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# PH-Functional *o*-Phosphinophenols—Synthesis via Methoxymethylethers and Screening Tests for Ni-Catalyzed Ethylene Polymerization

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ABSTRACT: *Various primary and secondary 2-phosphinoaryl methoxymethylethers were prepared via orthometallation of methyl- and methoxy-substituted aryl methoxymethylethers and subsequent reaction with aminochlorophosphines, followed by alcoholysis and reduction with excess $LiAlH_4$. Incomplete reduction provides 2-methoxymethoxy-substituted cyclotetraphosphines, isolated and characterized by X-ray crystal structure analysis in one case. An example of the facile P-alkylation of primary to secondary representatives is also given. Secondary 2-phosphinophenols, obtained by selective cleavage of the MOM-protection group, and even the primary 2-phosphino-4-methylphenol react with $Ni(COD)_2$ to form ethylene polymerization catalysts. 4-Methoxy groups cause a strong increase of the molecular weights and a bimodal molecular weight distribution of the polymerization products; neither effect is observed for tertiary phosphinophenolate/Ni polymerization catalysts.* © 2005 Wiley Periodicals, Inc. Heteroatom Chem 16:379–390, 2005; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20107

## *INTRODUCTION*

P-Tertiary 2-phosphinophenols have found considerable interest as ligands in transition metal complexes [1,2], and organonickel phosphinophenolate chelate complexes proved to be efficient moisture-tolerant polymerization or oligomerization catalysts [1,3,4]. P-Tertiary 2-phosphinophenol ethers became familiar by the formation of hemilabile P^O-chelate complexes [5] and the use of suitable asymmetric derivatives in highly enantioselective Rh-catalyzed hydrogenation reactions [6]. Primary [7–9] and secondary 2-phosphinophenols [9,10], however, have attracted much less attention. The use of primary 2-phosphinophenols is so far limited to the application as building blocks for phosphorus heterocycles [8,9], and secondary 2-phosphinophenols are

Dedicated to Prof. Dr. Alfred Schmidpeter on the occasion of his 75th birthday.

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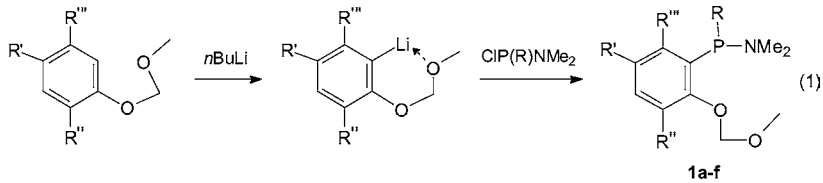
known to form dimeric $\mu$-P-bridging nickel phosphido complexes [11]. P-alkylation reactions of primary and secondary to secondary and tertiary 2-phosphinophenols have been reported, but require dimetallation and give inadequate yields because of the hydroxy substituent in *o*-position. A MOM-protected secondary 2-phosphinophenol proved to be more suitable for P-alkylation and thus provided access to asymmetric P-tertiary derivates, although reported so far only for 1,3-dibromopropane [9a]. MOM-protection provides also a convenient three-step synthesis of tertiary 2-phosphinophenols via direct orthometallation of aryl-methoxymethylethers, phosphinylation, and acidic O-deprotection [12,2i, 3a]. This and the potential use as hybrid ligands prompted us to study some primary and secondary 2-phosphinophenyl-methoxymethylethers.

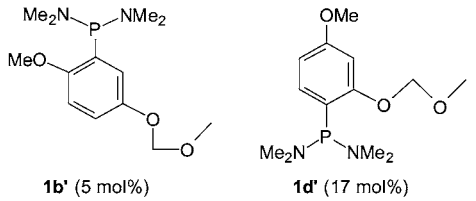
## *RESULTS AND DISCUSSION*

### *Syntheses*

4-Methylphenyl-methoxymethylether was treated with the equimolar amount of *n*-butyllithium in diethylether (−40 to −50°C) and subsequently with $ClP(NMe_2)_2$ to form the MOM-protected 2-diaminophosphino-4-methylphenol **1a** in good yield and with excellent selectivity (Scheme 1). Isomer signals could not be detected by $^{31}P$ or $^{1}H$ NMR, indicating that the ortholithiation was regiospecific, controlled only by the MOM group and not influenced by the methyl group. In the case of methoxy-substituted aryl methoxymethylethers, the metallation agent interacts also with the methoxy group and may lower the selectivity. 4-Methoxyphenyl-methoxymethylether reacts with *n*-butyllithium and $ClP(NMe_2)_2$ to **1b** in high yield but with slightly lower selectivity than observed for **1a**. About 5% of the isomer **1b′**, formed by metallation in ortho-position to the methoxy group and subsequent substitution, was identified by the characteristic coupling pattern of the proton NMR signals. 2-Methoxyphenyl-methoxymethylether reacts more selectively and provides only **1c** although the statistical chances for orthometallation next to the MOM and methoxy groups (1:1) are the same as in 4-methoxyphenyl-methoxymethylether (2:2). The metallation chances are no longer equal in the case of 3-methoxyphenyl-methoxymethylether. The atom H2 in ortho-position to the MOM and the methoxy group should statistically be favored to the hydrogen atoms H4 or H6, while the two alkoxy groups adjacent to the metallation site may also hinder each other sterically. The experiment shows considerably lowered selectivity. Lithiation with *n*BuLi at 0°C and subsequent reaction with $ClP(NMe_2)_2$ furnished a 59:41% mixture of the 3- and 5-methoxy-2-methoxymethyl benzenephosphonous acid diamides **1d** and **1d′**. Ortholithiation at −78°C in the presence of TMEDA improved the selectivity (83:17%) but not enough to obtain a sufficiently pure isomer. P-Secondary 2-(aminophenylphosphino)aryl methoxymethylethers **1e** [9a] and **1f** were obtained by reaction of the corresponding lithium reagents with $PhP(NMe_2)Cl$.



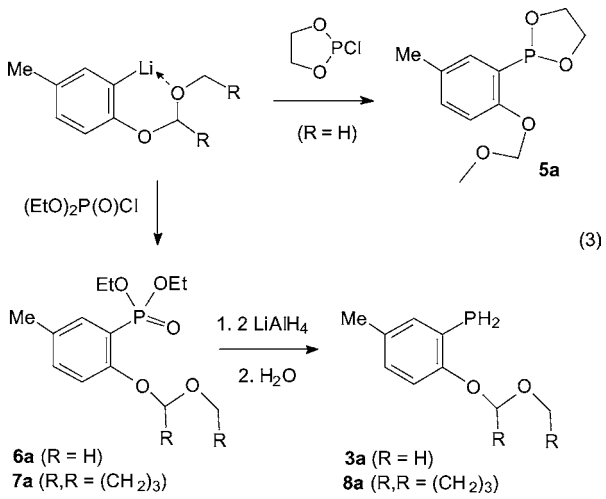

| 1 | a | b | c | d | e | f |
|---|---|---|---|---|---|---|
| R | $NMe_2$ | $NMe_2$ | $NMe_2$ | $NMe_2$ | Ph | Ph |
| R' | Me | MeO | H | H | Me | MeO |
| R'' | H | H | MeO | H | H | H |
| R''' | H | H | H | MeO | H | H |




SCHEME 1

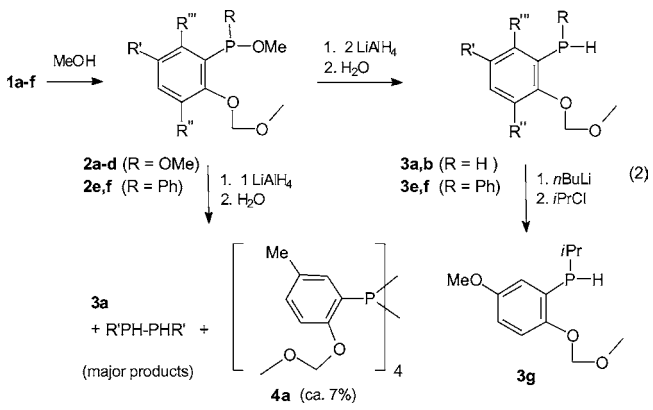
The conversion of the 2-(aminophosphino)aryl methoxymethylethers to the corresponding primary or secondary 2-phosphinoaryl methoxymethylethers was accomplished by alcoholysis and subsequent reduction with lithium aluminum hydride (Scheme 2). The resistance of the MOM protection group toward alcohols avoids the problem observed in the alcoholysis of 2-(aminophosphino)phenyl-silylethers, namely the attack of $-P(OR)_2$ by the deprotected *o*-hydroxyl group above 60°C [8,9], and allows the isolation of **2a–f** by distillation. The reduction to primary or secondary phosphides, hydrolyzed by water in work-up to **3a,b** or **3e,f**, requires excess $LiAlH_4$. Reduction of crude **2a** with only one equivalent of $LiAlH_4$ furnished a small amount of crystalline cyclotetraphosphine **4a** along with **3a** (low yield) and the corresponding diphosphine, which underwent disproportionation on heating. Finally, the facile P-alkylation of primary to secondary 2-methoxymethyl-arylphosphines, exemplified by the reaction of **2b** with *n*BuLi and isopropylbromide to **3g**, should be mentioned.

