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2-Thioanisyldichlorophosphine, new starting material for the preparation of multidentate phosphine ligands: syntheses and characterization of derivatives of 2-anisyl- and 2-thioanisyldichlorophosphines

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Abstract

A new aryldichlorophosphine, 2-thioanisyldichlorophosphine, and its anisyl analogue, 2-anisyldichlorophosphine, were prepared by using an organozinc halide reagent of 2-thioanisole or 2-anisole with ethereal solution of PCl_3 in refluxing conditions. From these aryldichlorophosphines, eight new multidentate phosphine ligands containing 2-thioanisyl, 4-thioanisyl, 2-anisyl, 1-naphthyl and 9-anthracenyl groups were synthesized and characterized. Characterization was based mainly on NMR spectroscopy and X-ray crystallography. The crystal structures of six ligands are reported. The electronic effects on basicity of ligands are discussed. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Dichlorophosphines; Phosphine ligands; ^{31}P-NMR spectroscopy; Basicity

1. Introduction

Phosphine ligands are commonly used in modifying activities and selectivities of homogeneous metal catalysts. In the preparation of phosphines, aryl- and alkylchlorophosphines are important intermediates [1]. The number of commercially available arylchlorophosphines is, however, limited, suggesting that the preparation is not always straightforward.

A century ago Michaelis prepared 4-anisyldichlorophosphine by aluminum trichloride-catalyzed Friedel–Crafts reaction [2]. Modifications of this original method have been commonly used in the preparation of aryldichlorophosphines since then [3–8]. The original method typically leads to a mixture of *ortho* and *para* isomers of substituted aromatic chlorophosphines, the *para* isomer being the main product. Deactivating, *meta*-directing groups prevent the substitution [7].

Several other methods have also been used in the preparation of dichlorophosphines. Large excess of PCl_3 [9], chlorobis(diethylamino)phosphine as an intermediate [10] and Grignard reagent combined with $ZnCl_2$ [11] are examples of these methods. These methods, however, failed in the synthesis of 2-thioanisyldichlorophosphine, and we had to search for new synthetic routes.

In this work we describe an improved route [11] for the preparation of *ortho*-substituted aryldichlorophosphines. The preparation and characterization of the title compound, 2-thioanisyldichlorophosphine (**1**), is reported. Also the corresponding 2-anisyldichlorophosphine (**2**) is prepared using the same method. Additionally, eight new phosphines (**3**–**10**) are synthesized from 2-anisyl- and 2-thioanisyldichlorophosphines.

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2. Experimental

$ZnCl_2$ (Aldrich) was dried in vacuum and diethyl ether (Lab Scan) was distilled from sodium–benzophenone ketyl under nitrogen before use. 2-Bromothioanisole (Aldrich), 4-bromothioanisole (Aldrich), 2-bromoanisole (Aldrich), 9-bromoanthracene (Aldrich), *n*-butyllithium (Aldrich), 1-bromonaph-thalene (Merck) and trichlorophosphine (Merck) were obtained from the indicated suppliers and used without further purifi-

Table 1
Crystallographic data

Ligand	3	4	5	7	8	9
Chemical formula	$C_{35}H_{25}PS$	$C_{27.5}H_{22}PSCl$ [a]	$C_{21}H_{21}PS_3$	$C_{35}H_{25}OP$	$C_{27}H_{21}OP$	$C_{21}H_{21}OPS_2$
Temperature (K)	120	120	293	120	120	120
Molecular weight (g mol^{-1})	508.58	450.93	400.53	492.52	392.41	384.47
Crystal size (mm)	0.3×0.3×0.3	0.2×0.2×0.4	0.2×0.3×0.3	0.2×0.3×0.4	0.2×0.3×0.3	0.3×0.4×0.4
Color	Orange	Colorless	Colorless	Orange–yellow	Colorless	Colorless
Crystal system	Triclinic	Trigonal	Triclinic	Triclinic	Orthorhombic	Monoclinic
Space group	$P\bar{1}$	$R\bar{3}$	$P\bar{1}$	$P\bar{1}$	$P2_12_12_1$	$P2_1/c$
Unit cell dimensions						
a (Å)	9.893(2)	37.209(5)	9.3640(10)	11.179(2)	7.8912(16)	18.038(4)
b (Å)	11.233(2)		11.141(2)	11.603(2)	15.170(3)	9.6995(19)
c (Å)	11.578(2)	9.0416(18)	11.8180(10)	11.708(2)	16.910(3)	23.160(5)
α (°)	95.94(3)		112.942(10)	119.30(3)		
β (°)	98.73(3)		103.038(11)	109.26(3)		105.65(3)
γ (°)	100.41(3)		105.715(12)	91.09(3)		
V (nm^3)	1239.5(4)	10841(3)	1013.8(2)	1219.8(4)	2024.2(7)	3902.0(13)
Z	2	18	2	2	4	8
$D_{calc.}$ (Mg m^{-3})	1.363	1.243	1.312	1.341	1.288	1.309
Absorption coefficient μ (mm^{-1})	0.219	0.324	0.446	0.141	0.151	0.361
$F(000)$	532	4230	420	516	824	1616
θ range (°)	3.82–27.49	3.79–25.00	2.02–24.99	2.06–26.00	2.91–24.98	1.89–26.37
h range	−12→12	−44→44	−1→11	−13→13	−8→8	−20→20
k range	−12→12	−44→44	−13→13	−13→13	−18→17	−12→12
l range	−15→15	−10→10	−14→13	−14→14	−20→19	−28→28
No. of collected reflections	10338	23624	4267	8239	3402	14256
No. of unique reflections	5220	4229	3554	4268	3402	7492
No. of observed reflections [$I>2\sigma(I)$]	4102	3492	2824	3515	3109	6411
No. of parameters	336	290	290	435	264	577
Final R indices [$I>2\sigma(I)$]	0.0379	0.0609	0.0342	0.0387	0.0336	0.0345
wR_2 [$I>2\sigma(I)$]	0.0937	0.1601	0.0890	0.0922	0.0737	0.0924
Goodness-of-fit	1.015	1.114	1.029	1.026	1.050	1.044

