Synthesis and Properties of Phenyl Phosphines with Meta-Positioned Methyl Groups and the X-ray Structure of Tris(3,5-dimethyl-4-methoxyphenyl)phosphine

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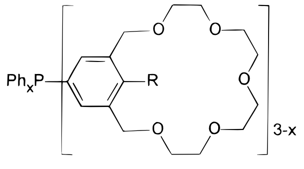
Summary: Nine phosphines, Ph_x(3,5-dimethyl-4-R-phenyl)$_{3-x}$ where R = H, F or OCH_3, have been synthesized, and the donor properties of the P(III) centers have been evaluated by measuring the A_1 ν(CO) frequencies of the $Ni(CO)_3L$ complexes. These data indicate that, compared to hydrogen, the methyl groups are electron donating, the fluoro groups are electron withdrawing, and the methoxy groups have little effect. The X-ray structure of tris(3,5-dimethyl-4-methoxyphenyl)phosphine has been obtained, and a prominent feature of the structure is that the methoxy groups are perpendicular to the phenyl ring faces and folded toward the ring faces adjacent to the phosphorus lone pair.

Introduction

The widespread use of phosphine-ligated metals as catalytic or stoichiometric reagents for organic reactions has resulted in both the commercial availability of a wide range of systems and a considerable interest in quantifying both the steric and electronic properties of a wide range of P(III) centers.[1−3] Recently, we began studies of hybrid, phosphine ligands of the types shown in **1**.[4] During those studies, it became evident that the chemical properties of phosphines with meta-positioned alkyl or alkoxy groups had not been extensively studied in a systematic manner, and a search of the CCDC database revealed only one reported X-ray structure, $P(3\text{-}C_6H_4CH_3)_3$.[5] As a result of this situation, we elected to prepare and study the series of nine phosphines shown as **2**−**4**, and we elected to determine the structure of **4c**. This anisole-based system was selected for several reasons including the fact that the conformational preference for OCH_3 groups on aromatic rings continues to be a topic of considerable theoretical and experimental interest.[6−11] Specifically, the neighboring CH_3 groups in **4c** would be expected to hinder the usual planar arrangement, **5**, observed in the ground and excited states for unsubstituted anisoles providing instead perpendicular, **6**, or gauche, **7**, arrangements.[11] In addition, with perpendicular or gauche arrangements, the OCH_3 groups could be folded either toward or away from the phenyl group faces that are oriented toward the P(III) lone pair.



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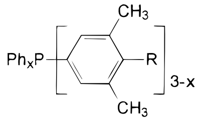
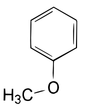


2 - 4

	x		
R	2	1	0
H	2a	2b	2c
F	3a	3b	3c
OCH_3	4a	4b	4c



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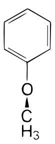

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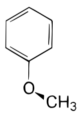

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Experimental Section

Reagents and Materials. Chlorodiphenylphosphine, dimethyl phenylphosphonite, triphenyl phosphite, 2,6-dimethylanisole, 5-bromo-*m*-xylene, 4-bromo-2,6-dimethylaniline, and *n*-butyllithium (2.5 M in hexane) were obtained from Aldrich Chemical Co., Inc. $Ni(CO)_4$ was purchased from Strem Chemicals, Inc. Prior to use, both tetrahydrofuran (THF, over sodium and benzophenone) and chlorodipenylphosphine were distilled.

4-Bromo-2,6-dimethylanisole was prepared as previously described,[12] and 4-bromo-1,3-dimethyl-2-fluorobenzene was

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prepared from 4-bromo-2,6-dimethylaniline by using the methods reported for 1,3-dimethyl-2-fluorobenzene.[13]

Methods and Instruments. Reactions and purifications were carried out under a blanket of argon. IR and NMR spectra were recorded on FT instruments. The ^1H, 400 MHz, and $^{31}P\{H\}$, 80 MHz, NMR spectra are referenced to TMS (internal) and 85% phosphoric acid (external). The IR instrument was calibrated with solutions of $Ni(CO)_3PPh_3$, for which the A_1 $\nu(CO)$ stretching band has been reported to be 2068.9 cm^{-1}.[14] Elemental analyses were carried out by Midwest Microlab Ltd., Indianapolis, IN. The X-ray analysis was carried out by the Molecular Structure Center, Indiana University, Bloomington, IN 47405.