Suitable precursors for the reduction to compounds of type **3** can also be prepared directly from 2-lithioaryl methoxymethylethers. While lithium 2-lithiophenolates generated from O-unprotected phenols react unselectively with 2-chloro-1,3,2-dioxaphospholane [13] affording mixtures of mono-, di-, and triorganophosphines, the reaction of the *o*-lithiophenyl-methoxymethylethers proceeds selectively to mono-substitution products, exemplified by **5a** (Scheme 3). Similarly, chlorodiethylphosphate can be used to synthesize the phosphonate **6a**, which is not isolated, and is reduced by $LiAlH_4$ to **3a**. However, the total yield of **3a** is no better than in the synthesis via **1a** and **2a**. Crude **6a** ($\delta^{31}$P 17.7, > 90% $\Sigma_{intens.}$), obtained from the solution by evaporation of diethyl ether, is a highly viscous material and decomposes upon distillation attempts in high vacuum. An analogous attempt with the 2-perhydropyranyl instead of the MOM-protection group, affording **7a** and **8a**, respectively, revealed similar behavior and even lower yields. The complete conversion of chlorodiethylphosphate, the lack of LiCl precipitation in the ethereal solution, and the thermal behavior could be accounted for by coordination of the lithium chloride, but this aspect, somewhat related to alkali metal complexes of (aza)crown ethers with a phosphine oxide side arm [14], was not studied within this work.

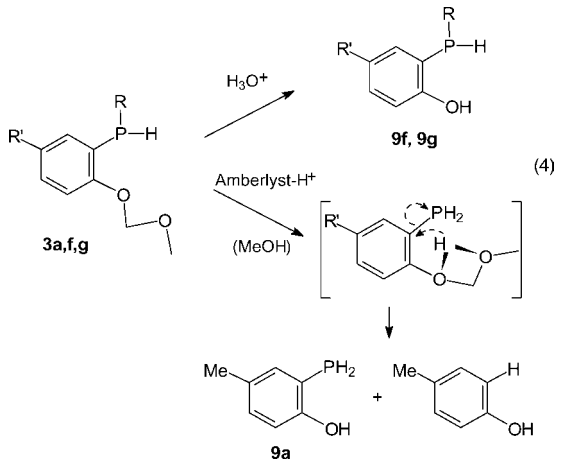



SCHEME 3

The O-dealkylation of tertiary 2-phosphinophenyl-methylethers or -isopropylethers is known but requires prolonged reflux with concentrated aqueous HI or HBr [15] or reaction with $BBr_3$ in $CH_2Cl_2$ followed by methanolysis [2j]. The deprotection of MOM-protected tertiary 2-phosphinophenols can be accomplished under much less drastic conditions, namely treatment with methanolic hydrochloric acid at 40°C [12, 2i, 3a] or even with dilute hydrochloric acid. This allows selective 2-O-deprotection in the presence of 4-methoxy groups [3a], also in the case of the P-secondary 2-phosphino-4-methoxyphenyl methoxymethylethers **3f** and **3g** (Scheme 4). The yield of **9f** is rather low but that of **9g** is adequate. Deprotection of primary 2-phosphinoaryl methoxymethylethers was attempted, so far only for **3a** and **8a**, with acid-charged ion exchange resin Amberlyst 15H in methanol (4 h 50°C, 15 h 20°C) but led to extensive P—C bond cleavage besides O-deprotection and furnished **9a** only in low yield and contaminated with *p*-cresol. The P—C cleavage in the absence of water might have been supported by *ortho*-directed protonation via the MOM group, facilitated by the absence of steric hindrance, but it needs




SCHEME 2




SCHEME 4

further studies to clarify whether the decomposition is due to intra- or inter-molecular processes.

## *Structural Aspects*

Structural evidence of the compounds **1–9** is given by the characteristic $^{1}H$, $^{13}C$, and $^{31}P$ NMR data. The appearance of a phosphorus singlet for the crystalline **4a** at $\delta - 58.2$ is in accordance with a symmetric tetraorganocyclotetraphosphine $(PR)_4$ which usually display a singlet in the range $\delta$ from $-45$ to $-77$ [16] while cyclotetramers with organophosphorus substituents, e.g. phosphoniumylidyl groups [17], or other cyclooligophosphines $(PR)_n$ exhibit more complex spectra due to P—P coupling [16]. The assignment is confirmed by crystal structure analysis (Fig. 1). The molecule is a folded four-membered ring of phosphorus atoms with all-*trans* substituents in equatorial positions and possesses $\bar{4}$-symmetry. The phosphorus atoms are pyramidal (angle sum 290.3°) and occupy positions alternating 0.32 Å above and below the best $P_4$ plane. The contact between the opposite pairs of phosphorus atom across the ring is 3.011 Å. The folding angle amounts to 133.4°, the torsion angles are ±32.5°. The torsion angle C(2)—C(1)—P—P#1 is rather small (−18.0°) and shows that the aryl planes with the 4-methyl end are packed approximately in the same direction as one P—P# bond, while the other is nearly perpendicular (C(2)—C(1)—P—P#2 −105.7°). The bond lengths and angles correspond to those of other cyclotetraphosphines [16–18].

## *Polymerization of Ethylene*

Organonickel phosphinophenolate chelate complexes formed in situ from tertiary 2-phosphinophenols

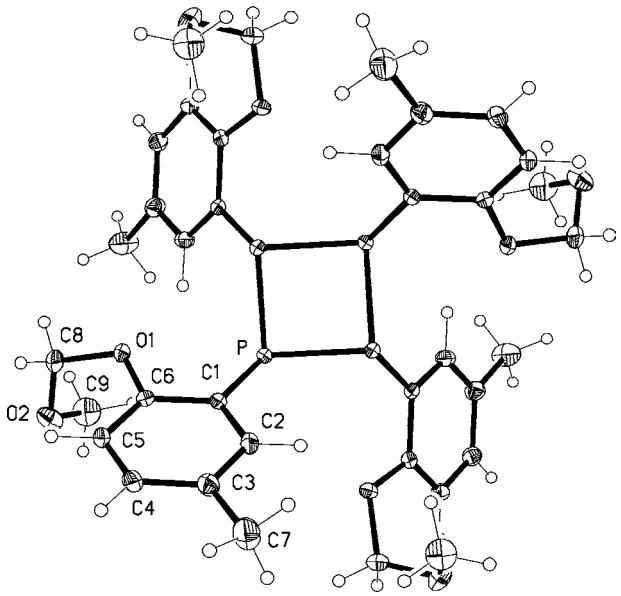



**FIGURE 1** Molecular structure of **4a** (thermal ellipsoids with 30% probability). Selected bond lengths (Å) and angles (°): P—C(1) 1.8347(17), P—P#1 2.2253(6); C(1)—P—P#1 104.31(6), C(1)—P—P#2 100.86(6), P#1—P—P#2 85.134(13), P—C(1)—C(2) 124.99(12), P—C(1)—C(6) 116.79(13); symmetry transformations used to generate equivalent atoms: #1 $-y+\frac{1}{4}, x+\frac{1}{4}, -z+\frac{1}{4}$; #2y $-\frac{1}{4}, x+\frac{1}{4}, -z+\frac{1}{4}$.

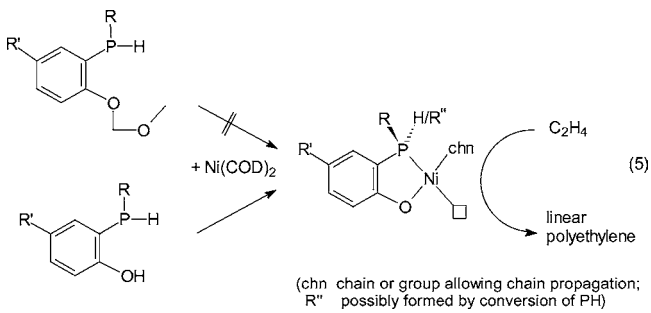
and $Ni(COD)_2$ (COD 1,5-cyclooctadiene) or other related isolated complexes catalyze the polymerization or oligomerization of ethylene [3,4]. Ligand tuning revealed that the polymer chain length increases for various $PR_2$ groups in the order $Ph_2P <$ Ph*t*BuP ≈ Ph*i*PrP < $Et_2P$ < $tBu_2P$ < $iPr_2P$ < $cHex_2P$. This is accounted for by an increase of the chain lengths with the basicity of the phosphino groups, superimposed upon a sterically induced decrease in the case of $\alpha$-branched alkyl groups [3a], and raises the question of the effect of primary and secondary phosphino groups. Screening tests of the batch polymerization of ethylene by catalysts prepared in situ from equimolar amounts of ligands **9** and $Ni(COD)_2$ revealed that the primary phosphinophenol **9a** gives rise to rather low activity, but secondary 2-phosphinophenols lead to highly active polymerization catalysts, if suitable conditions are provided (Table 1). Addition of the brown precatalyst solution prepared from **9g** and $Ni(COD)_2$ to a preheated (80°C) solution of ethylene in toluene caused instant formation of inactive black nickel but slow heating (20 to 80°C in 15–20 min) in the initial phase in toluene in the presence of ethylene allowed formation of a catalyst that converted 94% of the ethylene to almost linear polyethylene with vinyl end groups. The turnover number (4350) was