[a] $(oSP(naf)_2)\cdot^{1/2}(CH_2Cl_2)$.

Table 2
Selected bond lengths (Å)

Ligand	3	4	5	7	8	9
P1–C1	1.8432(19)	1.832(3)	1.847(2)	1.8516(19)	1.832(2)	1.8312(18)
P1–C7	1.8434(18)	1.829(3)	1.835(2)	1.8559(19)	1.840(2)	1.8349(18)
P1–C13	1.8543(18)	1.833(3)	1.832(2)	1.851(2)	1.8349(19)	1.8384(18)
S1–C2	1.7688(19)	1.765(4)	1.772(2)			
S1–C4						1.7640(18)
S1–C19	1.8022(19)	1.794(5)	1.786(3)			1.791(2)
S2–C10			1.766(2)			1.7644(18)
S2–C20			1.784(3)			1.795(2)
S3–C16			1.763(2)			
S3–C21			1.770(5)			
O1–C2				1.370(2)	1.377(2)	
O1–C19				1.431(2)	1.432(3)	
O3–C14						1.376(2)
O3–C21						1.431(2)

Table 3
Selected bond angles (°)

Ligand	3	4	5	7	8	9
C1–P1–C7	104.71(8)	103.28(15)	100.06(9)	104.62(8)	103.14(9)	99.94(8)
C1–P1–C13	102.38(8)	100.44(14)	100.89(9)	98.92(8)	104.13(9)	101.81(8)
C7–P1–C13	114.30(8)	104.70(15)	104.21(9)	110.83(8)	100.55(9)	101.42(8)
C2–S1–C19	102.91(9)	102.7(2)	104.01(5)			
C4–S1–C19						103.65(9)
C10–S2–C20			103.37(13)			102.78(10)
C16–S3–C21			104.53(16)			
C2–O1–C19				118.37(16)	117.60(17)	
C14–O3–C21						117.33(15)

cation. Standard Schlenk techniques were applied in synthesis. Characterization of the compounds was based mainly on ^{1}H-, ^{13}C- and ^{31}P-NMR spectroscopy. NMR spectra were recorded on a Bruker AM200 and Bruker DPX400 spectrometers. ^{1}H and ^{13}C spectra were referenced to TMS, and ^{31}P spectra to 85% H_3PO_4. X-ray diffraction data were collected with a Nonius KappaCCD or with a Nonius Mach3 diffractometer using Mo–K_α radiation.

2.1. Syntheses and characterization of starting materials

2.1.1. 2-Thioanisyldichlorophosphine (**1**)

2-Bromothioanisole (3.0 ml, 5 g, 25 mmol) was lithiated in diethyl ether (40 ml) at 0°C with *n*-butyl lithium (10 ml, 2.5 M in hexane, 25 mmol). The reaction mixture was stirred for 2 h at 0°C, after which an ethereal solution (40 ml) of $ZnCl_2$ (3.3 g, 25 mmol) was added. Stirring was continued for 2 h at room temperature (r.t.) to ensure the formation of organozinc halide reagent, which was then added to a solution of PCl_3 (6.6 ml, 75 mmol) in diethyl ether (30 ml) at 0°C. The reaction mixture was then refluxed for 40 h, cooled to r.t. and the solvent was distilled at the normal pressure. The crude product was distilled under reduced pressure. The product (1.5 g, 6.6 mmol, 26.3%) was obtained as a colorless liquid. b.p. 100–104°C/0.1 torr. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.5 (s, H_7, 3H), 7.4–7.6 (m, H_4–H_6, 3H), 8.1 (d, $^{3}J_{H-H}$ 8.0 Hz, H_3, 1H). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$) δ 20.5 (d, $^{4}J_{C-P}$ 4.1 Hz, C_7, 1C), 128.4 (s, C_5, 1C), 130.4 (d, $^{3}J_{C-P}$ 3.9 Hz, C_3, 1C), 132.5 (s, C_4, 1C), 132.9 (s, C_6, 1C), 140.6 (d, $^{1}J_{C-P}$ 38.2 Hz, C_1, 1C), 142.1 (d, $^{2}J_{C-P}$ 52.6 Hz, C_2, 1C). ^{31}P{^{1}H}-NMR (162 MHz, $CDCl_3$) δ 150.5 (s). Anal. Calc. for $C_7H_7Cl_2PS$: C, 37.4; H, 3.1; S, 14.2. Found: C, 38.0; H, 3.5; S, 14.8%.

