Syntheses and Characterization of New Tertiary Phosphane Ligands Prepared from *p*-Anisyl- and *p*-Thioanisyldichlorophosphanes

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The syntheses and spectroscopic parameters of the new tertiary phosphane ligands (p-MeOC$_6$H$_4$)(o-MeOC$_6$H$_4$)$_2$P (**1**), (p-MeOC$_6$H$_4$)(o-MeSC$_6$H$_4$)$_2$P (**2**), (p-MeSC$_6$H$_4$)(o-MeSC$_6$H$_4$)$_2$P (**3**), (p-MeSC$_6$H$_4$)(o-MeOC$_6$H$_4$)$_2$P (**4**), (p-MeOC$_6$H$_4$)(o-NC$_5$H$_4$)$_2$P (**5**), and (p-MeSC$_6$H$_4$)(o-NC$_5$H$_4$)$_2$P (**6**) are reported. Single-crystal X-ray structures of all the compounds (**1–6**) have been determined. The dependence of the ^{31}P-NMR chemical shifts on the substituent groups of the phosphanes is discussed.

Introduction

Aromatic tertiary phosphanes, such as triphenylphosphane, are important ligands that find widespread use in homogeneous organometallic catalysts. They stabilize the low oxidation states of the metal centers and can be used to modify both the electronic and steric properties of the catalysts. The incorporation of substituents at the *ortho*-, *meta*-, or *para*-positions of the aromatic rings offers a means of tailoring the properties of the ligands. Such substituents affect both the metal−phosphorus bond lengths and the associated angles.[1]

Ways of quantifying the electronic and steric properties of phosphanes have been extensively studied since 1970. Tolman's electronic and steric parameters (ν and θ, respectively) have formed the basis for these studies over the last 30 years.[1,2,3] The improvements in NMR techniques and molecular modelling have introduced new possibilities for delineating the properties of phosphanes.[4,5,6,7]

In the present study, we have prepared and characterized a series of new ligands derived from *p*-anisyl- and *p*-thioanisyldichlorophosphanes. The ligands have been designed with a view to modifying triphenylphosphane by introducing heteroatoms at various positions on the phenyl rings. This should allow different coordination modes in metal complexes. The electronic and steric properties of these ligands, assessed on the basis of their experimental ^{31}P-NMR shifts and crystal structures, are discussed.

Results and Discussion

Syntheses

The new mixed *ortho*/*para*-substituted tertiary phosphane ligands were prepared from *para*-substituted aryldichlorophosphanes. Friedel−Crafts reaction of phosphorus trichloride with anisole or thioanisole in the presence of aluminium chloride as catalyst furnished the desired aryldichlorophosphanes.[8] These were then allowed to react with *ortho*-substituted organolithium compounds, which were obtained by halogen−metal interchange reactions.[9] Organolithium compounds bearing anisyl-, thioanisyl-, and pyridyl groups were employed in order to modify the functionality of the new ligands. These groups induce both steric and electronic changes in the phosphane ligands. The ligands thus obtained, bearing *o*-anisyl and *o*-thioanisyl substituent groups, are potentially tridentate. However, experimental findings indicate that the *o*-thioanisyl ligands behave as bidentate ligands in metal complexes,[10] while the *o*-anisyl ligands behave mainly as monodentate ligands.[11][12] The *o*-pyridyl ligands are also potentially tridentate, but in fact form either monodentate complexes or behave as bridging ligands so as to form bimetallic coordination compounds.[13][14] The introduction of pyridyl groups can also have a modifying effect on the solubilities of phosphanes and their complexes.[15]

^{31}P-NMR Spectra

The behaviour of phosphanes as ligands is dependent on the electron-donating and -accepting properties of the phosphorus atom. The catalytic properties of phosphanes are, for example, regulated by the basicities of these ligands. ^{31}P-NMR spectrometry is an important tool for obtaining information concerning the chemical nature of the phosphorus atom. The ^{31}P-NMR chemical shifts have been shown to be dependent on the R groups of a phosphane PR$_3$.[16][17] Indeed, the chemical shifts of tertiary phosphane ligands can be estimated empirically (Equation 1):[16]

$$\delta = -62 + \sum_{n=1}^{3} \sigma_n^P$$

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Here, σ^P values are increments that are characteristic for each substituent group. The reference value corresponds to PMe_3 ($\delta = -62$ vs. 85% H_3PO_4).

The increments (σ^P) for the various substituent groups incorporated in the new tertiary phosphane ligands reported herein can be calculated from the published ^{31}P-NMR chemical shifts (Table 1). In these ligands, all three substituent groups are similar. On using the aforementioned increments to calculate theoretical ^{31}P-NMR chemical shifts for the six new ligands prepared in this work, a relatively good agreement with the experimental values is observed (Table 2). This indicates that with information on the substituent increments at hand, the electronic properties of the phosphane can be predicted with reasonable accuracy. This helps in the targeted modification of the phosphanes towards known applications.

