh, 12.41. FAB-MS: *m/e* 802 (3%, M^+), 767 (53%, $M^+ - Cl$), 694 (100%, $M^+ - COD$). Spectroscopic data (major diastereoisomer): $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 131.8 (d, $^1J_{PRh} = 220.5$ Hz); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 28.1 (s, $C(CH_3)_3$), 29.6 (s, $C(CH_3)_3$), 30.4 (s, $C(CH_3)_3$), 32.4 (d, $^2J_{CRh}$= 2.8 Hz, CH_2 cyclooctadiene), 32.6 (s, $C(CH_3)_3$), 34.7 (d, $^2J_{CRh}$= 1.9 Hz, CH_2 cyclooctadiene), 55.4 (s, OCH_3), 56.1 (s, OCH_3), 73.1 (d, $^1J_{CRh} = 13.4$ Hz), 73.3 (d, $^1J_{CRh} = 13.4$ Hz, both =*C*H− cyclooctadiene), phenylic carbons at 113.2, 114.1, 114.5, 114.9 (all s), 120.7 (d, $J_{CP} = 3.8$ Hz), 123.5 (d, $J_{CP} = 4.8$ Hz), 125.0, 125.7 (both s), 129.1 (d, $J_{CP} = 17.2$ Hz), 130.2, 132.3, 134.1, 134.4 (all s); ^1H NMR (CD_2Cl_2) δ 1.26 (s, 9H, $C(CH_3)_3$), 1.51 (s, 9H, $C(CH_3)_3$), 1.81, 1.94, 2.18, 2.30 (all m, 2H, CH_2 cyclooctadiene), 3.04 (br, 1H, =C*H*− cyclooctadiene), 3.04, 3.50 (both s, 3H, OCH_3), 3.86, 5.33, 5.59 (all br, 1H, =C*H*− cyclooctadiene), 5.59 (s, 1H, O*H*), phenylic protons at: 6.11 (d, 1H), 6.27 (d, 1H), 6.35 (s, 1H), 6.66 (d, 1H), 6.95, 7.05, 7.12, 7.23,7.25, 7.52, 7.73, 7.99 (all dd, 1H).

Preparation of [Rh(COD-1.5)(1-phenolate)] (3). A solution of **2** (1.596 g, 1.99 mmol) in thf (75 mL) was treated with a 0.1 M solution of *n*-butyllithium in hexane (19.9 mL, 1.99 mmol) at room temperature. After the mixture was stirred for 2 h, the solvent was evaporated in vacuo. The residue was washed with cold hexane (65 mL), filtered off, and then extracted with boiling diethyl ether (80 mL). After storage at 5 °C overnight the ethereal solution was cold filtered and the precipitate was washed with cold ethyl ether (6 mL) and then dried in vacuo at 50 °C for 3 h. Yield: 0.921 g of yellow microcrystalline material (60%). Anal. Calcd for $C_{42}H_{48}O_5PRh$: C, 65.79; H, 6.31; P, 4.04; Rh, 13.42. Found: C, 65.52; H, 6.21; P, 3.81; Rh, 13.18. FAB-MS: *m/e* 767 (58%, M^+), 659 (100%, $M^+ - COD$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 135.95 (d, $^1J_{PRh} = 241.4$ Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 27.2 (s, $C(CH_3)_3$), 29.3 (s, $C(CH_3)_3$), 29.9 (s, $C(CH_3)_3$), 31.4 (s, $C(CH_3)_3$), 32.6, 36.0 (both d, $^2J_{CRh} = 1.9$ Hz, CH_2 cyclooctadiene), 56.4 (s, OCH_3), 57.0 (both s, OCH_3), 66.6 (d, $^1J_{CRh} = 13.4$ Hz), 68.5 (d, $^1J_{CRh} = 12.4$ Hz, both =*C*H− cyclooctadiene), phenylic carbons at 112.9 (dd), 113.6 (dd), 113.9 (dd), 115.2 (s), 121.4 (d), 123.9 (dd), 124.8 (s), 125.3 (s), 127.9 (d), 130.2 (s), 132.3 (s), 132.9 (s), 133.3 (s). ^1H NMR (CD_2Cl_2): δ 1.54 (s, 9H, $C(CH_3)_3$), 1.83 (s, 9H, $C(CH_3)_3$), 2.21 (2H), 2.30 (4H), 2.47 (2H; all m, CH_2 cyclooctadiene), 3.65 (s, 3H, OCH_3) 3.69, 3.93 (both br, 1H, =C*H*− cyclooctadiene), 4.00 (s, 3H, OCH_3), 5.85 (br, 2H, =C*H*− cyclooctadiene), phenylic protons at 6.12 (d, 1H), 6.70 (d, 1H), 6.98 (d, 1H), 7.21 (ddd, 1H), 7.23 (d, 1H), 7.31 (ddd, 1H), 7.33 (d, 1H), 7.47 (ddd, 1H), 7.61 (ddd, 1H), 7.74 (ddd, 1H), 8.05 (dd, 1H), 8.20 (dd, 1H).