2.1.2. 2-Anisyldichlorophosphine (**2**)

2-Anisyldichlorophosphine was prepared using the method described above. The mixture was refluxed for 20 h. 2-Anisyldichlorophosphine (**2**) (3.9 g, 18.7 mmol, 37.4%) was obtained as a colorless liquid. b.p. 86–89°C/0.1 torr. ^{1}H-NMR (200 MHz, $CDCl_3$) δ 3.9 (s, H_7, 3H), 6.9 (dd, $^{3}J_{H-H}$ 8.1 Hz, $^{4}J_{H-P}$ 6.0 Hz, H_3, 1H), 7.1 (t, $^{3}J_{H-H}$ 7.7 Hz, H_5, 1H), 7.5 (t, $^{3}J_{H-H}$ 7.7 Hz, H_4, 1H), 7.9 (dd, $^{3}J_{H-H}$ 7.7 Hz, $^{4}J_{H-P}$ 3.4 Hz, H_6, 1H). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$) δ 56.1 (s, C_7, 1C), 111.0 (s, C_3, 1C), 121.7 (s, C_5, 1C), 127.4 (d, $^{1}J_{C-P}$ 59.9 Hz, C_1, 1C), 130.8 (s, C_6, 1C), 134.2 (s, C_4, 1C), 160.7

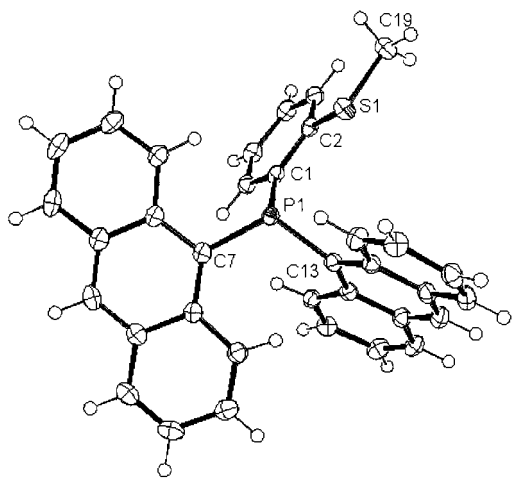


Fig. 1. Crystal structure of (2-thiomethylphenyl)bis(9-anthracenyl)-phosphine.

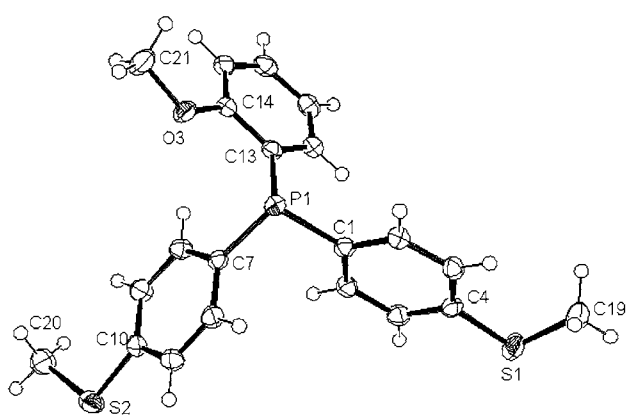
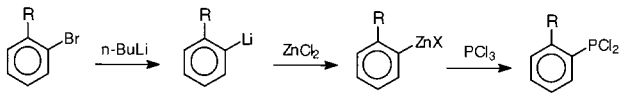
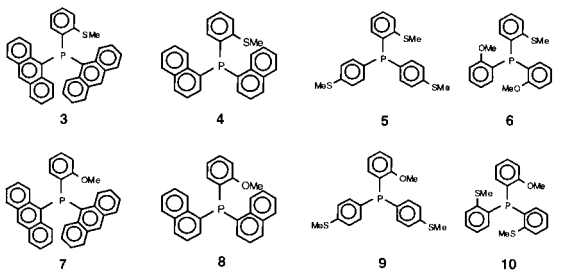


Fig. 2. Crystal structure of (2-methoxyphenyl)bis(4-thiomethylphenyl)phosphine.



1 R = -SMe
2 R = -OMe

Scheme 1. Synthetic route for the preparation of 2-thioanisyl- and 2-anisyldichlorophosphine.



Scheme 2. Structures of the ligands prepared in this work.