Table 1. Increments of substituted phenyl groups

Ligand	Empirical shift [ppm]	σ^P increment [ppm]
(o-$MeSC_6H_4)_3P$	−30.2[18]	10.60
(p-$MeSC_6H_4)_3P$	−8.3[19]	17.90
(o-$MeOC_6H_4)_3P$	−37.1[18], −38.5[19]	8.30, 7.83
(p-$MeOC_6H_4)_3P$	−10.2[19], −9.60[20]	17.27, 17.47
(o-$NC_5H_4)_3P$	−1.3[21]	20.23

Table 2. Comparison of empirical and theoretical ^{31}P-NMR shifts of the new ligands

Ligand	Empirical shift [ppm]	Theoretical shift [ppm]
1	−27.7	−28.13
2	−23.1	−23.53
3	−21.1	−22.90
4	−25.9	−27.50
5	−2.3	−4.27
6	−1.6	−3.64

Tolman[2] has estimated the electron-donating properties of tertiary phosphanes by measuring the IR frequencies of the carbonyl groups in $Ni(CO)_3(PR_3)$. The frequencies obtained with various ligands were compared to that with tri-*tert*-butylphosphane, which proved to be the most basic ligand in the series. Based on the experimental results, Tolman calculated the substituent contributions (χ_i) of various attached groups. The relationship can be expressed empirically by Equation 2:

$$\nu(CO) = 2056.1 + \sum_{i=1}^{3} \chi_i cm^{-1}$$

Here, the frequency 2056.1 cm^{-1} is that seen with tri-*tert*-butylphosphane attached to Ni. The larger the χ_i value, the less basic the ligand.

Tolman and Allman recognized that there is no general correlation between basicity and ^{31}P-NMR chemical shifts of phosphane ligands.[3][22] However, the basicities of the corresponding phosphane oxides have been shown to be directly related to the ^{31}P-NMR chemical shifts.[23] Phosphane oxides were chosen to minimize the effect of the lone pair on phosphorus on the chemical shift, which allows the electronic effects to dominate. However, it seems that within certain chemically related groups of phosphanes, a relationship between ^{31}P-NMR shifts and basicity can be found. For example, the values for trialkylphosphanes correlate quite well: P(tBu)$_3$: ν(CO) = 2056.1 cm^{-1} vs. $\delta = 63$; P(iPr)$_3$: ν(CO) = 2059.2 cm^{-1} vs. $\delta = 19.4$; PEt_3: ν(CO) = 2061.7 cm^{-1} vs. $\delta = -20.0$; PMe_3: ν(CO) = 2064.1 cm^{-1} vs. $\delta = -62$.[2][3]

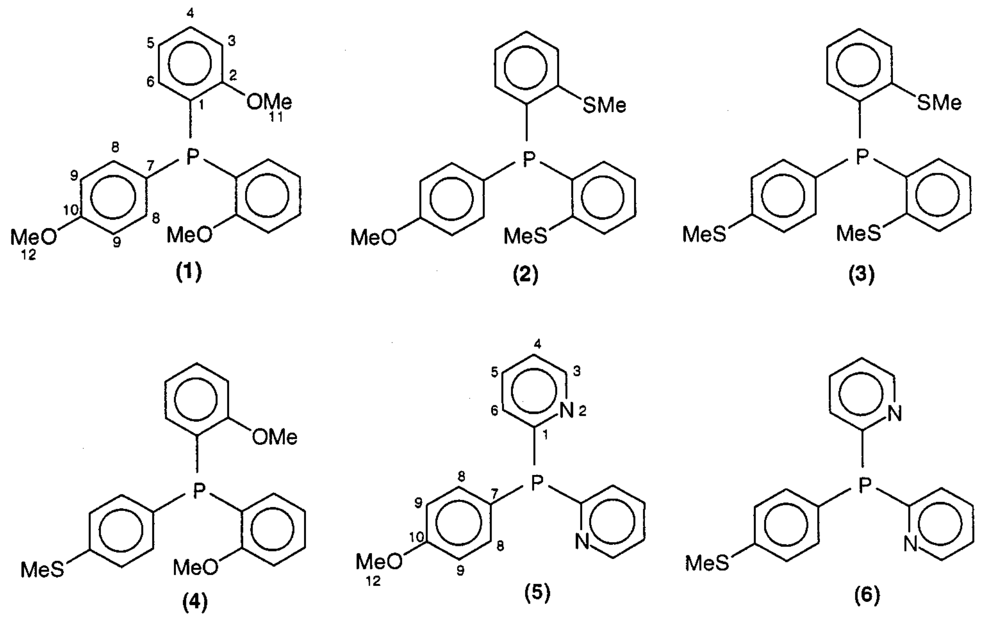
A similar kind of correlation, although of opposite direction, can be noted in the series of anisyl-substituted phosphane ligands. ν(CO) values of these ligands can be calculated by using the substituent contributions of o-C_6H_4-OCH_3 (0.9 cm^{-1}) and p-$C_6H_4OCH_3$ (3.4 cm^{-1}) reported by Tolman.[2] When the experimental ^{31}P-NMR shifts are compared with these calculated ν(CO) values, a reasonably good agreement is seen: (o-$MeOC_6H_4)_3P$: ν(CO) = 2058.8 cm^{-1} vs. $\delta = -37.1$; (p-$MeOC_6H_4$)(o-$MeOC_6H_4)_2P$: ν(CO) = 2061.3 cm^{-1} vs. $\delta = -27.7$; (p-$MeOC_6H_4)_3P$: ν(CO) = 2066.3 cm^{-1} vs. $\delta = -10.2$.