IR Studies. The $Ni(CO)_3L$ IR studies were carried out in situ (deoxygenated dichloromethane filtered through a column of activated alumina) as previously described.[14–16]

Preparation of (3,5-Dimethylphenyl)diphenylphosphine (2a). Compounds **2**–**4** (**a**–**c**) were prepared by the following procedure. 5-Bromo-*m*-xylene (4.31 g, 0.0233 mol, dissolved in 250 mL of THF) was cooled in a liquid nitrogen/ethyl acetate slush. *n*-Butyllithium (9.2 mL, 0.023 mol) in hexane was added via syringe over a period of 1 h to the cooled and stirred solution. After stirring for an additional 1 h at this temperature, 5.14 g of chlorodipenylphosphine dissolved in 5 mL of THF was added over a period of 1.5 h. The mixture was warmed to room temperature, and 30 mL of 0.02 M HCl(aq) was added. Following the removal of most of the THF (rotary evaporator), the resulting aqueous mixture was extracted with 2 × 50 mL portions of dichloromethane, which was subsequently separated and removed. The resulting oil was crystallized from 75 mL of absolute ethanol, providing 3.97 g (59%) of colorless crystals; mp 62–64 °C. ^1H NMR ($CDCl_3$): δ 2.26 (s, 6 H), 6.94 (d, J = 8.80 Hz, 2 H), 6.98 (s, 1 H) 7.3–7.4 (m, 10 H). Anal. Calcd for $C_{20}H_{19}P$: C, 82.74; H, 6.60. Found: C, 82.64; H, 6.68.

Preparation of Bis(3,5-dimethylphenyl)phenylphosphine (2b). 5-Bromo-*m*-xylene (4.31 g, 0.0233 mol) was reacted sequentially with 9.2 mL of *n*-butyllithium and 1.97 g of dimethyl phenylphosphonite, yielding 1.72 g (46%) of colorless crystals following crystallization from absolute ethanol; mp 91–92 °C. ^1H NMR ($CDCl_3$): δ 2.28 (s, 12 H), 6.96 (d, J = 8.40 Hz, 4 H), 6.98 (s, 2 H) 7.3–7.4 (m, 5 H). Anal. Calcd for $C_{22}H_{23}P$: C, 82.99; H, 7.28. Found: C, 82.78; H, 7.32.

Preparation of Tris(3,5-dimethylphenyl)phosphine (2c). 5-Bromo-*m*-xylene (4.31 g, 0.0233 mol) was reacted sequentially with 9.2 mL of *n*-butyllithium and 2.40 g of triphenyl phosphite, yielding 1.66 g (62%) of colorless crystals following crystallization from absolute ethanol; mp 158–159 °C. ^1H NMR ($CDCl_3$): δ 2.27 (s, 18 H), 6.94 (d, J = 8.60 Hz, 6 H), 6.96 (s, 3 H). Anal. Calcd for $C_{24}H_{27}P$: C, 83.20; H, 7.86. Found: C, 83.07; H, 7.85.

Preparation of (3,5-Dimethyl-4-fluorophenyl)diphenylphosphine (3a). 4-Bromo-1,3-dimethyl-2-fluorobenzene (5.00 g, 0.0246 mol) was reacted sequentially with 10.0 mL of *n*-butyllithium and 5.43 g of chlorodiphenylphosphine, yielding 4.08 g (54%) of colorless crystals following crystallization from absolute ethanol; mp 76–77 °C. ^1H NMR ($CDCl_3$): δ 2.20 (d, J = 2.20 Hz, 6 H), 6.97 (t, J = 14.30 Hz, 2 H), 7.25–7.40 (m, 10 H). Anal. Calcd for $C_{20}H_{18}FP$: C, 77.91; H, 5.88. Found: C, 77.66; H, 5.90.

Preparation of Bis(3,5-dimethyl-4-fluorophenyl)phenylphosphine (3b). 4-Bromo-1,3-dimethyl-2-fluorobenzene (4.72 g, 0.0233mol) was reacted sequentially with 9.2 mL of *n*-butyllithium and 1.97 g of dimethyl phenylphosphonite, yielding 1.87 g (45%) of colorless crystals following crystallization from absolute ethanol; mp 99–100 °C. ^1H NMR ($CDCl_3$): δ 2.21 (d, J = 1.80 Hz, 12 H), 6.97 (t, J = 14.60 Hz, 4 H), 7.25–7.40 (m, 5 H). Anal. Calcd for $C_{22}H_{21}F_2P$: C, 74.56; H, 5.97. Found: C, 74.34; H, 5.96.