Table 4
^{31}P-NMR chemical shifts of the PR_3-type phosphines and the corresponding calculated increment values of the substituent groups

Ligand	^{31}P chemical shift (δ, ppm)	σ^P increment (δ, ppm)
$(o\text{-MeSC}_6H_4)_3P$	−30.2 [32]	10.60
$(p\text{-MeSC}_6H_4)_3P$	−8.3 [33]	17.90
$(o\text{-MeOC}_6H_4)_3P$	−37.1 [32]	8.30
$P(naf)_3$	−32.6 [34]	9.80
$P(antr)_3$	−44.0 [9]	6.00

Table 5
Comparison of measured and calculated ^{31}P-NMR shifts of prepared ligands

Ligand	Measured shift (δ, ppm)	Calculated shift (δ, ppm)
3 ($SPanthr_2$)	−38.4	−39.40
4 ($SPnaf_2$)	−29.7	−31.80
5 (oSpSSP)	−13.9	−15.60
6 (oSoOOP)	−34.1	−34.80
7 ($OPanthr_2$)	−40.4	−41.70
8 ($OPnaf_2$)	−31.9	−34.10
9 (oOpSSP)	−15.3	−17.90
10 (oOoSSP)	−30.0	−32.50

(d, $^2J_{C-P}$ 22.4 Hz, C_2, 1C). ^{31}P{^{1}H}-NMR (162 MHz, $CDCl_3$) δ 164.6 (s). Anal. Calc. for $C_7H_7Cl_2OP$: C, 40.2; H, 3.4. Found: C, 40.7; H, 3.4%.

2.2. Syntheses of phosphine ligands

2.2.1. General method

The organic reagent containing bromine group was lithiated by *n*-butyl lithium in sodium-dried diethyl ether at 0°C. The mixture was stirred for 1–2 h at 0°C, after which 2-aryldichlorophosphine in Et_2O was added. The mixture was stirred an additional 1–2 h at 0°C. The precipitate was filtered and dried in vacuum. The product was recrystallized from ethanol or ethanol–toluene solution.

2.3. Characterization of phosphine ligands

2.3.1. (2-Thiomethylphenyl)bis(9-anthracenyl)phosphine ($SPanthr_2$) (**3**)

Yield 0.7 g, 1.3 mmol, 64.3%. m.p. 231–232°C. ^{1}H-NMR (200 MHz, $CDCl_3$) δ 2.3 (s, H_{15}, 3H), 6.9 (m, H_6, 1H), 7.0 (m, H_5, 1H), 7.1 (m, H_{11}, 4H), 7.2–7.4 (m, H_3, H_4 and H_{10}, 6H), 8.0 (d, $^3J_{H-H}$ 8.1 Hz, H_{12}, 4H), 8.5 (s, H_{14}, 2H), 8.7 (dd, $^3J_{H-H}$ 8.9 Hz, $^4J_{H-P}$ 3.4 Hz, H_9, 4H). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$) δ 17.2 (d, $^3J_{C-P}$ 7.9 Hz, C_{15}, 1C), 124.8 (s, C_{11}, 4C), 125.3 (s, C_5, 1C), 126.0 (s, C_{10}, 4C), 126.6 (s, C_{14}, 2C), 126.9 (s, C_9, 4C), 127.1 (s, C_3, 1C), 128.7 (s, C_4, 1C), 129.5 (s, C_{12}, 4C), 130.7 (s, C_{13}, 4C), 131.5 (s, C_8, 4C), 133.0 (s, C_6, 1C), 135.5 (d, $^1J_{C-P}$ 14.1 Hz, C_7, 2C), 136.8 (d, $^1J_{C-P}$ 10.9 Hz, C_1, 1C), 144.4 (d, $^2J_{C-P}$ 33.0 Hz, C_2, 1C). ^{31}P{^{1}H}-NMR (162 MHz, $CDCl_3$) δ −38.4 (s). MS [M + 1] Anal. Calc. for $C_{35}H_{26}PS$, 509.149; found, 509.148.

2.3.2. (2-Thiomethylphenyl)bis(1-naphthyl)phosphine ($SPnaf_2$) (**4**)

Yield 0.2 g, 0.5 mmol, 53.4%. m.p. 204–205°C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.5 (s, H_{17}, 3H), 6.7 (dd, $^3J_{H-H}$ 7.4 Hz, $^3J_{H-P}$ 3.8 Hz, H_6, 1H), 7.0 (m, H_5, 1H), 7.3 (m, H_3, H_4, H_8 and H_9, 6H), 7.4 (t, $^3J_{H-H}$ 7.7 Hz, H_{13}, 2H), 7.5 (t, $^3J_{H-H}$ 7.4 Hz, H_{12}, 2), 7.9 (m, H_{10} and H_{11}, 4H), 8.5 (dd, $^3J_{H-H}$ 8.0 Hz, H_{14}, 2H). ^{13}C{^{1}H}-NMR (50 MHz, $CDCl_3$) δ 17.1 (d, $^4J_{C-P}$ 10.2 Hz, C_{17}, 1C), 125.3 (s, C_5, 1C), 125.7 (s, C_9, 2C), 126.0 (s, C_{12}, 2C), 126.2 (s, C_{14}, 2C), 126.3 (s, C_{13}, 2C), 126.4 (s, C_{10}, 2C), 126.7 (s, C_3, 1C), 128.6 (s, C_4, 1C), 129.5 (s, C_{11}, 2C), 129.6 (s, C_8, 2C), 132.8 (s, C_6, 1C), 133.5 (s, C_{15}, 2C), 134.5 (s, C_{16}, 2C), 134.9 (d, $^1J_{C-P}$ 7.3 Hz, C_1, 1C), 135.7 (d, $^1J_{C-P}$ 23.2 Hz, C_7, 2C), 144.3 (d, $^2J_{C-P}$ 29.1 Hz, C_2, 1C). ^{31}P{^{1}H}-NMR (162 MHz, $CDCl_3$) δ −29.7 (s). MS [M + 1] Anal. Calc. for $C_{27}H_{22}PS$, 409.118; found, 409.114.