**TABLE 1** Polymerization of Ethylene with Catalysts Generated from PH-Functional 2-Phosphinophenols and Ni(COD)$_2$ in Toluene

| *Experiment* | *Conditions: Ligand ($\mu$mol),[a] T (°C), p (bar)* | *$C_2H_4$ Quantity (g), Conversion (%), TON (mol/mol)* | *Polymer Data mp (°C), d (g/cm$^3$), Crystallinity (%)* | *DTA (°C)[c] (endo, exo)* | *$M_w$, $M_n$ (g/mol)* | *$\alpha$-Olefin (%), Me/Vin, Me/1000 C* |
|---|---|---|---|---|---|---|
| 1 | **9a** (100), 100, 50 | 14.8, 31, 1640 | 130.5–132, 0.954 | 122.5, 116 | $M_{NMR}$, 13.000[g] | >98, 2.2, 2.4[g] |
| 2 | **9e** (114), 120, 47 | 11.7, 75, 2240 | 123–124, n.d. | 131, 119 | 16.400, 8.100[d,e] | n.d. |
| 3 | **9f** (99) 80, 50 | 12.2, 70.5, 3100 | 124–126, 0.96, 85[b] | 133, n.d. | 696.800, 7.230[d,f] | 97, 1.2, 2.8[b] |
| 4 | **9g** (100) 80, 50 | 13.0, 94, 4350 | 129–131, 0.97, 85[b] | 137, n.d. | 812.600, 9.500[d] | 95, 2.1, 2.1[b] |
| 5 | **9h** (220), 140, 40 | 9.6, 51, 790 | 126–128, n.d. | 135, 119 | 18.000, 13.800 | 96, 1.5, 3.4[g] |

[a]Equimolar amount of Ni(COD)$_2$.
[b]Determined by IR from PE plates (BASF).
[c]Endothermic peak on heating, exothermic peak on cooling.
[d]Bimodal.
[e]ca. 99% $M_w$ ca. 9.000, ca. 1% $M_w$ ca. 500.000 g/mol.
[f]Hard polymer layer at the wall of the autoclave $M_w$ 948.000, $M_n$ 21.500.
[g]Determined by $^1$H NMR integration.

limited by the ethylene/catalyst ratio in this case. For **9e, 9f** and 2-isopropylphosphino-4-methylphenol **9h** [9a] conversions are lower, but conditions are not optimized. The low activity of the catalyst in experiment 5 (TON 790) is attributable to the low ethylene/catalyst ratio along with partial catalyst decomposition at 140°C. The moderate conversion (51%) at this high temperature, on the other hand, shows that the PH-based catalyst does not decompose too rapidly. The molecular weights of the polyethylenes obtained in experiments 1–5 are all considerably higher than those of polyethylenes prepared with 2-diphenylphosphinophenol/Ni(COD)$_2$ catalysts under similar conditions [3]. The $M_w$ values accomplished by the secondary 2-phosphino-4-methylphenolate catalysts **9e**/Ni and **9h**/Ni are comparable to those brought about by 2-diethylphosphinophenolate/Ni catalysts, while $M_w$ values of HDPE obtained with 2-phosphino-4-methoxyphenolate catalysts **9f**/Ni and **9g**/Ni are much higher and by far the highest values achieved so far with 2-phosphinophenolate/Ni catalysts. The considerable increase of the $M_w$ values was not observed with catalysts derived from 4-methoxy-substituted tertiary 2-phosphinophenols; on the contrary, there the $M_w$ values became strongly reduced by 4-methoxy groups [3a]. The uncommon effect of the 4-methoxy group is coupled with a bimodal molecular weight distribution and a larger high-molecular weight fraction, observed also, but only in traces (estimated ca. 1%), in the polyethylene formed by the 2-phosphino-4-methylphenolate catalyst **9e**/Ni (exp. 2). It is improbable that the effect is caused by small contaminations of **9f** and **9g** by the corresponding methoxymethyl ethers, as these proved to be inactive in the screening tests and should rather lower the molecular weights, as is typical for ether and particularly phosphine additives [3a,4c]. The necessity of removing the O-protection group to generate nickel catalysts indicates a crucial role of P$^\cap$O$^-$-chelate structures in catalysis with P-secondary moieties, as is known with P-tertiary 2-phosphinophenols. This, the same selectivity for linear $\alpha$-olefins and the fact that the bimodal molecular distribution can be caused by stirring problems after formation of more viscous high polymers, lead us to propose a mechanism similar to that discussed for SHOP-type catalysts [19,1a,3] (Scheme 5). However, the present lack of evidence on P$^\cap$O$^-$-chelate complexes derived from secondary 2-phosphinophenols, the formation of a dimeric cyclopentadienylnickel $\mu$-P bridging phosphido complex with free OH from nickelocene and **3a** [11] and the unusual effect of 4-methoxy groups show that further studies on HP$^\cap$O$^-$-chelate complexes or on the destiny of the PH-ligands are required to obtain a more detailed and reliable picture of the mechanism.




**SCHEME 5**

## *EXPERIMENTAL*

All manipulations were performed under dry argon, using Schlenk techniques and freshly distilled ketyl-dried solvents. The arylmethoxymethyl ethers [3a,20] and 4-methylphenyl-perhydropyran-2-ylether [21] were prepared according to known procedures, other chemicals were purchased. Ethylene (99.5%, Air Liquide) was used without further treatment. NMR spectra were recorded at 25°C on a multinuclear FT-NMR spectrometer ARX300 (Bruker) at 300.1 ($^1$H), 75.5 ($^{13}$C), and 121.5 ($^{31}$P) MHz. Shift references are tetramethylsilane for $^1$H and $^{13}$C and $H_3PO_4$ (85%) for $^{31}$P. Coupling constants, unless indicated otherwise, refer to $J_{HH}$ in $^1$H and $J_{PC}$ in $^{13}$C NMR data. Assignment numbers of the phenol ring follow the nomenclature, those of phenyl- or alkylphosphino groups are denoted *i*, *o*, *m*, *p* and $\alpha$, $\beta$, $\gamma$, $\delta$, respectively. IR spectra were measured on a FTIR-spectrometer System 2000 (Perkin Elmer), mass spectra on a single-focusing mass spectrometer AMD40 (Intectra). Melting points were determined in a capillary and are uncorrected. TG/DTA were carried out with SETARAM TGDTA 92-16 (5 K/min) under argon) and elemental analyses with a CHNS-932 analyzer from LECO using standard conditions. Analyses of oligomers were performed on a gas chromatograph Hewlett Packard 5890, column 30 m HP-5 (crosslinked 5%PhMe silicone), 30–180°C, 20 min isotherm, 6°C/min; percentages given refer to mass% (uncorrected). $^1$H NMR and GPC measurements of polyethylenes were carried out as described in [3a].

### *Phosphonous and Phosphinous Amides*

*2-[Bis(dimethylamino)phosphino]-4-methylphenyl-methoxymethylether (***1a***).* A solution of *n*BuLi (1.6 N in hexane, 115 mL, 184 mmol) was slowly added at −40 to −50°C to a solution of 4-methylphenyl-methoxymethylether (28.0 g, 184 mmol) in diethyl ether (200 mL). Stirring was continued while the solution warmed to room temperature. After 2 h at 20°C the solution was cooled to −20°C, then chlorobis(dimethylamino)phosphine (28.4 g, 184 mmol) dissolved in ether (30 mL) was added dropwise. The mixture was stirred for 1 h, the precipitate was separated, and the solvent was evaporated in vacuum. The residue was distilled at 94–95°C/0.04 Torr to give 31.0 g (62%) of colorless **1a**. Anal. Calcd for $C_{13}H_{23}N_2O_2P$ (270.31): C, 57.76; H, 8.58; N, 10.36. Found: C, 57.33; H, 8.29; N, 9.85. $^1$H-NMR ($C_6D_6$): $\delta$ 2.21 (s, 3H, Me), 2.71 (d, $^3J_{PH} = 9.3$ Hz, 12H, $NMe_2$), 3.26 (s, 3H, OMe), 4.93 (s, 2H, $OCH_2O$), 6.95 (m, $^3J = 8.3$, $^4J \approx 2.4$, $^5J_{PH} \approx 1.4$ Hz, 1H, 5-H), 7.04 (dd, $^3J = 8.3$, $^4J_{PH} = 4.4$ Hz, 1H, 6-H), 7.38 (dd, $^3J_{PH} = 4.0$, $^4J = 2.4$ Hz, 1H, 3-H). $^{31}$P{$^1$H} NMR ($C_6D_6$): $\delta$ 98.1.