Reaction of Complex 3 with Hydroxy Phosphonite 1 under Syngas. A solution of complex **3** (406 mg, 0.529 mmol) in toluene (30 mL) was treated with the hydroxy phosphonite (294.7 mg, 0.529 mmol) at room temperature. After the mixture was stirred for 1 h, a sample of the reaction solution (2 mL) was evaporated to dryness. A ^{31}P NMR spectrum measured in toluene-d_8 showed no signals other than those of the starting compounds. The reaction solution was transferred to the autoclave and stirred under syngas (20 bar) at 80 °C for 4 h. The autoclave was cooled and depressurized and the solution transferred to a Schlenk tube. The reaction solution was concentrated to half its original volume in vacuo and stored at −23 °C for 2 weeks. The colorless crystals that formed were filtered off, washed with hexane, and dried in vacuo. Yield: 93 mg (49%) of 3,3′-di-*tert*-butyl-5,5′-dimethoxybiphenyl-2,2′-diol (mp 228 °C). The filtrate was evaporated to dryness in vacuo, giving a brown solid, consisting of five $HRh(CO)_2P_2$ complexes. $^{31}P\{^1H\}$ NMR: δ 171.3 (d), $J_{PRh} = 201.1$ Hz, P(1); 171.5 (dd), $J_{PRh} = 198.3$ Hz, P(2); 171.7 (dd), $J_{PRh} = 198.3$ Hz, P(3); 171.9 (d), $J_{PRh} = 197.0$ Hz, P(4); 172.4 (d), $J_{PRh} = 201.1$ Hz, P(5). ^1H NMR: δ −10.07 (dt, $J_{HP} = 14.6$ Hz, $J_{HRh} = 3.5$ Hz), H(1); −10.13 (dt, $J_{HP} = 15.4$ Hz, $J_{HRh} = 3.9$ Hz), H(2); −10.13 (dt, $J_{HP} = 15.4$ Hz, $J_{HRh} = 3.9$ Hz), H(3); −10.13 (dt, $J_{HP} = 15.4$ Hz, $J_{HRh} = 3.4$ Hz), H(4); −10.14 (dt, $J_{HP} = 13.5$ Hz, $J_{HRh} = 3.7$ Hz), H(5). IR (toluene, 0.2 mm CaF_2): ν(CO) 1942.6 (s), 2009.4 (s), ν(Rh−H) 1955.4 (m, sh) cm^{-1}. FAB MS: *m/e* 915 (M^+, 10%) 875 (50%), 859 ($M^+ - 2CO$, 62%), 687 ($M^+ - CO - H$ − phosphorine, 100%), 659 ($M^+ - 2\ CO - H$ − phosphorine, 73%), 602 (50%).