Preparation of Tris(3,5-dimethyl-4-fluorophenyl)phosphine (3c). 4-Bromo-1,3-dimethyl-2-fluorobenzene (4.72 g, 0.0233mol) was reacted sequentially with 9.2 mL of *n*-butyllithium and 2.40 g of triphenyl phosphite, yielding 1.35 g (43%) of colorless crystals following crystallization from absolute ethanol; mp 158–160 °C. ^1H NMR ($CDCl_3$): δ 2.21 (d, J = 1.80 Hz, 18 H), 6.90 (t, J = 14.70 Hz, 6 H). Anal. Calcd for $C_{24}H_{24}F_3P$: C, 71.99; H, 6.04. Found: C, 71.78; H, 6.08.

Preparation of (3,5-Dimethyl-4-methoxyphenyl)diphenylphosphine (4a). 4-Bromo-2,6-dimethylanisole (5.00 g, 0.0233 mol) was reacted sequentially with 9.2 mL of 2.5 M *n*-butyllithium and 5.14 g of chlorodiphenylphosphine, yielding 1.22 g (16%) of colorless crystals following crystallization from absolute ethanol; mp 88–89 °C. ^1H NMR ($CDCl_3$): δ 2.22 (s, 6 H), 3.73 (s, 3 H), 6.97 (d, J = 7.70 Hz, 2 H), 7.3–7.4 (m, 10 H). Anal. Calcd for $C_{21}H_{21}OP$: C, 78.73; H, 6.61. Found: C, 78.47; H, 6.64.

Preparation of Bis(3,5-dimethyl-4-methoxyphenyl)phenylphosphine (4b). 4-Bromo-2,6-dimethylanisole (5.00. g, 0.0233 mol) was reacted sequentially with 9.2 mL of 2.5 M *n*-butyllithium and 1.98 g of dimethyl phenylphosphonite, yielding 0.97 g (22%) of colorless crystals following crystallization from absolute ethanol; mp 90–92 °C. ^1H NMR ($CDCl_3$): δ 2.23 (s, 12 H), 3.73 (s, 6 H), 6.97 (d, J = 7.60 Hz, 4 H), 7.3–7.4 (m, 5 H). Anal. Calcd for $C_{24}H_{27}O_2P$: C, 76.17; H, 7.19. Found: C, 75.95; H, 7.36.

Preparation of Tris(3,5-dimethyl-4-methoxyphenyl)phosphine (4c). 4-Bromo-2,6-dimethylanisole (5.04 g, 0.0234 mol) was reacted sequentially with 9.2 mL of 2.5 M *n*-butyllithium and 2.40 g of triphenyl phosphite, yielding 1.71 g (50%) of colorless crystals following crystallization from absolute ethanol; mp 171–173 °C. ^1H NMR ($CDCl_3$): δ 2.24 (s, 18 H), 3.73 (s, 9 H), 6.97 (d, J = 8.00 Hz, 6 H). Anal. Calcd for $C_{27}H_{33}O_3P$: C, 74.29; H, 7.62. Found: C, 74.12; H, 7.60.

Single-Crystal X-ray Diffraction Study of 4c. Crystals of **4c** were grown by slowly evaporating a dichloromethane and ethanol solution (1:10 ratio) at −10 °C. A small, nearly equidimensional fragment was cleaved from a longer needle, attached to a glass fiber, and cooled to −170 °C for characterization and data collection. Data were collected using a standard $\theta-2\theta$ scan with fixed backgrounds at each extreme of the scan. A systematic search of reciprocal space located a set of diffraction maxima which could be indexed as orthorhombic, space group *Pcab*. The structure was solved using MULTAN78 and Fourier techniques. All hydrogen atoms were visible and were refined isotropically in the final cycles. No absorption correction was applied.