The fairly good correlation of ν(CO) values and ^{31}P-NMR shifts in these examples suggests that ^{31}P-NMR chemical shifts give adequately reliable information concerning the basicities of closely related phosphane ligands. Therefore, the basicity order of the new ligands should be **6** > **5** > **3** > **2** > **4** > **1**. This order is also supported by the observation that electron-donating substituents increase while electron-withdrawing substituents decrease the basic strengths of the ligands.[2][24]

Molecular Structures

The X-ray crystal structures of all six ligands are essentially very similar. There are no significant differences in bond lengths or bond angles between the ligands. For example, the C−P bond lengths all fall within a range of just 0.025 Å. Similarly, the variations in the C_{arom}−O, C_{methyl}−O, C_{arom}−S, and C_{methyl}−S bond lengths are relatively small: 0.017, 0.021, 0.023, and 0.055 Å, respectively. Furthermore, the relative orientation of the MeO or MeS groups does not seem to have a systematic effect on the bond lengths. The small geometrical variations suggest that the structural impact of the *ortho* or *para* groups or the pyridyl ring on the overall form of the ligands is only minor. The X-ray crystal structures of the ligands **2** and **6** are presented in Figures 1 and 2.

The steric effects of phosphanes as ligands are often expressed in terms of the Tolman cone angles θ.[1][3] These are estimated by assuming an average M−P bond length of 2.28 Å. Substituent groups in the *para* positions of the aryl rings do not significantly influence the steric properties of the ligands. This is illustrated by the similar cone angles found for PPh_3 and (pTol)$_3$P, both $\theta = 145°$.[1] Of the ligands prepared in this work, (p-$MeOC_6H_4$)(o-$NC_5H_4)_2P$ (**5**) and (p-$MeSC_6H_4$)(o-$NC_5H_4)_2P$ (**6**) should therefore resemble PPh_3 from a steric point of view. The four other ligands (p-$MeOC_6H_4$)(o-$MeOC_6H_4)_2P$ (**1**), (p-$MeOC_6H_4$)(o-



Scheme 1. Schematic structures of the reported ligands; numbering corresponds to the NMR data

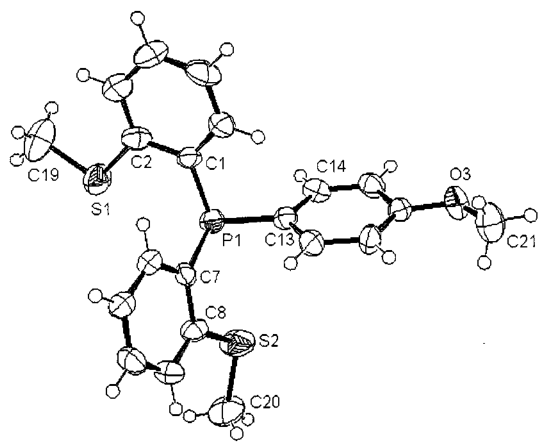


Figure 1. X-ray crystal structure of (p-$MeOC_6H_4$)(o-$MeSC_6H_4$)$_2$P (**2**)

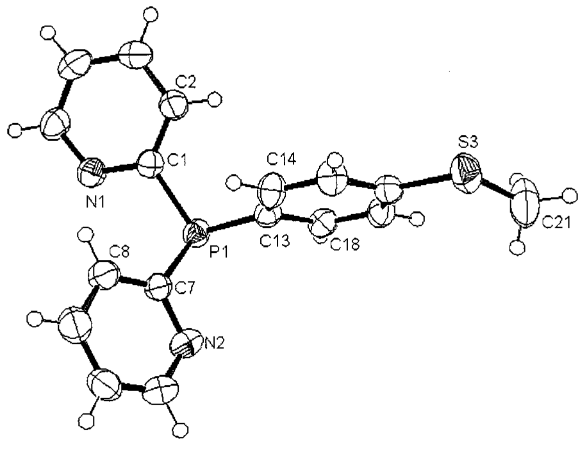


Figure 2. X-ray crystal structure of (p-$MeSC_6H_4$)(o-NC_5H_4)$_2$P (**6**)