*2-[Bis(dimethylamino)phosphino]-4-methoxyphenyl-methoxymethylether (***1b***).* The reaction between 4-methoxyphenyl-methoxymethylether (10.5 g, 62.5 mmol) in diethyl ether (70 mL), *n*BuLi (1.6 N in hexane, 39.4 mL, 63 mmol), and chlorobis(dimethylamino)phosphine (9.7 g, 62.5 mmol) gave 15.5 g (87%) of colorless oily **1b**, bp 0.04 Torr/136–138°C. Anal. Calcd for $C_{13}H_{23}N_2O_3P$ (286.31): C, 54.55; H, 8.04; N, 9.78. Found: C, 54.14; H, 8.25; 9.48. MS (70 eV, EI, 35°C): *e*/*z* (%) = 286 (44) [M], 271 (31) [M−$CH_3^+$], 242 (50) [M−$NMe_2^+$], 106 (62) [MeO−$C_6H_3^+$], 58 (100), 45 (77) [$CH_2OMe^+$]. $^1$H-NMR ($C_6D_6$): $\delta$ 2.69 (d, $^3J_{PH} = 9.3$ Hz, 12H, $NMe_2$), 3.25 (s, 3H, $OCH_3$), 3.41 (s, 3H, $OCH_3$), 4.91 (s, 2H, $OCH_2O$), 6.71 (ddd, $^3J = 8.8$, $^4J = 3.1$, $^5J_{PH} = 1.7$ Hz, 1H, 5-H), 7.09 (dd, $^3J = 8.8$, $^4J_{PH} = 4.6$ Hz, 1H, 6-H), 7.28 (dd, $^3J_{PH} = 3.8$, $^4J = 3.1$ Hz, 1H, 3-H). $^{13}$C{$^1$H}(DEPT) NMR (toluene-$D_8$): $\delta$ 41.8 (d, $^2J = 17.9$ Hz, $NMe_2$), 55.1 ($OCH_3$), 55.8 ($OCH_3$), 95.8 ($OCH_2O$), 114.1, 116.2 (CH-5, CH-6), 118.2 (d, $^2J_{PC} = 8.1$ Hz, CH-3), 131.4 (d, $^1J = 12.9$ Hz, $C_q$-2), 153.1 (d, $^2J = 15.1$ Hz, $C_q$-1), 155.3 ($C_q$-4). $^{31}$P{$^1$H} NMR ($C_6D_6$): $\delta$ 97.5.

**1b** was contaminated by ca. 5% of 3-bis(dimethylamino)phosphino-4-methoxyphenyl-methoxymethylether **1b′**: $\delta$ 3.21 (s, OMe), 3.33 (s, OMe), 2.70 (d, $^3J_{PH} = 9.3$ Hz, $NMe_2$), 4.94 (s, $OCH_2O$), 6.50 (dd, $^3J = 8.8$, $^4J_{PH} = 4.7$ Hz, 5-H), ca. 7.05 (superimposed, 6-H), 7.49 (dd, $^3J_{PH} = 3.8$, $^4J = 3.1$ Hz, 2-H).

*6-[Bis(dimethylamino)phosphino]-2-methoxyphenyl-methoxymethylether (***1c***).* The reaction between 2-methoxyphenyl-methoxymethylether (13.8 g, 82.1 mmol), *n*BuLi (1.6 N in hexane, 51.5 mL, 82.5 mmol) and chlorobis(dimethylamino)phosphine (12.7 g, 82.2 mmol) gave 19.0 g (81%) of **1c**, bp 0.04 Torr/120°C, mp 35–36°C after crystallization from *n*-pentane at −25°C. Anal. Calcd for $C_{13}H_{23}N_2O_3P$ (286.31): C, 54.55; H, 8.04; N, 9.78. Found: C, 54.41; H, 8.14; 9.76. $^1$H-NMR ($C_6D_6$): $\delta$ 2.70 (d, $^3J_{PH} = 9.2$ Hz, 12H, $NMe_2$), 3.27 (s, 3H, $OCH_3$), 3.58 (s, 3H, $OCH_3$), 5.29 (s, 2H, $OCH_2O$), 6.58 (dt, $^3J = 8.0$, $^4J = 1.5$, $^5J_{PH} = 1.5$ Hz, 1H, 3-H), 7.00 (td, $^3J = 8.0$, $^4J_{PH} = 1.5$ Hz, 1H, 4-H), 7.24 (m, $^3J = 8.0$, $^3J_{PH} = 3.7$, $^4J = 1.5$ Hz, 1H, 5-H). $^{13}$C{$^1$H}, CH-COSY NMR ($C_6D_6$): $\delta$ 41.7 (d, $^2J = 18.1$ Hz, $NMe_2$), 55.4 ($OCH_3$), 57.6 (d, $^6J = 8.3$ Hz, $OCH_3$), 98.5 (d, $^4J = 4.1$ Hz, $OCH_2O$), 113.2 (CH-3), 123.9 (CH-4), 124.3 (d, $^2J_{PC} = 5.3$ Hz, CH-5), 135.3 (d, $^1J = 12.0$ Hz, $C_q$-6), 147.6 (d, $^2J = 16.4$ Hz, $C_q$-1), 152.8 (d, $^3J = 1.9$ Hz, $C_q$-2). $^{31}$P{$^1$H} NMR ($C_6D_6$): $\delta$ 97.3. MS (70 eV, EI, 30°C): *e*/*z* (%) = 286 (39) [$M^+$],

271 (21) [M—$CH_3^+$], 243 (19), 242 (49) [M—$NMe_2^+$], 198 (16), 183 (15), 139 (19), 119 (15) [M—$P(NMe_2)_2^+$], 106 (60) [MeO—$C_6H_3^+$], 76 (31), 58 (100), 45 (58) [$CH_2OMe^+$].

*2-[Bis(dimethylamino)phosphino]-3-methoxyphenyl-methoxymethylether (***1d***).* *n*BuLi (1.7 N in hexane, 39.5 mL, 67.2 mmol) was added dropwise at −78°C to 3-methoxyphenyl-methoxymethylether (11.2 g, 66.7 mmol) dissolved in diethyl ether (100 mL), TMEDA was added (7.8 g, 67.1 mmol), the solution was allowed to warm to 20°C and stirred for further 2 h. Then, at −40°C, chlorobis(dimethylamino)phosphine (10.0 g, 64.7 mmol) was added. The mixture was stirred for 1 h at room temperature, was filtered, washed and distilled to give 12.7 g (67.6%) of a mixture of **1d** and **1d′** (83:17%), bp 0.04 Torr/128–132°C. **1d**: $^1$H-NMR ($C_6D_6$): $\delta$ 2.76 (d, $^3J_{PH} = 9.2$ Hz, 12H, $NMe_2$), 3.23 (s, 3H, $OCH_3$), 3.35 (s, 3H, $OCH_3$), 4.94 (s, 2H, $OCH_2O$), 6.35 (m, $^3J = 8.2$, $^4J = 2.2$, $^4J_{PH} = 0.8$ Hz, 1H, 6-H), 6.90 (m, $^3J = 8.2$, $^4J = 2.3$ Hz, 1H, 4-H), 7.06 (m, $^3J = 8.2$, $^4J_{PH} = 1.7$ Hz, 1H, 5-H). $^{31}P\{^1H\}$ NMR ($C_6D_6$): $\delta$ 96.7.

*2-(Dimethylaminophenylphosphino)-4-methoxyphenyl-methoxymethylether (***1f***).* The reaction between 4-methoxyphenyl-methoxymethylether (26.0 g, 160 mmol) in diethyl ether (250 mL), *n*BuLi (1.6 N in hexane, 100 mL, 160 mmol), and chlorodimethylaminophenylphosphine (29.5 g, 160 mmol) (at −20°C) gave 39.5 g (80%) of **1f**, bp 0.04 Torr/154°C. $^1$H NMR ($C_6D_6$): $\delta$ 2.57 (d, $^3J_{PH} = 9.0$ Hz, 6H, $NMe_2$), 3.05 (s, 3H, $OCH_3$), 3.37 (s, 3H, $OCH_3$), 4.73 (s, 2H, $OCH_2O$), 6.74 (ddd, $^3J = 8.8$, $^4J = 3.1$, $^5J_{PH} = 1.1$ Hz, 1H, 5-H), 7.08–7.15 (m, 4H, aryl), 7.18 (dd, $^3J_{PH} = 4.2$, $^4J = 3.1$ Hz, 1H, 3-H), 7.44–7.51 (m, 2H, aryl). $^{31}P\{^1H\}$ NMR ($C_6D_6$): $\delta$ 58.1.