2.3.3. (2-Thiomethylphenyl)bis(4-thiomethylphenyl)-phosphine (oSpSSP) (**5**)

Yield 0.2 g, 0.5 mmol, 40.4%. m.p. 113–115°C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.4 (s, H_{11}, 3H), 2.5 (s, H_{12}, 6H), 6.8 (dd, $^3J_{H-H}$ 7.8 Hz, $^3J_{H-P}$ 3.9 Hz, H_6, 1H), 7.1 (m, H_5, 1H), 7.2 (m, H_8 and H_9, 8H), 7.3 (m, H_3 and H_4, 2H). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$) δ 15.2 (s, C_{12}, 1C), 17.2 (d, $^4J_{C-P}$ 7.9 Hz, C_{11}, 2C), 125.3 (s, C_5, 1C), 126.0 (d, $^2J_{C-P}$ 6.7 Hz, C_8, 4C), 126.5 (s, C_3, 1C), 129.3 (s, C_4, 1C), 132.1 (d, $^1J_{C-P}$ 9.2 Hz, C_7, 2C), 133.0 (s, C_6, 1C), 134.3 (d, $^3J_{C-P}$ 20.4 Hz, C_9, 4C), 136.7 (d, $^1J_{C-P}$ 10.0 Hz, C_1, 1C), 139.9 (s, C_{10}, 2C), 143.5 (d, $^2J_{C-P}$ 27.4 Hz, C_2, 1C). ^{31}P{^{1}H}-NMR (162 MHz,

$CDCl_3$) δ −13.9 (s). MS [M + 1] Anal. Calc. for $C_{21}H_{22}PS_3$, 401.062; found, 401.059.

2.3.4. (2-Thiomethylphenyl)bis(2-methoxyphenyl)-phosphine (oSoOOP) (6)

Yield 0.3 g, 0.8 mmol, 62.2%. m.p. 180–182°C. ^{1}H-NMR (200 MHz, $CDCl_3$) δ 2.4 (s, H_{13}, 3H), 3.7 (s, H_{14}, 6H), 6.7 (m, H_{12}, 2H), 6.8 (dd, $^3J_{H-H}$ 7.5 Hz, $^3J_{H-P}$ 3.8 Hz, H_6, 1H), 6.9 (m, H_9 and H_{11}, 4H), 7.0 (m, H_5, 1H), 7.3 (m, H_3, H_4 and H_{10}, 4H). ^{13}C{^{1}H}-NMR (50 MHz, $CDCl_3$) δ 17.4 (d, $^4J_{C-P}$ 10.2 Hz, C_{13}, 1C), 55.7 (s, C_{14}, 2C), 110.3 (s, C_9, 2C), 120.9 (s, C_{11}, 2C), 124.4 (d, $^1J_{C-P}$ 13.1 Hz, C_7, 2C), 125.2 (s, C_5, 1C), 126.8 (d, $^3J_{C-P}$ 2.9 Hz, C_3, 1C), 130.0 (s, C_4, 1C), 130.1 (s, C_{10}, 2C), 133.3 (s, C_6, 1C), 133.9 (s, C_{12}, 2C), 136.4 (d, $^1J_{C-P}$ 10.2 Hz, C_1, 1C), 143.8 (d, $^2J_{C-P}$ 29.1 Hz, C_2, 1C), 161.6 (d, $^2J_{C-P}$ 17.4 Hz, C_8, 2C). ^{31}P{^{1}H}-NMR (162 MHz, $CDCl_3$) δ −34.1 (s). MS [M + 1] Anal. Calc. for $C_{21}H_{22}O_2PS$, 369.108; found, 369.107.