$MeSC_6H_4$)$_2$P (**2**), (p-$MeSC_6H_4$)(o-$MeSC_6H_4$)$_2$P (**3**), and (p-$MeSC_6H_4$)(o-$MeOC_6H_4$)$_2$P (**4**) should be sterically analogous to (o-$MeOC_6H_4$)$_2$PPh and (o-$MeSC_6H_4$)$_2$PPh ligands. The steric requirements of these ligands are affected by the conformations of the o-anisyl and o-thioanisyl groups, and therefore the cone angles may not have strictly defined values. The cone angles of these ligands have not been determined

Experimental Section

The ligands were characterized mainly on the basis of ^1H-, ^{13}C-, and ^{31}P-NMR data. NMR spectra were recorded on Bruker AM200 and Bruker DPX400 spectrometers. ^1H- and ^{13}C-NMR spectra were referenced to TMS; ^{31}P-NMR spectra to 85% H_3PO_4. − Elemental analyses were carried out on a Perkin−Elmer 2400 Series II CHNS/O analyzer. − Exact mass peaks were measured on a Kratos MS-80 spectrometer. − X-ray crystal structures were determined with either an Enraf−Nonius Kappa-CCD or a Nicolet R3m diffractometer. − Commercial reagents were used without further purification. Diethyl ether was distilled from sodium/benzophenone ketyl under nitrogen prior to use. Standard Schlenk techniques were used for the syntheses.

Starting Materials: p-Anisyldichlorophosphane and p-thioanisyldichlorophosphane were prepared according to a published procedure for p-anisyldichlorophosphane.[25][26] The reaction time for the preparation of p-thioanisyldichlorophosphane was extended to 90 h. p-Anisyldichlorophosphane was collected at 98−100°C/0.3 Torr; p-thioanisyldichlorophosphane at 125−126°C/0.15 Torr.

(p-Methoxyphenyl)bis(o-methoxyphenyl)phosphane (1): o-Bromoanisole (1.0 g, 0.7 mL, 5.4 mmol) was lithiated with n-butyllithium (nBuLi) (2.2 mL, 2.5 M in hexane, 5.4 mmol) in sodium-dried diethyl ether (Et_2O) (20 mL) at 0°C. The mixture was stirred for 1 h at 0°C, and then a solution of p-anisyldichlorophosphane (0.6 g, 2.7 mmol) in Et_2O (15 mL) was added. The resulting mixture was stirred for a further 1 h at 0°C and the precipitate formed was filtered off and dried in vacuo. The product (0.5 g, 1.5 mmol, 55.1%) was recrystallized from ethanol. Single crystals suitable for X-ray crystallographic analysis were obtained by slow evaporation of the solvents from a dichloromethane/hexane solution at −20°C. M.p. 146−149°C. − $C_{21}H_{21}O_3P$: calcd. C 71.6, H 6.0; found C 71.7, H 6.0. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.7 (s, 6 H, H^{11}), 3.8 (s, 3 H, H^{12}), 6.7 (dd, $^{3}J_{H-H}$ = 6.0 Hz, $^{3}J_{H-P}$ = 2.2 Hz, 2 H, H^{6}), 6.8 (m, 6 H, H^{3}, H^{5}, and H^{9}), 7.2 (t, $^{3}J_{H-H}$ = 7.6 Hz, 2 H, H^{8}), 7.3 (t, $^{3}J_{H-H}$ 7.7 Hz, 2 H, H^{4}). − $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ = 55.1 (s, 1 C, C^{12}), 55.6 (s, 2 C, C^{11}), 110.1 (s, 2 C, C^{3}), 113.9 (d, $^{2}J_{C-P}$ = 7.9 Hz, 2 C, C^{8}), 120.8 (s, 2 C, C^{5}), 125.7 (d, $^{1}J_{C-P}$ = 12.3 Hz, 2 C, C^{1}), 126.8 (d, $^{1}J_{C-P}$ = 6.9 Hz, 1 C, C^{7}), 130.0 (s, 2 C, C^{4}), 133.5 (s, 2 C, C^{6}), 135.6 (d, $^{3}J_{C-P}$ = 22.5 Hz, 2 C, C^{9}), 160.1 (s, 1 C, C^{10}), 161.2 (d, $^{2}J_{C-P}$ = 15.9 Hz, 2 C, C^{2}). − $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$): δ = −27.7 (s).