## *Phosphonous and Phosphinous Esters*

*2-(Dimethoxyphosphino)-4-methylphenyl-methoxymethylether (***2a***).* Dry methanol (25.0 mL, 0.62 mol) was added to **1a** (29.3 g, 108.4 mmol). Gaseous dimethylamine evolved. The temperature was slowly increased to 60°C and kept for 2.5 h to complete the reaction. After evaporation of methanol in vacuum, the residue was distilled to give 23.8 g (90%) of colorless liquid **2a**, bp. 0.04 Torr/92–96°C. Anal. Calcd for $C_{11}H_{17}O_4P$ (244.23): C, 54.10; H, 7.02. Found: C, 53.96; H, 7.00. $^1$H-NMR ($C_6D_6$): $\delta$ 2.14 (s, 3H, Me), 3.22 (s, 3H, OMe), 3.42 (d, $^3J_{PH} = 10.6$ Hz, 6H, POMe), 4.92 (s, 2H, $OCH_2O$), 6.97 (m, $^3J = 8.3$, $^4J \approx 2.2$, $^5J_{PH} \approx 0.6$ Hz, 1H, 5-H), 7.03 (dd, $^3J = 8.3$, $^4J_{PH} = 3.7$ Hz, 1H, 6-H), 7.70 (m, 1H, 3-H).

*2-(Dimethoxyphosphino)-4-methoxyphenyl-methoxymethylether (***2b***).* Dry methanol (3.8 g, 119 mmol) reacted with **1b** (8.5 g, 29.7 mmol) to give 7.1 g (92%) of colorless liquid **2b**, bp 0.04 Torr/101°C. Anal. Calcd for $C_{11}H_{17}O_5P$ (260.23): C, 50.77; H, 6.58. Found: C, 50.60; H, 6.77. MS (70 eV, EI, 35°C): *e/z* (%) = 260 (30) [M], 245 (51) [M—$CH_3^+$], 217 (20), 185 (48) [M—MOM—$OMe^+$], 93 (43) [$P(OMe)_2^+$], 63 (22), 45 (100) [$CH_2OMe^+$].

**2b**: $^1$H-NMR ($C_6D_6$): $\delta$ 3.24 (s, 3H, OMe), 3.39 (d, $^3J_{PH} = 10.7$ Hz, 6H, POMe), 3.41 (s, 3H, OMe), 4.91 (s, 2H, $OCH_2O$), 6.79 (ddd, $^3J = 8.9$, $^4J = 3.2$, $^5J_{PH} = 1.1$ Hz, 1H, 5-H), 7.04 (dd, $^3J = 8.9$, $^4J_{PH} = 4.2$ Hz, 1H, 6-H), 7.53 (dd, $^4J = 3.2$, $^3J_{PH} = 2.3$ Hz, 1H, 3-H). $^{13}C\{^1H\}$ ($C_6D_6$): $\delta$ 52.8 (d, $^2J = 9.5$ Hz, POMe), 55.3 (OMe), 55.8 (OMe), 95.3 ($OCH_2O$), 116.1 (d, $^2J_{PC} = 4.6$ Hz, CH-3), 116.3, 117.1 (CH-5, CH-6), 130.4 (d, $^1J = 29.0$ Hz, $C_q$-2), 154.0 (d, $^2J = 18.0$ Hz, $C_q$-1), 155.2 ($C_q$-4). $^{31}P\{^1H\}$ NMR ($C_6D_6$): $\delta$ 152.8.

**2b** was contaminated by ca. 5% of 3-dimethoxyphosphino-4-methoxyphenyl-methoxymethylether **2b′**: $^1$H-NMR ($C_6D_6$): $\delta$ 3.18 (s, OMe), 3.31 (s, OMe), POMe doublet superimposed, 4.86 (s, $OCH_2O$), 6.48 (dd, $^3J = 8.9$, $^4J_{PH} = 4.2$ Hz, 5-H), 7.10 (ddd, $^3J = 8.9$, $^4J = 3.1$, $^5J_{PH} = 1.2$ Hz, 6-H), 7.76 (dd, $^4J = 3.1$, $^3J_{PH} = 2.1$ Hz, 2-H). $^{31}P\{^1H\}$ NMR ($C_6D_6$): $\delta$ 153.1.

*6-(Dimethoxyphosphino)-2-methoxyphenyl-methoxymethylether (***2c***).* **2c** was synthesized as reported for **2a** from **1c** (12.2 g, 42.7 mmol) and dry methanol (5.5 g, 170.6 mmol) to yield 10.2 g (90%) of **2c**, bp 0.04 Torr/102–104°C. Anal. Calcd for $C_{11}H_{17}O_5P$ (260.23): C, 50.77; H, 6.58. Found: C, 50.32; H, 6.94. $^1$H-NMR ($C_6D_6$): $\delta$ 3.21 (s, 3H, $OCH_3$), 3.39 (d, $^3J_{PH} = 10.7$ Hz, 6H, OMe), 3.60 (s, 3H, $OCH_3$), 5.33 (s, 2H, $OCH_2O$), 6.58 (dt, $^3J = 8.1$, $^4J \approx {}^5J_{PH} \approx 1.1$ Hz, 1H, 3-H), 6.97 (td, $^3J = 8.1$, 7.8, $^4J_{PH} = 0.6$ Hz, 1H, 4-H), 7.52 (m, $^3J = 7.8$, $^3J_{PH} = 1.9$, $^4J = 1.5$ Hz, 1H, 5-H). $^{13}C\{^1H\}$ NMR ($C_6D_6$): $\delta$ 52.9 (d, $^2J = 10.0$ Hz, OMe), 55.3 ($OCH_3$), 57.8 (d, $^6J = 8.3$ Hz, $OCH_3$), 98.8 (d, $^4J = 1.8$ Hz, $OCH_2O$), 115.0 (CH-3), 122.6 (d, $^2J_{PC} = 4.1$ Hz, CH-5), 124.1 (CH-4), 134.6 (d, $^1J = 28.0$ Hz, $C_q$-6), 148.7 (d, $^2J = 20.6$ Hz, $C_q$-1), 152.4 (d, $^3J = 2.4$ Hz, $C_q$-2). $^{31}P\{^1H\}$ NMR ($C_6D_6$): $\delta$ 153.6. MS (70 eV, EI, 35°C): *e/z* (%) = 260 (9) [$M^+$], 259 (17), 245 (28) [M—$CH_3^+$], 217 (31), 199 (19), 185 (36), 93 (51) [$P(OMe)_2^+$], 63 (21), 45 (100).

*2-(Methoxyphenylphosphino)-4-methoxyphenyl-methoxymethylether (***2f***).* **2f** was synthesized as reported for **2a** from **1f** (39.5 g, 120 mmol) and dry methanol (8.0 g, 250 mmol) affording 26.5 g (70%) of **2f**, bp 0.1 Torr/142–143°C. Anal. Calcd for $C_{16}H_{19}O_4P$

(306.30): C, 62.74; H, 6.25. Found: C, 62.38; H, 6.17. $^1$H NMR ($C_6D_6$): $\delta$ 3.01 (s, 3H, OMe), 3.37 (s, 3H, OMe), 3.43 (d, $^3J_{PH} = 14.1$ Hz, 3H, POMe), 4.63, 4.80 ($2d_{AB}$, $^2J = 6.9$ Hz, 2H, $OCH_2O$), 6.71 (ddd, $^3J = 8.9$, $^4J = 3.1$, $^5J_{PH} = 0.6$ Hz, 1H, 5-H), 6.97 (dd, $^3J = 8.9$, $^4J_{PH} = 4.5$ Hz, 1H, 6-H), 7.02–7.18 (m, $^3J = 8.0$ Hz, 3H, Ph), 7.48 (t, $^3J_{PH} = 4.0$, $^4J = 3.1$ Hz, 1H, 3-H), 7.72–7.80 (m, 2H, Ph). $^{31}$P{$^1$H} NMR ($C_6D_6$): $\delta$ 108.4.

*(1,3,2-Dioxophospholane)-2-yl-4-methylphenyl-methoxymethylether (***5a***).* A solution of *n*BuLi (1.6 N in hexane, 14.5 mL, 63 mmol) was added slowly (1 mL/min) at −50°C to a solution of 4-methyl-phenyl-methoxymethylether (3.60 g, 23.7 mmol) in diethylether (40 mL). After warming to room temperature, it was allowed to stir for further 3–5 h. Then the suspension was cooled to −80°C, and 2-chloro-1,3,2-dioxaphospholane (3.0 g, 23.7 mmol) dissolved in diethyl ether (3 mL) was added within 10 min. After stirring overnight at room temperature, the mixture was filtered, the solvent removed in vacuum, and the residue distilled to give 3.3 g (58%) of **5a**, bp 105–110°C/0.02 Torr. Anal. Calcd. for $C_{11}H_{15}O_4P$ (242.21): C, 54.55; H, 6.24. Found: C, 53.82; H, 6.53. $^1$H-NMR ($C_6D_6$): $\delta$ 2.28 (s, 3H, Me), 3.51 (s, 3H, OMe), 3.97–4.10 (m, 4H, $OCH_2$), 5.21 (s, 2H, $OCH_2O$), 6.97 (dd, $^3J = 8.3$, $^4J_{PH} = 3.1$ Hz, 1H, 6-H), 7.07 (dd, $^3J_{PH} = 2.8$, $^4J = 2.2$ Hz, 1H, 3-H), 7.12 (dd, $^3J = 8.3$, $^4J = 2.2$ Hz, 1H, 5-H). $^{13}$C NMR ($CDCl_3$): $\delta = 19.7$ (s, $CH_3$), 55.2 (s, $OCH_3$), 63.4 (d, $^2J = 9.4$ Hz, $POCH_2$), 93.4 (s, $OCH_2O$), 113.5 (s, C-6), 128.5 (d, $^1J = 5.9$ Hz, C-2), 129.5 (s, C-4), 129.9 (s, C-5), 132.7 (s, C-3), 155.9 (d, $^2J = 14.1$ Hz, C-1). $^{31}$P{$^1$H} NMR ($CDCl_3$): $\delta$ 161.8.