2.3.5. (2-Methoxyphenyl)bis(9-anthracenyl)phosphine (OPanthr$_2$) (7)

Yield 0.2 g, 0.4 mmol, 17.1%. m.p. 232–233°C. ^{1}H-NMR (200 MHz, $CDCl_3$) δ 3.4 (s, H_{15}, 3H), 6.6–6.9 (m, H_3, H_5 and H_6, 3H), 7.1 (m, H_{11}, 4H), 7.3 (m, H_4 and H_{10}, 5H), 8.0 (d, $^3J_{H-H}$ 8.5 Hz, H_{12}, 4H), 8.5 (s, H_{14}, 2H), 8.8 (dd, $^3J_{H-H}$ 8.9 Hz, $^4J_{H-P}$ 3.4 Hz, H_9, 4H). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$) δ 55.3 (s, C_{15}, 1C), 110.1 (s, C_3, 1C), 121.1 (s, C_5, 1C), 124.7 (s, C_{11}, 4C), 125.7 (s, C_{10}, 4C), 126.1 (d, $^1J_{C-P}$ 12.8 Hz, C_1, 1C), 127.1 (s, C_{14}, 2C), 127.3 (s, C_9, 4C), 129.4 (s, C_{12}, 4C), 129.8 (s, C_4, 1C), 130.4 (s, C_{13}, 4C), 131.5 (s, C_8, 4C), 132.7 (s, C_6, 1C), 135.5 (d, $^1J_{C-P}$ 14.0 Hz, C_7, 2C), 161.4 (d, $^2J_{C-P}$ 18.5 Hz, C_2, 1C) ppm. ^{31}P{^{1}H}-NMR (162 MHz, $CDCl_3$) δ −40.4 (s). MS [M + 1] Anal. Calc. for $C_{35}H_{26}OP$, 493.172; found, 493.173.

2.3.6. (2-Methoxyphenyl)bis(1-naphthyl)phosphine (OPnaf$_2$) (8)

Yield 0.3 g, 0.8 mmol, 32.3%. m.p. 222–224°C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.8 (s, H_{17}, 3H), 6.6 (dd, $^3J_{H-H}$ 7.6 Hz, $^3J_{H-P}$ 4.4 Hz, H_6, 1H), 6.8 (t, $^3J_{H-H}$ 7.4 Hz, H_5, 1H), 7.0 (m, H_3 and H_4, 2H), 7.3 (t, $^3J_{H-H}$ 7.6 Hz, H_9, 2H), 7.35 (t, $^3J_{H-H}$ 7.6 Hz, H_8, 2H), 7.42 (t, $^3J_{H-H}$ 7.6 Hz, H_{13}, 2H), 7.5 (t, $^3J_{H-H}$ 7.2 Hz, H_{12}, 2H), 7.9 (dd, $^3J_{H-H}$ 8.2 Hz, H_{10} and H_{11}, 4H), 8.5 (dd, $^3J_{H-H}$ 8.2 Hz, H_{14}, 2H). ^{13}C{^{1}H}-NMR (50 MHz, $CDCl_3$) δ 55.8 (s, C_{17}, 1C), 110.3 (s, C_3, 1C), 121.2 (s, C_5, 1C), 123.9 (d, $^1J_{C-P}$ 9.2 Hz, C_1, 1C), 125.7 (s, C_9, 2C), 125.9 (s, C_{12}, 2C), 126.1 (s, C_{14}, 2C), 126.3 (s, C_{13}, 2C), 126.8 (s, C_{10}, 2C), 128.5 (s, C_{11}, 2C), 129.4 (s, C_8, 2C), 130.5 (s, C_4, 1C), 132.6 (s, C_6, 1C), 133.4 (d, $^2J_{C-P}$ 10.2 Hz, C_{15}, 2C), 134.9 (s, C_{16}, 2C), 135.7 (d, $^1J_{C-P}$ 23.2 Hz, C_7, 2C), 161.7 (d, $^2J_{C-P}$ 17.2 Hz, C_2, 1C). ^{31}P{^{1}H}-NMR (162 MHz, $CDCl_3$) δ −31.9 (s). MS [M + 1] Anal. Calc. for $C_{27}H_{22}OP$, 393.141; found, 393.136.

2.3.7. (2-Methoxyphenyl)bis(4-thiomethylphenyl)-phosphine (oOpSSP) (9)

Yield 0.4 g, 1.0 mmol, 71.6%. m.p. 103–106°C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.5 (s, H_{12}, 6H), 3.8 (s, H_{11}, 3H), 6.7 (dd, $^3J_{H-H}$ 7.6 Hz, $^3J_{H-P}$ 4.8 Hz, H_6, 1H), 6.9 (m, H_3 and H_5, 2H), 7.2 (m, H_8 and H_9, 8H), 7.3 (t, $^3J_{H-H}$ 8.6 Hz, H_4, 1H). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$) δ 15.2 (s, C_{12}, 2C), 55.7 (s, C_{11}, 1C), 110.2 (s, C_3, 1C), 121.0 (s, C_5, 1C), 125.4 (d, $^1J_{C-P}$ 11.3 Hz, C_1, 1C), 125.9 (d, $^2J_{C-P}$ 6.8 Hz, C_8, 4C), 130.4 (s, C_4, 1C), 132.6 (d, $^1J_{C-P}$ 8.7 Hz, C_7, 2C), 133.5 (s, C_6, 1C), 134.2 (d, $^3J_{C-P}$ 20.6 Hz, C_9, 4C), 139.5 (s, C_{10}, 2C), 161.0 (d, $^2J_{C-P}$ 15.1 Hz, C_2, 1C). ^{31}P{^{1}H}-NMR (162 MHz, $CDCl_3$) δ −15.3 (s). MS [M + 1] Anal. Calc. for $C_{21}H_{22}OPS_2$, 385.085; found, 385.080.