(*p*-Methoxyphenyl)bis(*o*-thiomethylphenyl)phosphane (2): *o*-Bromothioanisole (2.0 g, 1.3 mL, 9.8 mmol) was lithiated with *n*BuLi (3.9 mL, 2.5 M in hexane, 9.8 mmol) in sodium-dried diethyl ether (20 mL) at 0°C. The mixture was stirred for 2 h at 0°C, and then a solution of *p*-anisyldichlorophosphane (1.0 g, 4.9 mmol) in Et_2O (20 mL) was added. The resulting mixture was stirred for a further 2 h at 0°C and the precipitate formed was filtered off and dried in vacuo. The product (1.1 g, 2.9 mmol, 59.2%) was recrystallized from ethanol/toluene. Single crystals suitable for X-ray crystallographic analysis were obtained by slow evaporation of the solvents from a dichloromethane/hexane solution. M.p. 155−157°C. − $C_{21}H_{21}OPS_2$: calcd. C 65.6, H 5.5, S 16.7; found C 65.5, H 5.5, S 16.3. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.4 (s, 6 H, H^{11}), 3.8 (s, 3 H, H^{12}), 6.7 (dd, $^{3}J_{H-H}$ = 7.5 Hz, $^{3}J_{H-P}$ = 3.8 Hz, 2 H, H^{6}), 6.9 (d, $^{3}J_{H-H}$ = 7.7 Hz, 2 H, H^{9}), 7.1 (m, 2 H, H^{5}), 7.2 (t, $^{3}J_{H-H}$ = 7.8 Hz, 2 H, H^{8}), 7.3 (m, 4 H, H^{3} and H^{4}). − $^{13}C\{^{1}H\}$ NMR (50 MHz, $CDCl_3$): δ = 17.3 (d, $^{4}J_{C-P}$ = 8.7 Hz, 2 C, C^{11}), 55.1 (s, 1 C, C^{12}), 114.4 (d, $^{2}J_{C-P}$ = 8.7 Hz, 2 C, C^{8}), 125.3 (s, 2 C, C^{5}), 125.9 (d, $^{1}J_{C-P}$ = 7.3 Hz, 1 C, C^{7}), 126.8 (d, $^{3}J_{C-P}$ = 4.4 Hz, 2 C, C^{3}), 129.2 (s, 2 C, C^{4}), 133.1 (s, 2 C, C^{6}), 136.1 (d, $^{3}J_{C-P}$ = 23.2 Hz, 2 C, C^{9}), 136.8 (d, $^{1}J_{C-P}$ = 8.7 Hz, 2 C, C^{1}), 143.5 (d, $^{2}J_{C-P}$ = 27.6 Hz, 2 C, C^{2}), 160.5 (s, 1 C, C^{10}). − $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$): δ = −23.1 (s).

(*p*-Thiomethylphenyl)bis(*o*-thiomethylphenyl)phosphane (3): *o*-Bromothioanisole (2.0 g, 1.3 mL, 9.8 mmol) was lithiated with *n*BuLi (3.9 mL, 2.5 M in hexane, 9.8 mmol) in sodium-dried diethyl ether (30 mL) at 0°C. The mixture was stirred for 2 h at 0°C, and then a solution of *p*-thioanisyldichlorophosphane (1.1 g, 4.9 mmol) in Et_2O (20 mL) was added. The resulting mixture was stirred for a further 2 h at 0°C and the precipitate formed was filtered off and dried in vacuo. The product (0.9 g, 2.2 mmol, 45.0%) was twice recrystallized, first from ethanol/toluene and then from hexane/ethanol. Crystals were used for X-ray crystallographic analysis without further crystallization. M.p. 144°C. − $C_{21}H_{21}PS_3$: calcd. C 63.0, H 5.3, S 24.0; found C 62.9, H 5.4, S 24.0. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.4 (s, 6 H, H^{11}), 2.5 (s, 3 H, H^{12}), 6.7 (dd, $^{3}J_{H-H}$ = 7.3 Hz, 2 H, H^{6}), 7.1 (m, 2 H, H^{5}), 7.2 (m, 4 H, H^{8} and H^{9}), 7.3 (m, 4 H, H^{3} and H^{4}). − $^{13}C\{^{1}H\}$ NMR (50 MHz, $CDCl_3$): δ = 15.1 (s, 1 C, C^{12}), 17.3 (d, $^{4}J_{C-P}$ = 8.7 Hz, 2 C, C^{11}), 125.3 (s, 2 C, C^{5}), 126.1 (d, $^{2}J_{C-P}$ = 8.7 Hz, 2 C, C^{8}), 126.8 (d, $^{3}J_{C-P}$ = 4.4 Hz, 2 C, C^{3}), 129.3 (s, 2 C, C^{4}), 131.3 (d, $^{1}J_{C-P}$ = 10.2 Hz, 1 C, C^{7}), 133.3 (s, 2 C, C^{6}), 134.7 (d, $^{3}J_{C-P}$ = 20.3 Hz, 2 C, C^{9}), 136.2 (d, $^{1}J_{C-P}$ = 10.2, 2 C, C^{1}), 140.0 (s, 1 C, C^{10}), 143.7 (d, $^{2}J_{C-P}$ = 29.1 Hz, 2 C, C^{2}). − $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$): δ = −21.1 (s).