Results and Discussion

Synthesis. Compounds **2**–**4** have been obtained by reactions involving carbanions generated by low-temperature lithium/bromine exchange reactions and Ph_2PCl (for **2**–**4a**), $PhP(OMe)_2$ (for **2**–**4b**), and $P(OPh)_3$ (for **2**–**4c**). NMR spectra of the crude reaction mixtures were consistent with the conclusion that all are formed in high yield, but the purified products were obtained in 22–59% yields. Following purification by crystallization from ethanol, all compounds were found to be colorless, air-stable crystals. The ^{31}P NMR signals for **2**–**4** along with those from the previously reported crown ether analogues, **1**, R = H and OCH_3, are summarized in Table 1. As shown, the shifts for all 14 compounds span a narrow range from −4.0 to −7.4 δ. Further, for the

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Table 1. $^{31}P\{H\}$ Chemical Shifts (δ) in $CDCl_3$

	ligand series and substituent in position 4				
	2 (H)	**3** (F)	**4** (OMe)	**1** (H)[4]	**1** (OMe)[4]
a	−4.6	−5.7, d (*J* = 3.0 Hz)	−5.6	−5.0	−5.7
b	−4.3	−6.6, d (*J* = 3.7 Hz)	−6.2	−4.4	−6.5
c	−4.0	−7.4	−7.0	−4.1	

Table 2. A_1 ν(CO) Stretching Frequencies (cm^{-1}) for $Ni(CO)_3L$ Complexes

	2(H)	**3** (F)	**4** (OMe)	**1** (H)	**1** (OMe)
a	2067.7	2068.5	2067.6	2069.1	2068.9
b	2067.0	2067.9	2066.5	2068.8	2068.7
c	2065.9	2067.7	2065.4	2068.5	

Table 3. Selected Hammett Substituent Constants

	position	
group	meta	para
H	0	0
F	0.34	0.15
CH_3	−0.06	−0.14
OCH_3	0.10	−0.28

phosphines in series **1** and **2** with hydrogen atoms in the 4 positions, the chemical shifts increase with increasing numbers of phenyl rings, but the opposite trend is observed for those with OCH_3 or F in that position. That these trends are observed for both the ligands reported here and the crown-ether-based phosphines, **1**, may be an additional indication that the crown ether groups can be considered to be comparable to the simpler methyl groups.

$Ni(CO)_3L$ IR Data. The electronic characteristics of phosphines have been studied by a variety of experimental methods including the use of titrations involving perchloric acid in nitromethane[17,18] and calorimetry,[19−21] along with both IR[14−16] and NMR[22] measurements of $Ni(CO)_3L$ complexes. The ν(CO) bands from $Ni(CO)_3L$ complexes in particular have been used to characterize the properties of a large number of P(III) systems, and these data have an advantage in that comparisons can be made with data from electrostatic−covalent (E−C) calculations.[23,24]

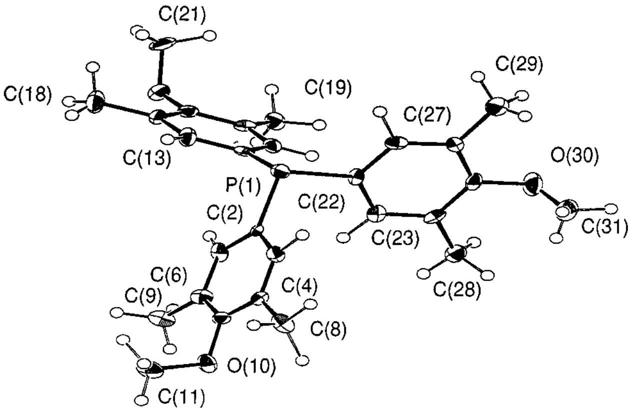

Figure 1. ORTEP drawing of **4**.

Table 4. Crystallographic Data

formula	$C_{27}H_{33}O_3P$
space group	*Pcab*
cell dimensions, Å, at −170 °C	*a* = 12.320(3), *b* = 37.838(9), *c* = 10.216(3)
vol, $Å^3$	4762.17
λ, Å	0.71069
calcd density, g/cm^3	1.218
Z molecules/cell	8
μ, cm^{-1}	1.408
max and min 2θ, deg	6, 50
no. of unique reflns collected	5445
no. with *F* > 0.0	3446
no. with *F* > 2.33σ(*F*)	1554
no. of unique intensities	4189
final residuals	
$R(F)^a$	0.0523
$R_w(F)^b$	0.0413
goodness of fit for last cycle	1.465
max Δ/σ for last cycle	0.03

[a] $R = \sum||F_o| - |F_c||/|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ where $w = 1/\sigma^2(|F_o|)$.