2.3.8. (2-Methoxyphenyl)bis(2-thiomethylphenyl)-phosphine (oOoSSP) (10)

Yield 0.4 g, 1.1 mmol, 47.0%. m.p. 156–159°C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.4 (s, H_{14}, 6H), 3.8 (s, H_{13}, 3H), 6.6 (m, H_6, 1H), 6.8 (d, $^3J_{H-H}$ 7.2 Hz, H_{12}, 2H), 6.86 (t, $^3J_{H-H}$ 7.4 Hz, H_3, 1H), 6.91 (d, $^3J_{H-H}$ 8.4 Hz, H_5, 1H), 7.0 (m, H_{11}, 2H), 7.3 (m, H_4, H_9 and H_{10}, 5H). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$) δ 17.4 (s, C_{14}, 2C), 55.7 (s, C_{13}, 1C), 110.3 (s, C_3, 1C), 121.1 (s, C_5, 1C), 124.0 (d, $^1J_{C-P}$ 12.6 Hz, C_1, 1C), 125.2 (s, C_{11}, 2C), 126.7 (s, C_9, 2C), 129.2 (s, C_{10}, 2C), 130.2 (s, C_4, 1C), 133.4 (s, C_{12}, 2C), 134.0 (s, C_6, 1C), 135.9 (d, $^1J_{C-P}$ 9.2 Hz, C_7, 2C), 144.0 (d, $^2J_{C-P}$ 29.3 Hz, C_8, 2C), 161.6 (d, $^2J_{C-P}$ 16.3 Hz, C_2, 1C). ^{31}P{^{1}H}-NMR (162 MHz, $CDCl_3$) δ −30.0 (s). MS [M + 1] Anal. Calc. for $C_{21}H_{22}OPS_2$, 385.085; found, 385.081.

2.4. Crystallography

X-ray diffraction data were collected with a Nonius KappaCCD (compounds **3**, **4**, **7**, **8**, and **9**) or with a Nonius Mach3 (compound **5**) diffractometer using Mo–K_α radiation ($\lambda = 0.71073$ Å). For compound **5**, cell parameters were obtained from 25 automatically centered reflections. Data collection ($\omega/2\theta$ scan mode) and cell refinement were carried out with the CAD4 EXPRESS diffractometer program [12] and data reduction with XCAD4 program [13]. For other compounds the data were collected using ϕ or combined ϕ/ω scans with a COLLECT [14] data collection program. Denzo and Scalepack [15] programs were used for cell refinements and data reduction. All structures were solved by direct methods using SHELXS97 [16] or SIR97 [17] programs with the WINGX [18] graphical user interface or by using SHELXTL version 5.1 [19] program package. The structure refinements were carried out with the SHELXL97 [20]. For compounds **3**, **4**, and **8**, the hydrogens were constrained to ride on their parent atom (C–H = 0.95 Å, $U_{iso} = 1.2$ (C_{eq}) for aromatic hydrogens and C–H = 0.98 Å, $U_{iso} = 1.5$ (C_{eq}) for methyl H

atoms). For compounds **5** and **9** all hydrogens were located from the difference Fourier map and refined isotropically (compound **5**: $U_{iso} = 0.05$ for aromatic hydrogens, $U_{iso} = 0.08$ for methyl hydrogens, compound **9**: $U_{iso} = 0.04$ for aromatic hydrogens, $U_{iso} = 0.05$ for methyl hydrogens). Crystallographic data are summarized in Table 1 and selected bond lengths and angles in Tables 2 and 3. The crystal structures of (2-thiomethylphenyl)bis(9-anthracenyl)phosphine and (2-methoxyphenyl)bis(4-thiomethylphenyl)phosphine are shown in Figs. 1 and 2.

3. Results and discussion

3.1. Dichlorophosphines

In order to prepare *ortho*- and *meta*-substituted aryldichlorophosphines, a method that utilizes a Grignard reagent for activating the *ortho* or *meta* position in the aromatic ring has been developed [11]. In this method, the Grignard reagent of the *ortho*- or *meta*-substituted aryl group was transmetalated with $ZnCl_2$ to the corresponding organozinc halide reagent. This was then allowed to react with PCl_3 under THF in refluxing conditions.

For the preparation of **1**, the lithiation procedure in combination with 20-fold excess of PCl_3 was first examined. A dilute solution of 2-lithiothioanisole was added dropwise to the ethereal solution of PCl_3, after which the mixture was refluxed. The reaction produced tris(2-thiomethylphenyl)phosphine, instead of the title compound. We therefore chose the combination of organolithium and organozinc halide reagents in diethyl ether for the preparation of a reagent, which was then allowed to react with PCl_3 (Scheme 1). The main improvement compared with the original method [11] was the formation of compounds **1** and **2** without side products.