(*p*-Thiomethylphenyl)bis(*o*-methoxyphenyl)phosphane (4): *o*-Bromoanisole (1.9 g, 1.2 mL, 9.8 mmol) was lithiated with *n*BuLi (3.9 mL, 2.5 M in hexane, 9.8 mmol) in sodium-dried diethyl ether (30 mL) at 0°C. The mixture was stirred for 1 h at 0°C, and then a solution of *p*-thioanisyldichlorophosphane (1.1 g, 4.9 mmol) in Et_2O (20 mL) was added. The resulting mixture was stirred for a further 2

Table 3. Crystallographic data

Ligand	**1**	**2**	**3**	**4**	**5**	**6**
Chemical formula	$C_{21}H_{21}O_3P$	$C_{21}H_{21}OPS_2$	$C_{21}H_{21}PS_3$	$C_{21}H_{21}O_2PS$	$C_{17}H_{15}N_2OP$	$C_{17}H_{15}N_2PS$
Molecular weight [g mol^{-1}]	352.35	384.47	400.53	368.41	294.28	310.34
Crystal size [mm]	0.2 × 0.2 × 0.2	0.3 × 0.3 × 0.3	0.1 × 0.1 × 0.3	0.4 × 0.4 × 0.2	0.4 × 0.4 × 0.2	0.3 × 0.3 × 0.2
Color	Colorless	Colorless	Colorless	Colorless	Colorless	Colorless
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	*P*2$_1$/*c*	*P*2$_1$/*c*	*P*-1	*P*-1	*P*2$_1$/*n*	*P*2$_1$/*c*
Unit cell dimensions [°]						
a [nm]	7.678(2)	8.002(2)	8.083(2)	8.357(2)	8.300(2)	9.406(2)
b [nm]	30.928(6)	14.917(3)	10.110(2)	11.126(2)	10.944(2)	9.350(2)
c [nm]	7.780(2)	16.304(3)	13.454(3)	11.786(2)	16.967(3)	17.877(4)
α [°]	90	90	72.09(3)	103.57(3)	90	90
β [°]	102.45(3)	92.63(3)	74.97(3)	107.60(3)	100.84(3)	98.50(3)
γ [°]	90	90	82.52(3)	104.49(3)	90	90
Volume [nm^3]	1804.1(6)	1944.1(7)	1008.9(4)	952.5(3)	1513.7(5)	1554.9(6)
Z	4	4	2	2	4	4
Density$_{calcd.}$ [Mg m^{-3}]	1.297	1.314	1.319	1.285	1.291	1.326
Absorption coefficient μ [mm^{-1}]	0.169	0.362	0.448	0.265	0.181	0.305
F(000)	744	808	420	388	616	648
θ range [°]	2.72−24.99	2.50−25.00	3.03−25.00	2.01−28.22	3.07−26.00	2.46−26.00
h range	−8 → 9	0 → 9	−9 → 9	−11 → 11	−10 → 10	0 → 11
k range	−36 → 29	0 → 17	−12 → 12	−13 → 14	−13 → 13	0 → 11
l range	−9 → 8	−19 → 19	−15 → 15	−15 → 15	−20 → 20	−22 → 21
No. of collected reflns.	7645	3749	6761	12254	18305	3047
No. of unique reflns.	3068	3409	3488	4456	2952	3047
No. of obsd. reflns., $I > 2\sigma(I)$	2317	1404	2163	3894	2637	2705
No. of parameters	227	227	227	227	235	190
Final *R* indices $I > 2\sigma(I)$	0.0651	0.0730	0.0551	0.0523	0.0371	0.0333
w*R*2 $I > 2\sigma(I)$	0.1586	0.1076	0.1305	0.1448	0.0984	0.0821
Goodness-of-fit	1.094	1.006	1.045	1.055	1.037	1.048
T [K]	120(2)	293(2)	293(2)	293(2)	293(2)	293(2)

Table 4. Selected bond lengths [Å]

	(1)	(2)	(3)	(4)	(5)	(6)
P(1)−C(1)	1.842(4)	1.842(6)	1.843(3)	1.8332(16)	1.8395(16)	1.8373(16)
P(1)−C(7)	1.834(4)	1.833(6)	1.838(3)	1.8283(17)	1.8392(16)	1.8439(17)
P(1)−C(13)	1.836(4)	1.826(6)	1.829(4)	1.8352(17)	1.8194(16)	1.8288(16)
C(2)−S(1)		1.759(6)	1.759(4)			
C(8)−S(2)		1.768(6)	1.753(4)			
C(16)−S(3)			1.762(4)	1.7763(19)		1.7613(17)
C(16)−O(3)	1.377(5)	1.366(7)			1.360(2)	
S(1)−C(19)		1.783(6)	1.795(4)			
S(2)−C(20)		1.769(6)	1.756(5)			
S(3)−C(21)			1.740(5)	1.776(3)		1.780(2)
C(2)−O(1)	1.375(5)			1.365(2)		
C(8)−O(2)	1.369(5)			1.368(2)		
C(16)−S(3)				1.7763(19)		1.7613(17)
O(1)−C(19)	1.429(5)			1.423(2)		
O(2)−C(20)	1.435(5)			1.414(3)		
O(3)−C(21)	1.431(5)	1.426(7)			1.422(3)	
N(1)−C(1)					1.345(2)	1.351(2)
N(1)−C(5)					1.337(2)	1.333(2)
N(2)−C(7)					1.343(2)	1.347(2)
N(2)−C(11)					1.338(2)	1.341(3)