Table 5. Selected Bond Distances (Å) for 4c

C(5)−O(10)	1.409(6)	O(30)−C(31)	1.429(8)
O(10)−C(11)	1.436(7)	P(1)−C(2)	1.844(6)
C(15)−O(20)	1.394(6)	P(1)−C(12)	1.820(6)
O(20)−C(21)	1.447(7)	P(1)−C(22)	1.840(5)
C(25)−O(30)	1.388(6)		

Table 6. Selected Bond Angles (deg) for 4c

C(2)−P(1)−C(12)	103.81(28)	C(15)−O(20)−C(21)	113.5(5)
C(2)−P(1)−C(22)	102.02(27)	C(25)−O(30)−C(31)	112.4(6)
C(12)−P(1)−C(22)	101.75(28)		
C(5)−O(10)−C(11)	112.7(5)		

The A_1 stretching frequencies for $Ni(CO)_3L$ (L = **2**−**4**) have been recorded in CH_2Cl_2, and the values for these along with those for the previously reported[4] examples of **1** are presented in Table 2. Compared to the value of 2068.9 cm^{-1} for PPh_3,[14] these data are consistent with the conclusion that the meta-positioned methyl groups are electron donors, with each group decreasing the ν(CO) band by ca. 0.5 cm^{-1}. As expected, the fluorine substituents are electron-withdrawing groups, increasing the band positions by ca. 0.6 cm^{-1}. The OCH_3 groups are also electron donors, but clearly the effect is small, a maximum of ca. 0.2 cm^{-1} per group. Together, these effects can be expressed: (# CH_3)(0.5 cm^{-1}) + (# F)(−0.6 cm^{-1}) + (# OCH_3)(0.2 cm^{-1}) + observed ν(CO) = 2069 (the value for PPh_3). Hammett parameters[25] for these substituents are summarized in Table 3, and these values are reflected in the IR data presented in Table 2 because the meta-positioned methyl groups and the para-positioned methoxy groups are electron donors, whereas the fluoro group is electron withdrawing. However, the observed magnitudes of the shifts are not entirely in line with the values in that the meta-positioned methyl groups are better donors (ca. 0.5 cm^{-1}) than the para-positioned methoxy groups (ca. 0.2 cm^{-1}). Previously reported[15] ν(CO) data for $PhP_x(4\text{-}C_6H_4\text{-}OCH_3)_{3-x}$ (*x* = 2, 2068.2 cm^{-1}; *x* = 0, 2066.1 cm^{-1}) also indicate the methoxy group is expected to have a larger effect than observed in **4a**−**c**. Only small effects from para-positioned methoxy groups were also observed for

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Table 7. C−C−O−C Dihedral Angles for 4c and Tris(4-methoxyphenyl)phosphine

4c	angle	$P(4\text{-}C_6H_4OCH_3)_3$[26]	angle	$P(4\text{-}C_6H_4OCH_3)_3$[27]	angle
C(4)C(5)O(10)C(11)	102.6	C(7)C(8)O(2)C(11)	−4.7	C(7)C(8)O(2)C(23)	−176.2
C(6)C(5)O(10)C(11)	−82.2	C(9)C(8)O(2)C(11)	175.7	C(9)C(8)O(2)C(23)	4.5
C(14)C(15)O(20)C(21)	87.1	C(14)C(15)O(3)C(18)	−176.6	C(13)C(14)O(3)C(24)	175.5
C(16)C(15)O(20)C(21)	−94.5	C(16)C(15)O(3)C(18)	2.8	C(15)C(14)O(3)C(24)	−4.72
C(24)C(25)O(30)C(31)	−85.3	C(21)C(22)O(4)C(25)	−3.4	C(19)C(20)O(4)C(25)	3.82
C(26)C(25)O(30)C(31)	98.3	C(23)C(22)O(4)C(25)	178.8	C(21)C(20)O(4)C(25)	177.20

the related ligands **1**; see Table 2. For **1**, it can be argued that the methoxy effect is almost nil because there appears to be another factor that decreases the ν(CO) values as the number of crown ether rings increases even though the number of $-CH_2OR$ groups, which are likely electron withdrawing, also increases. If this additional factor is ca. 0.3 cm^{-1}, as observed for ligand **1**, then the methoxy effect is even smaller than the first analysis might indicate. The likely reason for the limited impact of the methoxy groups in **1** and **4** is that steric interactions hinder the conjugation of the oxygen lone pairs with the aromatic ring protons. Additional evidence that the ortho-positioned groups function in this manner is presented below.