## *Phosphinoaryl-methoxymethylethers from Phosphonous and Phosphinous Esters*

*4-Methyl-2-phosphinophenyl-methoxymethyl-ether (***3a***).* A solution of **2a** (22.5 g, 92.1 mmol) in diethyl ether (100 mL) were added slowly at 0°C to $LiAlH_4$ (7.0 g, 184.2 mmol) in diethyl ether (400 mL). After stirring for 12 h at room temperature, degassed water was added dropwise until the evolution of hydrogen ceased. The suspension was filtered, and the solid residue carefully washed with ether. The filtrate was dried with sodium sulfate, the solvent was removed, and the residue was distilled at 56–60°C/0.03 Torr to give 9.3 g (55%) of highly air sensitive, colorless **3a**. Anal. Calcd for $C_9H_{13}O_2P$ (184.18): P, 16.82. Found: P, 16.5. $^1$H NMR ($C_6D_6$): $\delta$ 2.02 (s, 3H, 4-Me), 3.13 (s, 3H, OMe), 3.91 (d, $^1J_{PH} = 201.2$ Hz, 2H, $PH_2$), 4.84 (s, 2H, $OCH_2O$), 6.85 (m, $^3J = 8.3$, $^4J = 2.1$, $^5J_{PH}$ = 0.4–0.6 Hz, 1H, 5-H), 6.94 (dd, $^3J = 8.3$, $^4J_{PH} = 3.2$ Hz, 1H, 6-H), 7.10 (m, $^3J_{PH} = 6.9$, $^4J = 2.1$, $J \approx 0.5$ Hz, 1H, 3-H). $^{31}$P{$^1$H} NMR ($CDCl_3$): $\delta = -138.7$.

*Tetra(2-methoxymethyloxy-5-methylphenyl)cyclo-tetraphosphane diethylether solvate (***4a***).* Reduction of crude **2a** (27.8 g, 115 mmol) with a smaller excess of $LiAlH_4$ (5.0 g, 131.6 mmol) and worked up as above furnished ca. 10 g crude product. Crystals formed overnight were separated and washed with a small portion of diethyl ether to give 1.5 g (7%) of **4a**, mp 144–145°C, medium soluble in $Et_2O$ or $CDCl_3$, less soluble in $C_6D_6$. Anal. Calcd for $C_{40}H_{54}O_9P_4$ (802.76): C, 59.85; H 6.78. Found: C, 59.48; H, 6.83. $^1$H NMR ($CDCl_3$): $\delta$ 2.33 (s, 12H, 5-Me), 3.28 (s, 12H, OMe), 5.02 (s, 8H, $OCH_2O$), 6.95 (d, $^3J = 8.3$ Hz, 4H, 12-H), 7.03 (dd, $^3J = 8.3$, $^4J = 2.0$ Hz, 4H, 4-H), 7.92 (d, $^4J = 2.0$ Hz, 4H, 6-H); $Et_2O$: 1.21, 3.47 (t, q $^3J = 7.1$ Hz). $^{13}$C NMR ($CDCl_3$): $\delta$ 20.7 (Me), 55.9 (OMe), 94.0 ($OCH_2O$), 112.6 (C-3), 127.7 ($C_q$-5), 129.6, 130.8 (C-4, C-6), 134.1 (br, $C_q$-1), 155.5 (br, $C_q$-2); $Et_2O$: 15.3, 65.8. $^{31}$P{$^1$H} NMR ($CDCl_3$): $\delta$ − 58.2. Crystal data see Table 2.

**TABLE 2** Crystal Data and Structure Refinement of **4a**

| | |
|---|---|
| Empirical formula | $C_{38}H_{50}O_9P_4$ |
| Formula weight | 774.66 |
| Temperature | 143(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Tetragonal |
| Space group | $I4_1/a$ |
| Unit cell dimensions | $a = 17.6234(14)$ Å $\alpha = 90°$<br>$b = 17.6234(14)$ Å $\beta = 90°$<br>$c = 13.4490(16)$ Å $\gamma = 90°$ |
| Volume | 4177.0(7) Å$^3$ |
| $Z$ | 4 |
| Density (calculated) | 1.232 mg/m$^3$ |
| Absorption coefficient | 0.230 mm$^{-1}$ |
| $F(000)$ | 1640 |
| Crystal size | 0.24 × 0.20 × 0.18 mm$^3$ |
| Theta range for data collection | 1.90–28.28° |
| Index ranges | $-22 < h < 23$, $-23 < k < 22$, $-15 < l < 17$ |
| Reflections collected | 24722 |
| Independent reflections | 2599 [$R$(int) = 0.1374] |
| Completeness to theta = 28.00° | 100.0% |
| Absorption correction | None |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data/restraints/parameters | 2599/0/106 |
| Goodness-of-fit on $F^2$ | 1.108 |
| Final $R$ indices [$I > 2\sigma(I)$] | $R1 = 0.0447$, $wR2 = 0.1228$ |
| $R$ indices (all data) | $R1 = 0.0594$, $wR2 = 0.1278$ |
| Largest diff. peak and hole | 0.425 and −0.386 e.Å$^{-3}$ |

The NMR spectra of the liquid fraction revealed mainly **3a** along with the corresponding P-secondary diphosphine NMR: $\delta^{31}$P −87.3, −90.7, *rac/meso* ca. 1:1; PH $\delta^1$H 4.31 (dd, $^1J_{PH} = 221$, $^2J_{PH}$13 Hz), a small amount of dissolved **4a** and an unknown impurity with $\delta^{31}$P −7.5.

*4-Methoxy-2-phosphinophenyl-methoxymethylether (***3b***).* Using the procedure described for **3a, 3b** was synthesized from **2b** (27.5 g, 110 mmol) in diethyl ether (90 mL) and $LiAlH_4$ (7.5 g, 20 mmol) in diethyl ether (400 mL), yield 15.1 g (71%) of colorless liquid, bp 77–78°C/0.04 Torr. Anal. Calcd for $C_9H_{13}O_3P$ (200.17): C, 54.00; H, 6.55. Found: C, 54.24; H, 7.00. MS (70 eV, EI): *e/z* (%) = 200 (10) [M]. $^1$H-NMR ($C_6D_6$): $\delta$ 3.14 (s, 3H, $OCH_3$), 3.26 (s, 3H, $OCH_3$), 3.90 (d, $^1J_{PH} = 201.9$ Hz, 2H, PH), 4.81 (s, 2H, $OCH_2O$), 6.65 (dd, $^3J = 8.9$, $^4J = 3.1$ Hz, 1H, 5-H), 6.96 (dd, $^3J = 8.9$, $^4J_{PH} = 3.4$ Hz, 1H, 6-H), 7.00 (dd, $^3J_{PH} \approx 6$, $^4J = 3.1$ Hz, 1H, 3-H). $^{13}$C{$^1$H} ($C_6D_6$): $\delta$ 55.6 ($OCH_3$), 56.0 ($OCH_3$), 95.1 ($OCH_2O$), 114.7, 115.1 (CH-5, CH-6), 117.5 (d, $^1J_{PC} = 7.0$ Hz, $C_q$-2), 120.5 (d, $^2J = 10.5$ Hz, CH-3), 152.1 (d, $^2J = 8.2$ Hz, $C_q$-1), 154.2 ($C_q$-4). $^{31}$P NMR ($C_6D_6$): $\delta$ − 137.2 (m, $^1J_{PH} = 202$, $J_{PH} = 6.7$, 3.5 Hz).

**3b** was contaminated by ca. 5% of the isomer 3-phosphino-4-methoxyphenyl-methoxymethylether (**3b′**): $^1$H-NMR ($C_6D_6$): $\delta$ 3.17 (s, OMe), 3.25 (s, OMe), 3.89 (d, $^1J_{PH} = 202.1$ Hz, PH),4.83 (s, $OCH_2O$), 6.35 (dd, $^3J = 8.9$, $^4J_{PH} = 3.4$ Hz, 5-H), 7.10 (ddd, $^3J = 8.9$, $^4J = 3.1$, $^5J_{PH} = 1.2$ Hz, 6-H), 7.29 (dd, $^3J_{PH} = 6.9$, $^4J = 3.0$ z, 2-H). $^{31}$P{$^1$H} NMR ($C_6D_6$): $\delta$ −138.3.