Table 5. Selected bond angles [°]

	(1)	(2)	(3)	(4)	(5)	(6)
C(1)−P(1)−C(7)	102.57(18)	101.8(3)	102.74(15)	102.04(8)	103.03(7)	102.52(7)
C(1)−P(1)−C(13)	100.94(18)	100.3(3)	100.74(15)	101.12(8)	103.02(7)	103.36(7)
C(7)−P(1)−C(13)	102.60(18)	103.4(3)	103.38(16)	103.81(8)	103.57(7)	100.63(7)
C(16)−O(3)−C(21)	116.4(3)	117.5(5)			118.98(16)	
C(16)−S(3)−C(21)			103.7(2)	103.30(12)		104.77(10)
C(2)−O(1)−C(19)	117.5(3)			118.54(17)		
C(8)−O(2)−C(20)	117.5(3)			118.51(19)		
C(2)−S(1)−C(19)		104.4(3)	103.44(19)			
C(8)−S(2)−C(20)		104.5(3)	105.6(2)			

h at 0°C and then the precipitate formed was filtered off and dried in vacuo. The product (1.1 g, 3.1 mmol, 62.0%) was recrystallized from ethanol. Single crystals suitable for X-ray crystallographic analysis were obtained by slow evaporation of the solvent from a dichloromethane solution. M.p. 151−152°C. − $C_{21}H_{21}O_2PS$: calcd. C 68.5, H 5.8, S 8.7; found C 68.0, H 5.5, S 9.1. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.5 (s, 3 H, H^{12}), 3.7 (s, 6 H, H^{11}), 6.7 (dd, $^3J_{H-H}$ = 7.3 Hz, $^3J_{H-P}$ = 1.7 Hz, 2 H, H^6), 6.8 (t, $^3J_{H-H}$ = 7.7 Hz, 2 H, H^5), 6.9 (t, $^3J_{H-H}$ = 5.1 Hz, 2 H, H^3), 7.2 (d, $^3J_{H-H}$ = 4.3 Hz, 4 H, H^8 and H^9), 7.3 (t, $^3J_{H-H}$ = 6.8 Hz, 2 H, H^4). − $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 15.2 (s, 1 C, C^{12}), 55.7 (s, 2 C, C^{11}), 110.2 (s, 2 C, C^3), 120.9 (s, 2 C, C^5), 125.1 (d, $^1J_{C-P}$ = 12.2 Hz, 2 C, C^1), 125.8 (d, $^2J_{C-P}$ = 7.0 Hz, 2 C, C^8), 130.1 (s, 2 C, C^4), 132.4 (d, $^1J_{C-P}$ = 9.7 Hz, 1 C, C^7), 133.7 (s, 2 C, C^6), 134.4 (d, $^3J_{C-P}$ = 21.6 Hz, 2 C, C^9), 139.1 (s, 1 C, C^{10}), 161.3 (d, $^2J_{C-P}$ = 15.9 Hz, 2 C, C^2). − $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = −25.9 (s).

(*p*-Methoxyphenyl)bis(*o*-pyridyl)phosphane (5): A solution of *n*BuLi (10 mL, 2.5 M in hexane, 25 mmol) in sodium-dried diethyl ether (40 mL) was cooled to −100°C by means of an ethanol/liquid nitrogen bath. A solution of *o*-bromopyridine (2.5 mL, 25 mmol) in diethyl ether (30 mL) was then rapidly added and the mixture was stirred for 1.5 h at −100°C. A solution of *p*-anisyldichlorophosphane (2.61 g, 12.5 mmol) in diethyl ether (30 mL) was then added dropwise and stirring was continued at −100°C for 1 h. After slowly warming to room temperature, the light-brown mixture was extracted with H_2SO_4 (2 N, 30 mL) and the aqueous layer was separated and made alkaline with NaOH. The crude product was extracted from the aqueous phase with diethyl ether. The solvent was evaporated from the combined extracts and the oily crude product was washed with methanol. The product (3.06 g, 10.4 mmol, 83.2%) was dried in vacuo. Single crystals were grown by vapor diffusion of hexane into a methanol/dichloromethane solution of the pyridylphosphane. M.p. 100−101°C. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.8 (s, 3 H, H^{12}), 7.0 (d, $^3J_{H-H}$ = 8.5 Hz, 2 H, H^9), 7.3 (m, 4 H, H^6 and H^8), 7.5 (t, $^3J_{H-H}$ = 7.3 Hz, 2 H, H^4), 7.7 (t, $^3J_{H-H}$ = 7.7 Hz, $^4J_{H-P}$ = 1.7 Hz, 2 H, H^5), 8.6 (m, 2 H, H^3). − $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ = 55.5 (s, 1 C, C^{12}), 115.2 (d, $^2J_{C-P}$ = 8.7 Hz, 2 C, C^8), 123.1 (s, 2 C, C^4), 127.0 (d, $^1J_{C-P}$ = 7.3 Hz, 1 C, C^7), 128.7 (d, $^2J_{C-P}$ = 18.9 Hz, 2 C, C^6), 136.4 (d, $^3J_{C-P}$ = 2.9 Hz, 2 C, C^5), 137.7 (d, $^3J_{C-P}$ = 23.2 Hz, 2 C, C^9), 150.8 (d, $^3J_{C-P}$ = 11.6 Hz, 2 C, C^3), 162.0 (s, 1 C, C^{10}), 164.8 (d, $^1J_{C-P}$ = 4.4 Hz, 2 C, C^1). − $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = −2.3 (s). − MS: Exact mass: 294.0886.