X-ray Diffraction Structure of 4c. The molecular structure of **4c** is shown in Figure 1, crystallographic data and selected bond distances and angles are presented in Tables 4−6. The carbon−carbon bond distances average 1.390 Å (mean absolute deviation 0.008 Å) and 1.503 (mean absolute deviation 0.008 Å) for the sp^2-sp^2 and sp^2-sp^3 carbon−carbon bonds, respectively. The phosphorus−carbon bond distances are also unremarkable with P(1)−C(2), P(1)−C(12), and P(1)−C(22) values of 1.844(6), 1.820(6), and 1.840(6) Å, respectively.

A prominent feature of the structure is that the methyl carbon atoms are out of the planes of the benzene rings, arrangement **6**, with the dihedral angles indicated in Table 7. The comparable dihedral angles from the previously reported X-ray data[26,27] for $P(4\text{-}C_6H_4OCH_3)_3$ without the flanking methyl groups are near 0°, arrangement **5** (see Table 7). This planar arrangement has also been established by X-ray methods for $H_3Ge(4\text{-}C_6H_4OCH_3)$[6] as well as the 4-positioned methoxy groups and $P(2,4,6\text{-}C_6H_2(OCH_3)_3)_3$.[28] Further, an optical spectroscopic $S_1 \leftarrow S_0$ fluorescence excitation study,[9] TOFMS studies,[7] and a CIS/6-31G* ab initio calculation[9] all clearly indicate that in the gas phase there is essentially one conformer for anisole with the heavy atoms in the plane of the benzene ring. The C−O−C bond angles, summarized in Table 6, are also indicative of the differences between the methoxy groups in **4c** and the phosphines cited for comparison because in the former and latter these angles average 113° and 118°, respectively. In addition the ring-carbon-to-oxygen distances for **4c** also appear to be slightly longer, with an average of 1.397 Å, than the comparable distances in $P(4\text{-}C_6H_4OCH_3)_3$, which average 1.367 Å. Longer ring-carbon-to-oxygen bonds are expected[11] for the observed orientations of the methoxy groups, and this too is consistent with the conclusion that the degree of conjugation between the aromatic rings and the methoxy groups in **4** is less than observed in the phosphines chosen for comparison. Finally, as shown in Figure 1, the methoxy groups are folded toward the ring faces, which are oriented toward the phosphorus lone pairs. These orientations result in P(1)−C(11), P(1)−C(21), and P(1)−C(31) distances of 6.66, 6.75, and 6.69 Å, respectively.

Comparisons of the structural features of **4c** to closely related phosphines are necessarily limited because, as noted in the Introduction, we were able to locate only one report[5] of an X-ray structure of a phosphine with multiple meta-positioned substituents, $P(3\text{-}C_6H_4CH_3)_3$. However, the C−P−C angles obtained for **4c**, 103.81 (28)°, 102.02 (27)°, and 101.75 (28)°, are similar to the average values of 102.2°, 101.2°, and 101.7° reported for PPh_3,[27,29,30] $P(4\text{-}C_6H_4OCH_3)_3$,[26,27] and $P(3\text{-}C_6H_4\text{-}CH_3)_3$,[5] respectively. As a result, these data suggest that meta-positioned methyl groups in **4c** have not increased these angles as observed for $P(2,4,6\text{-}C_6H_2(OCH_3)_3)_3$[28] and $P(2,6\text{-}C_6H_3(CH_3)_2)_3$,[31] which average 105.2° and 109.5°, respectively. To further describe **4c**, the rotation of the phenyl rings from vertical positions have been measured using an approach similar to that previously described.[32] Specifically, the torsion angles from the centroid of the three ipso carbons through the phosphorus atom back to the ipso and ortho carbons have been measured for **4c**, $P(3\text{-}C_6H_4CH_3)_3$, and three structure determinations of PPh_3. With this approach, larger torsion angles correspond to greater phenyl ring rotation around the P−C bonds. The average values of 141°, 136°, and 144° for **4c**, $P(3\text{-}C_6H_4CH_3)_3$, and PPh_3, respectively, also suggest that the meta-positioned methyl groups do not have a significant impact on the structure of **4c**, except for their effects on the positions of the methoxy methyl groups.

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Supporting Information Available: Full crystallographic data, bond lengths, and bond angles for **4c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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