*4-Methoxy-2-(phenylphosphino)phenyl-methoxymethylether (***3f***).* Using the procedure described for **3a, 3f** was synthesized from **2f** (23.3 g, 80 mmol) in diethyl ether (80 mL) and $LiAlH_4$ (4.6 g, 120 mmol) in diethyl ether (250 mL), yield 8.5 g (41%), bp 0.04 Torr/130–132°C. $C_{15}H_{17}O_3P$ (276.3), MS (70 eV, EI): *e/z* (%) = 276 (23) [$M^+$], 245 (23), 244 (100) [M−OMe−$H^+$], 231 (28), 229 (30),153 (21), 91 (17), 45 (54) [$CH_2OMe^+$]. $^1$H NMR ($C_6D_6$): $\delta$ 3.09 (s, 3H, $OCH_3$), 3.23 (s, 3H, $OCH_3$), 4.788, 4.79 ($2d_{AB}$, $^2J = 6.8$ Hz, 2H, $OCH_2O$), 5.37 (d, $^1J_{PH} = 219.2$ Hz, 1H, PH), 6.67 (dd, $^3J = 8.9$, $^4J = 3.1$ Hz, 1H, 5-H), 6.98 (m, $^3J_{PH} = 6.7$, $^4J = 3.1$ Hz, 1H, 3-H), 6.99–7.04 (m, 4H, aryl), 7.50–7.53 (m, 2H, aryl). $^{13}$C{$^1$H} ($C_6D_6$): $\delta$ 55.8 ($OCH_3$), 56.3 ($OCH_3$), 95.7 ($OCH_2O$), 116.0, 116.3 (CH-5, CH-6), 121.1 (d, $^2J = 9.2$ Hz, CH-3), 127.1 (d, $^1J = 14$ Hz, $C_q$-2), 129.29 (CH-*p*), 129.30 (d, $^3J = 5.8$ Hz, CH-*m*), 135.2 (d, $^1J = 11.3$ Hz, Cq-*i*), 135.6 (d, $^2J = 18.1$ Hz, CH-*o*), 153.6 (d, $^2J = 10.6$ Hz, $C_q$-1), 155.8 (d, $^3J = 3.8$ Hz, $C_q$-4). $^{31}$P NMR ($C_6D_6$): $\delta$ −53.2 (d quint, $^1J_{PH} = 220$ Hz).

*2(-Isopropylphosphino)-4-methoxyphenyl-methoxymethylether (***3g***).* A solution of *n*BuLi in hexane (1.6 N, 29.7 mL, 47.5 mmol) was added dropwise to a solution of **3b** (9.5 g, 47.5 mmol) in diethyl ether (150 mL) at −40°C and allowed to warm to room temperature. Stirring was continued for 1 h to afford a yellow phosphide solution. After cooling to −40°C, isopropyl bromide (5.9 g, 48 mmol) was added dropwise. The mixture was stirred for 4 h at 20°C and filtered. The solvent was removed, and the residue was distilled at 90–92°C/0.04 Torr to give 8.7 g (76%) of colorless liquid **3g**. $C_{12}H_{19}O_3P$ (242.3), MS (70 eV, EI): *e/z* (%) = 242 (23) [M], 211 (41) [$M^+$−OMe], 168 (36), 167 (100) [$M^+$−PH*i*Pr], 155 (40), 124 (28), 45 (35) [$CH_2OMe^+$]. $^1$H NMR ($C_6D_6$): $\delta$ 1.11 (dd, $^3J = 6.9$, $^3J_{PH} = 9.7$ Hz, 3H, $Me_A$), 1.13 (dd, $^3J = 7.1$, $^3J_{PH} = 16.9$ Hz, 3H, $Me_B$), 2.17–2.32 (m, $^3J \approx 7$, $^2J_{PH} \approx 2.7$ Hz, 1H, CH), 3.18 (s, 3H, $OCH_3$), 3.31 (s, 3H, $OCH_3$), 4.03 (dd, $^1J_{PH} = 206.9$, $^3J = 7.7$ Hz, 1H, PH), 4.85, 4.87 ($2d_{AB}$, $^2J = 6.8$ Hz, 2H, $OCH_2O$), 6.69 (dd, $^3J = 8.9$, $^4J = 3.1$ Hz, 1H, 5-H), 7.02 (dd, $^3J = 8.9$, $^4J_{PH} = 3.2$ Hz, 1H, 6-H), 7.12 (dd, $^3J_{PH} = 5.9$, $^4J = 3.1$ Hz, 1H, 3-H). $^{13}$C{$^1$H} ($C_6D_6$): $\delta$ 22.3 (d, $^2J = 19$ Hz, Me), 23.9 (2d, $J \approx 9$ Hz, CH, Me), 55.9 ($OCH_3$), 56.4 ($OCH_3$), 95.9 ($OCH_2O$), 115.6, 115.7 (CH-5, CH-6), 116.3 (d, $^1J = 2$ Hz, $C_q$-2), 122.2 (d, $^2J = 9$ Hz, CH-3), 154.0 (d, $^2J = 9$ Hz, $C_q$-1), 155.5 (d, $^3J = 4$ Hz, $C_q$-4). $^{31}$P{$^1$H} NMR ($C_6D_6$): $\delta$ − 34.0.

**3g** was contaminated by ca. 5% of the isomer 3-isopropylphosphino-4-methoxyphenyl-methoxymethylether (**3g′**) (cf. **1b′**): $^1$H-NMR ($C_6D_6$): $\delta$ 1.00 (dd, $^3J = 6.9$, $^3J_{PH} = 11.6$ Hz, $Me_A$), 1.17 (dd, $^3J = 7.0$, $^3J_{PH} = 14.8$ Hz, $Me_B$), CH superimposed, 3.25 (s, OMe), 3.36 (s, OMe), 4.08 (dd, $^1J_{PH} = 207.3$, $^3J = 7.6$ Hz, PH), 4.91, 4.92 ($2d_{AB}$, $^2J = 6.8$ Hz, $OCH_2O$), 6.70 (dd, part. superimp., 5-H), 7.09 (dd, $^4J = 3.0$ Hz, part. superimp., 6-H), 7.20 (dd, $^3J_{PH} = 5.7$, $^4J = 3.1$ Hz, 2-H). $^{31}$P{$^1$H} NMR ($C_6D_6$): $\delta$ − 35.4.

## *Phosphinoaryl-methoxymethylethers via Intermediate Phosphonates*

*4-Methyl-2-phosphinophenyl-methoxymethylether (***3a***).* 4-Methylphenyl-methoxymethylether (6.63 g, 41 mmol), dissolved in diethyl ether (40 mL), was treated with *n*BuLi (1.6 N in hexane, 26.0 mL, 41.3 mmol) as described for **5a**. The resulting suspension was cooled to −50°C and added in small portions (ca. 1 mL) to a solution of $(EtO)_2P(O)Cl$ (5.9 mL, 40.8 mmol) in diethyl ether (5 mL). After stirring overnight at 20°C ($^{31}$P NMR $\delta$ 17.7 (**6a**), >90% $\Sigma_{int}$), the suspension was added in small portions to $LiAlH_4$ (3.0 g, 79.0 mmol) in diethylether

(100 mL) at 0°C. The mixture was stirred for 1 h, then slowly heated and refluxed for 2 h. After stirring overnight and cooling to 0°C, degassed water was added dropwise until the evolution of hydrogen ceased. The solid hydroxides were filtered off and washed with ether, the filtrate was dried with $Na_2SO_4$ and distilled to give 3.5 g of **3a**, bp 67–72°C/0.2 Torr, contaminated by ca. 10% *p*-cresol (corrected total yield 42%). (NMR data of **3a** as given above.)

*4-Methyl-2-phosphinophenyl-perhydropyran-2-yl ether (**8a**).* A solution of 4-methylphenyl-perhydropyran-2-yl ether (9.2 g, 47.9 mmol) in diethyl ether (50 mL) was treated with *n*BuLi (1.6 N in hexane, 32.0 mL, 51.2 mmol) as described for **5a**. At −50°C a solution of $ClP(O)(OEt)_2$ (8.46 g, 49.0 mmol) in diethyl ether (7 mL) was added dropwise, and the mixture was stirred overnight at 20°C. $^1$H NMR ($CDCl_3$) assessment of the soluble part (a very viscous oil after removal of solvent) indicated ca. 55% of crude **7a** besides unconverted 4-methylphenyl-perhydropyran-2-yl ether, while 88% of the dissolved phosphorus compounds are phosphonates, mainly **7a**, $\delta^{31}$P 18.2, 84% $\Sigma_{int}$. The crude suspension was added in small portions to $LiAlH_4$ (4.0 g, 105 mmol) in diethyl ether (100 mL) at 0–5°C, the mixture was allowed to warm to room temperature and refluxed for 2 h. Then excessive $LiAlH_4$ was decomposed by dropwise addition of degassed water, insoluble components were filtered off, and the filtrate was dried with $Na_2SO_4$. Distillation and redistillation of the fraction 85–100°C/0.9 Torr gave 3.8 g of impure **8a** (corrected yield 2.7 g, 25%), bp 91–97°C/0.8 Torr, containing ca. 30% of 4-methylphenyl-tetrahydropyran-2-yl ether.