(*p*-Thiomethoxyphenyl)bis(*o*-pyridyl)phosphane (6): A solution of *n*BuLi (4 mL, 2.5 M in hexane, 10 mmol) in sodium-dried diethyl ether (20 mL) was cooled to −100°C by means of an ethanol/liquid nitrogen bath. A solution of *o*-bromopyridine (1.0 mL, 10 mmol) in diethyl ether (20 mL) was then rapidly added and the mixture was stirred for 75 min at −100°C. A solution of *p*-thioanisyldichlorophosphane (1.13 g, 5 mmol) in diethyl ether (20 mL) was then added dropwise and stirring was continued at −100°C for 1 h. After slowly warming to room temperature, the light-yellow mixture was extracted with H_2SO_4 (2 N, 30 mL) and the aqueous layer was separated and made alkaline with NaOH. The white solid product was obtained by extraction of the aqueous phase with diethyl ether. The product (0.60 g, 1.93 mmol, 38.7%) was dried in vacuo. Single crystals were grown by vapor diffusion of hexane into a methanol/dichloromethane solution of the pyridylphosphane. M.p. 122−123°C. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.5 (s, 3 H, H^{12}), 7.2 (m, 6 H, H^6, H^8, and H^9), 7.4 (t, $^3J_{H-H}$ = 7.7 Hz, 2 H, H^4), 7.6 (t, $^3J_{H-H}$ = 7.7 Hz, $^4J_{H-P}$ = 1.9 Hz, 2 H, H^5), 8.7 (d, $^3J_{H-H}$ = 4.7 Hz, 2 H, H^3). − ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$): δ = 14.8 (s, 1 C, C^{12}), 123.3 (s, 2 C, C^4), 126.5 (d, $^2J_{C-P}$ = 8.7 Hz, 2 C, C^8), 128.9 (d, $^2J_{C-P}$ = 20.3 Hz, 2 C, C^6), 132.3 (d, $^1J_{C-P}$ = 10.2 Hz, 1 C, C^7), 136.2 (s, 2 C, C^5), 136.6 (d, $^3J_{C-P}$ = 2.9 Hz, 2 C, C^9), 142.0 (s, 1 C, C^{10}), 150.9 (d, $^3J_{C-P}$ = 11.6 Hz, 2 C, C^3), 164.1 (d, $^1J_{C-P}$ = 4.4 Hz, 2 C, C^1). − ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = −1.6 (s). − MS: Exact mass: 310.0727.

X-ray Crystallography: X-ray diffraction data were collected with an Enraf−Nonius Kappa-CCD (compounds **1** and **3−6**) or a Nicolet R3m (compound **2**) diffractometer using Mo-K_α radiation (λ = 0.71073 Å). For **2**, cell parameters were obtained from 25 automatically centered reflections. Data collection (ω scan mode), data reduction, and cell refinement were carried out with the P3/P4 diffractometer program V4.27.[27] For the other compounds, the data were collected using ϕ or combined $\phi-\omega$ scans with the Collect[28] data collection program. Denzo and Scalepack[29] programs were used for cell refinements and data reduction. All structures were solved by direct methods using either SHELXS-97[30] or SIR-97[31] programs with the WinGX[32] graphical user interface, or by using the SHELXTL v5.1[33] program package. Structure refinements were carried out with SHELXL-97.[34] All non-hydrogen atoms were refined anisotropically. For compounds **1−5**, the hydrogens were constrained to ride on their parent atom [U_{iso} = 1.2(C_{eq}) for aromatic hydrogens and U_{iso} = 1.5(C_{eq}) for methyl H atoms]. For compound **6**, all hydrogens were located from the difference Fourier map and refined isotropically with constant U_{iso} = 0.05 for aromatic hydrogens and U_{iso} = 0.08 for methyl hydrogens. Crystallographic data are summarized in Table 3 and selected bond lengths and angles are given in Tables 4 and 5.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-114003 to CCDC-114008. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) +44 (0)1223/ 336033; E-mail: deposit@ccdc.cam.ac.uk].

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