P−C Activation of Hydroxy Phosphonite 1 and Formation of Complex 5. A solution containing [acacRh(COD-1.5)] (28.9 mg, 0.093 mmol) and phosphonite **1** (1.036 g, 1.861 mmol) in toluene (35 mL) was transferred into the autoclave via cannula. Syngas was applied (33 bar) and the reactor heated with stirring to 140 °C. Then the pressure was adjusted to 50 bar. After 8 h of reaction time, the autoclave was cooled and depressurized and the reaction solution transferred to a Schlenk tube. Evaporation of the solvent in vacuo afforded a brown oily residue, which was treated with 10 mL of hexane to give an amorphous brown precipitate. After filtration, 5 mL of hexane added to the filtrate gave a second fraction of precipitate, which was removed also. ^{31}P NMR showed the filtrate to contain only one phosphorus compound with a signal at δ 139.2 ppm (toluene-d_8, chemical shift in CD_2Cl_2 138.3 ppm). Evaporation of the solvent gave 0.783 g (1.407 mmol, 76%) of phosphite **4**. For details of analyses see the independent phosphite synthesis described in the next paragraph. The phosphite obtained (0.783 g, 1.407 mmol) was dissolved in thf (20 mL) and added at room temperature to a solution of $[ClRh(COD-1.5)]_2$ (0.347 g, 0.703 mmol) in thf (20 mL). After the mixture was stirred overnight, the solvent was removed in vacuo to form a yellow-brown solid, which was washed with cold hexane (3 × 5 mL) and recrystallized from toluene/hexane. Yield: 0.751 g (66%) of [ClRh(COD-1.5)(**4**)]. Anal. Calcd for $C_{42}H_{49}O_5PClRh$: C, 62.81; H, 6.15. Found: C, 63.01; H, 6.32. FAB-MS: *m/e* 802 (7%, M^+), 767 (38%, $M^+ - Cl$), 694 (89%, $M^+ - COD$), 659 (100%, $M^+ - COD - Cl$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 119.1 (d, $J_{PRh} = 273.3$ Hz), $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 28.4 (s, CH_2 cyclooctadiene), 31.6 (s, $C(CH_3)_3$), 33.4 (s, CH_2 cyclooctadiene), 35.9 (s, $C(CH_3)_3$), 56.0 (s, OCH_3), 71.0 (d, $J_{CRh} = 13.4$ Hz, =*C*H− cyclooctadiene), phenylic carbons at 113.4 (d, $J_{CP} = 16.2$ Hz), 113.8, 115.2 (both s), 121.9 (d, $J_{CP} = 5.7$ Hz), 124.3, 127.4, 127.7, 128.1, 131.5, 132.1 (all s), 133.0 (d, $J_{CP} = 5.7$ Hz), 135.7, 137.9 (all s), 141.8 (d, $J_{CP} = 11.5$ Hz), 142.3 (d, $J_{CP} = 3.9$ Hz), 149.4 (d, $J_{CP} = 8.6$ Hz), 156.0 (s). ^1H NMR (CD_2Cl_2): δ 1.37 (s, 18H, $C(CH_3)_3$), 1.98 (br m, 4H, CH_2 cyclooctadiene), 2.19, (br m, 4H, CH_2 cyclooctadiene), 3.58 (br, 2H, =C*H*− cyclooctadiene), 3.71 (s, 6H, OCH_3), 5.45 (br, 2H, =C*H*− cyclooctadiene), phenylic protons at 6.60 (d, 2H), 6.88 (d, 2H), 7.02 (m, 2H), 7.14 (m, 1H), 7.20 (m, 3H), 7.30 (m, 1 H), 7.45 (m, 2H).

Independent Synthesis of Phosphite 4. A solution of 3,3′-di-*tert*-butyl-5,5′-dimethoxy-1,1′-biphenyl-2,2′-diylphosphorochloridite[26] (1.303 g, 3.08 mmol) in diethyl ether (15 mL) was slowly treated with a mixture of 2-phenylphenol (0.524 g, 3.03 mmol) and triethylamine (0.533 g, 5.27 mmol) in diethyl ether (10 mL) at room temperature. After it was stirred for 4 h, the reaction mixture was filtered and the solvent removed in vacuo. The residue obtained was dried in vacuo at 80 °C for 3 h to give the product as an colorless oil. Yield: 1.657 g (97%). Anal. Calcd for $C_{34}H_{37}O_5P$: C, 73.36; H, 6.70. Found: C, 73.10; H, 6.73. EIMS (70 eV): *m/e* 556 (95%, M^+), 387 (100%, $M^+ - o$-$(C_6H_5)C_6H_4O$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 138.3. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 30.9 (s, $C(CH_3)_3$), 35.6 (s, $C(CH_3)_3$), 55.9 (s, OCH_3), phenylic carbons at 113.2 (s), 114.8 (s), 121.5 (d, $J_{CP} = 12.4$ Hz), 124.6, 127.4, 128.4, 128.8, 130.0, 131.7 (all s), 134.0 (d, $J_{CP} = 3.8$ Hz), 134.2, 138.2 (both s), 141.7 (d, $J_{CP} = 5.7$ Hz), 143.0, 149.1, 156.3 (all s). ^1H NMR (CD_2Cl_2): δ 1.34 (s, 18H, $C(CH_3)_3$), 3.83 (s, 6H, OCH_3), phenylic protons at 6.75 (m, 2H), 6.99 (m, 2H), 7.18 (m, 2H), 7.29 (m, 4H), 7.39 (m, 1H), 7.45 (m, 2H).

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Supporting Information Available: Tables of crystal data and structure refinement details, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates for **2**, **3** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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