**Crude 7a**: $^1$H NMR ($CDCl_3$): $\delta$ 1.21 (m, 6H, Me), 1.35–1.90 (m, 6H, $CH_2$), 2.17 (s, 3H, 4-Me), 3.81 (t, $^3J$ = 10.3 Hz, 2H, $OCH_2$), 3.95–4.20 (m, 4H, $POCH_2$), 5.40 (s, 1H, OCHO), 7.02 (d, $^3J$ = 7.2 Hz, 6-H), 7.15 (d br, $^3J + {}^4J \approx$ 8.2 Hz, 5-H), 7.66 (d br, $^3J_{PH}$ = 15.2 Hz, 3-H). $^{31}$P {$^1$H} NMR ($CDCl_3$): $\delta$ = 18.2.

**8a**: $^1$H NMR ($CDCl_3$): $\delta$ 1.50–1.90 (m, 6H, $CH_2$), 2.23 (s, 3H, $CH_3$), 3.55–3.64 (m, 1H, $OCH_2$), 3.83 (d, $^1J_{PH}$ = 204.2 Hz, 2H, $PH_2$), 3.87 (td, $J$ = 10.1, 3.1 Hz, 1H, $OCH_2$), 5.44 (t, $^3J$ = 3.0 Hz, 1H, O—CH—O), 6.94–7.23 (m, 3H, Ar). $^{13}$C NMR ($CDCl_3$): $\delta$ = 18.4 (Me), 20.2 ($OCH_2\underline{C}H_2$), 25.1 ($OCH\underline{C}H_2$), 30.2 ($C\underline{C}H_2C$), 61.5 ($OCH_2$), 95.8 (OCHO), 113.7 (C-6), 118.4 (d, $^1J$ = 9.3 Hz, C-2), 129.6 (d, $^4J$ = 2.3 Hz, C-5), 130.6 (d, $^3J$ = 4.2 Hz, C-4), 135.6 (d, $^2J$ = 9.7 Hz, C-3), 155.7 (d, $^2J$ = 8.0 Hz, C-1). $^{31}$P{$^1$H} NMR ($CDCl_3$): $\delta$ 138.2.

*4-Methoxy-2-(phenylphosphino)phenol (**9f**).* Degassed 2N hydrochloric acid (250 mL) was added to **3f** (2.4 g, 8.7 mmol) at 40°C. The mixture was extracted with diethyl ether (50 mL). The solvent was removed in vacuum, and the residue was distilled at 0.02 Torr/130–131°C to give 0.6 g (30%) of **9f** as colorless viscous liquid. $C_{13}H_{13}O_2P$ (232.2), MS (70 eV, EI): *e*/*z* (%) = 232 (95) [M], 154 (100) [M$^+$—Ph—H], 124 (40) [M$^+$—PHPh]. $^1$H NMR ($C_6D_6$): $\delta$ 3.26 (s, 3H, $OCH_3$), 5.06 (s br, 1H, OH), 5.22 (d, $^1J_{PH}$ = 222.4 Hz, 1H, PH), 6.54 (dd, $^3J$ = 8.7, $^4J_{PH}$ = 3.5 Hz, 1H, 6-H), 6.68 (dd, $^3J$ = 8.7, $^4J$ = 3.1 Hz, 1H, 5-H), 6.99–7.12 (m, 4H, aryl), 7.37–7.43 (m, 2H, aryl). $^{13}$C{$^1$H}(DEPT) ($C_6D_6$): $\delta$ 55.9 ($OCH_3$), 117.3, 117.8 (CH-5, CH-6), 121.6 (d, $^1J$ = 15.4 Hz, CH-3), 121.8 (d, $^2J$ = 11.7 Hz, $C_q$-2), 129.2 (CH-*p*), 129.5 (d, $^3J$ = 6.0 Hz, CH-*m*), 134.6 (d, $^2J$ = 16.5 Hz, CH-*o*), 134.7 (d, $^1J$ = 8.3 Hz, Cq-*i*), 153.2 (d, $^2J$ = 8.7 Hz, $C_q$-1), 154.7 (d, $^3J$ = 6.0 Hz, $C_q$-4). $^{31}$P{$^1$H} NMR ($C_6D_6$): $\delta$ − 61.8.

*2-(Isopropylphosphino)-4-methoxyphenol (**9g**).* **3g** (7.2 g, 29.8 mmol) was treated with degassed 2N hydrochloric acid and worked up as above affording 3.7 g (63%) of **9g** as colorless viscous liquid, bp 0.02 Torr/113–114°C. $C_{10}H_{15}O_2P$ (198.2), MS (70 eV, EI): *e*/*z* (%) = 198 (75) [M$^+$], 156 (50) [M—*i*Pr$^+$], 124 (100) [M—PH*i*Pr$^+$], 77 (35) [Ph$^+$]. $^1$H NMR ($C_6D_6$): $\delta$ 1.00–1.18 (m, 6H, $Me_A$, $Me_B$), 2.20–2.26 (m, $^3J$ = 7.0, $^2J_{PH} \approx$ 2.9 Hz, 1H, CH), 3.76 (s, 3H, $OCH_3$), 4.04 (dd, $^1J_{PH}$ = 207.1, $^3J$ = 7.8 Hz, 1H, PH), 6.15 (s br, 1H, OH), 6.81 (dd, $^3J$ = 8.8, $^4J$ = 3.1 Hz, 1H, 5-H), 6.84 (dd, $^3J$ = 8.8, $^4J_{PH}$ = 2.7 Hz, 1H, 6-H), 6.94 (dd, $^3J_{PH}$ = 6.0, $^4J$ = 3.1 Hz, 1H, 3-H). $^{13}$C{$^1$H} ($C_6D_6$): $\delta$ $^{13}$C{$^1$H} ($C_6D_6$): $\delta$ 21.9 (d, $^2J$ = 17.7 Hz, *i*Pr), 23.1 (d, $^2J$ = 8.1 Hz, *i*Pr), 23.9 (d, $^1J$ = 6.1 Hz, *i*Pr), 56.0 ($OCH_3$), 117.0, 117.3 (CH-5, CH-6), 118.8 (d, $^1J$ = 14.7 Hz, $C_q$-2), 122.2 (d, $^2J$ = 10.5 Hz, CH-3), 153.7 (d, $^2J$ = 10.6 Hz, $C_q$-1), 154.4 (d, $^3J$ = 4.6 Hz, $C_q$-4). $^{31}$P{$^1$H} NMR ($C_6D_6$): $\delta$ − 50.6.

## *Crystal Structure Analysis*

*Data Collection.* A crystal of **4a** was mounted on a glass fiber in inert oil and transferred to the cold gas stream of the diffractometer (Bruker SMART 1000 CCD). Data were collected with monochromated Mo $K_\alpha$ radiation.

*Structure Refinement.* The structure was refined anisotropically on $F^2$ using the program SHELXL-97 (Prof. G.M. Sheldrick, University of Göttingen, Germany). Hydrogen atoms were included using a riding model or rigid methyl groups. A badly resolved region of residual electron density was tentatively assigned as disordered diethyl ether (the only solvent used to obtain single crystals) but could not be refined satisfactorily. For this reason, the program SQUEEZE (part of the PLATON-System: Prof. A.L.

Spek, University of Utrecht, the Netherlands) was used in order to remove mathematically the effects of the solvent.

For selected bond lengths and angles of **4a** see Fig. 1. The crystallographic data are listed in Table 2; where appropriate, the values refer to the idealized composition of 1:1 tetraphosphine:ether. Complete crystallographic data for **4a** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 255528. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (int. code) +44-(1223)/336-033, e-mail: deposit@ccdc.cam.ac.uk].

### *Ethylene Polymerization*

The corresponding phosphinophenol ligand (Table 1, ca. 100 $\mu$mol) and $Ni(COD)_2$ (ca. 27.5 mg, 100 $\mu$mol) were dissolved, each in 10 mL of toluene, cooled to 0°C (10 min) and mixed. The mixture was stirred at room temperature for 5 min and transferred via a Teflon cannula into the argon-filled stainless steel autoclave (75 mL), equipped with a manometer, two valves, a safety diaphragm, and Teflon-coated magnetic stirrer. The autoclave was pressurized (ca. 50 bar ethylene unless indicated otherwise), closed and after weight control transferred into the preheated bath. After heating for 12–15 h, cooling to room temperature and weight control, unconverted ethylene was allowed to escape via a cooling trap (−78°C, usually ≤0.1 g butenes condensed). The solvent and liquid products were separated by flash distillation at about $80°C/10^{-2}$ Torr. The residual polymer was stirred for 1 d with methanol/hydrochloric acid (1:1), thoroughly washed with methanol and dried in vacuum. Conversion and characteristic polymer data are given in Table 1.

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