4-Chlorobutanol forms when the aryl lithium compound is refluxed in THF with $ZnCl_2$ [21]. In order to prevent the formation of this side product, diethyl ether was used as a solvent. *n*-Butyl lithium was used instead of magnesium, because the formation of the Grignard reagent in diethyl ether was very slow. The target compounds were separated by distillation in reduced pressure.

3.2. Tertiary phosphine ligands

2-Thioanisyl- and 2-anisyldichlorophosphines were used as starting materials in the preparation of new tertiary phosphine ligands. In these reactions the chlorides were replaced by 2-thioanisyl, 4-thioanisyl, 2-anisyl, 1-naphthyl and 9-anthracenyl groups in order to find a variation in the steric and electronic properties of 2-thioanisyl and 2-anisyl containing ligands. The effects of these modifications will be studied in catalytic applications in the future. The schematic structures of prepared phosphine ligands are shown in Scheme 2.

The Lewis basicity of the ligands reflects the electronic effects of the substituents in the aromatic ring. Electron-donating substituents such as alkyl groups increase the basicity of ligands, while electron-withdrawing substituents such as aromatic groups with electronegative substituents decrease it [22]. The basicity of the ligands can be varied systematically by altering the substituents on the phosphorus atom [23].

Basicities of phosphines have been measured by many different methods. Simple titrations to measure pK_a values of phosphines are difficult because the tertiary phosphines are typically insoluble in water. Nonaqueous titrimetry [22,24], infrared technique [25], ultraviolet photoelectron spectra [26] and NMR studies [27–29] are the examples from the methods that have been used in estimating the basicities of phosphines.

^{31}P-NMR is an important tool to get information from 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 phosphine PR_3 [30,31]. The chemical shifts of tertiary phosphine ligands can be estimated by an empirical equation [30]:

$$\delta = -62 \sum_{n=1}^{3} \sigma_n^{\mathrm{P}} \quad (1)$$

where σ^{P} values are increments that are characteristic for each substituent group. The reference value represents PMe_3 (δ −62 ppm vs. 85% H_3PO_4).

The increments (σ^{P}) for the different substituent groups used in constructing the new tertiary phosphine ligands reported in this paper can be calculated from the ^{31}P-NMR chemical shifts reported in the literature (Table 4). In these ligands, all three substituent groups are the same. When these increments were used to calculate ^{31}P-NMR chemical shifts for the new ligands, relatively good agreement was obtained with the experimental values (Table 5). These values indicate that, having information of the substituent increments, the environment of the phosphorus atom can be estimated with reasonable accuracy.

It has been postulated that there is no general correlation between basicity and ^{31}P-NMR chemical shifts of the phosphine ligands [29,35]. Instead, the basicity of phosphines has been shown to be directly related to the ^{31}P-NMR chemical shifts of corresponding phosphine oxides [36]. Evidently within certain chemically related groups of phosphines, a relationships can also be found between the ^{31}P-NMR shifts and basicity. We have previously [37] prepared a group of tertiary phosphine ligands derived from 4-anisyl- and 4-thioanisyldichlorophosphines. The ^{31}P-NMR chemical shifts of these ligands were connected to the basicities determined by the IR frequencies of the carbonyl groups in $Ni(CO)_3(PR_3)$ [23].

Large aromatic groups are known to have relatively low basicities [22]. The low frequency of the ^{31}P-NMR chemical shifts of phosphines containing naphthyl and anthracenyl groups agree with this. Correspondingly, phosphine ligands having anisyl substituents bound to phosphorus atom are more basic [23]. The same behavior can also be connected to thioanisyl-substituted phosphine ligands. The experimental and calculated ^{31}P-NMR chemical shifts of the ligands prepared in this work are in good agreement with the common trend described before.

Bidentate ligands are catalytically promising and for example, diphosphines are commonly used in homogeneous metal catalysts. Experimental results show that the phosphine ligands containing 2-thiomethyl groups behave typically as a bidentate ligands in metal complexes [38]. The behavior of 2-methoxyphenyl phosphine ligands depends on the nature of the metal center used in the complexes. With Cr, Mo, W, Rh and Ir, 2-methoxyphenyl-substituted ligands behave mainly as a monodentate ligands [39,40]. With molybdenum the coordination can also be fluxional [41]. In these kinds of hemilabile complexes, the phosphorus atom is bound strongly to a transition metal, while the oxygen atom may be coordinatively labile. The oxygen can dissociate from the metal allowing the formation of a free coordination site, which may be important in homogeneous catalysis [42]. Heterodonor atoms in the *para* position of aromatic rings do not take part in metal coordination. Their effect on the ligands is mainly electronic.

4. Supplementary data

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 120178–120183 for compounds **3**–**5** and **7**–**9**. Copies of this information may be obtained free of charge from The Director, CCDC, 12, Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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