Pure phosphotriesters as versatile ligands in transition metal catalysis: efficient hydrosilylation of ketones and diethylzinc addition to aldehydes

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Pure phosphotriesters as versatile ligands in transition metal catalysis: efficient hydrosilylation of ketones and diethylzinc addition to aldehydes

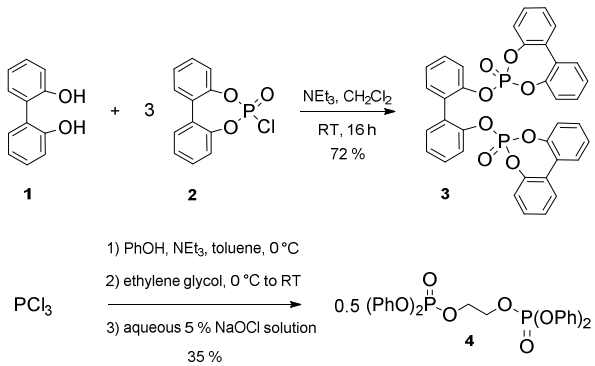
M. Bouhachicha,[a] A. Ngo Ndimba,[a] T. Roisnel,[b] C. Lalli*[a] and G. Argouarch*[a]

This work aims to highlight the underrated role played by pure phosphotriesters (or phosphates) ligands in catalysis, when compared to other phosphorus-containing donors such as for example phosphane oxides or phosphites. To probe this and to enlarge the very narrow catalytic scope of these Lewis bases, easily accessible mono- and bidentate phosphotriesters were tested as donors in two important transition metal-based catalytic transformations: the zinc-catalyzed hydrosilylation of ketones and the titanium-promoted diethylzinc addition to aldehydes. In both cases, the reactions were successful and the corresponding alcohols were obtained in high yields.

Since the beginning of modern transition metal catalysis, tremendous amount of new organic compounds were conceived to play the crucial role of ligands in many catalytic reactions. Additionally, new plethoric molecules have also emerged as powerful organocatalysts. To achieve this, chemists have innovated continuously in the search for new catalytic systems, and their optimization. In reviewing the literature, the architectures of all these catalysts show a prodigious variety of organic motifs with various functional groups; one might therefore wonder why only handful examples of pure phosphotriesters as efficient donors for this purpose have been reported to date. For instance, Miura and co-workers have shown that in palladium-catalyzed oxidative coupling of arylboronic acids with internal alkynes to produce 1,4-diaryl-1,3-butadienes, simple triaryl phosphates such as triphenylphosphate (TPP) compete well with their parent phosphites, or even outdo them in the case of diarylacetylenes.[1] In the field of organocatalysis, only two recent studies were reported in which BINOL-based chiral phosphates allowed highly enantioselective reactions. Ishihara and co-workers used chiral triaryl phosphates as nucleophilic catalysts to promote the enantioselective iodolactonization of 4-arylmethyl-4-pentanoic acids in the presence of *N*-haloimides,[2] whereas Luo's group successfully applied chiral trityl phosphates as latent carbocation catalysts to asymmetric Friedel-Crafts reactions in particular.[3]

In order to go beyond these few examples,[4] and taking into consideration the appealing coordination properties of the phosphoryl (P=O) fragment towards oxophilic metals,[5] we started to examine the potential of phosphates as suitable donors in the zinc-catalyzed hydrosilylation of ketones[6] and the titanium-promoted addition of diethylzinc to aldehydes.[7] These two well-documented transition metal-catalyzed reactions produce alcohols which are valuable building blocks in modern chemistry.

In this study, beside the easily available TPP $(PhO)_3P=O$, two new bidentate phosphorus triesters **3** and **4** were prepared (Scheme 1). According to a frequently employed method for the synthesis of phosphates,[8] reaction between 2,2'-biphenol (**1**) and an excess of **2**[9] in the presence of a base readily led to the formation of the tris-biphenyl bisphosphate **3** in good yield (72%). In contrast, preparation of compound **4** following a similar nucleophilic substitution turned out to be ineffective.[10] However, mixing of 1 equiv. of PCl_3 and 2 equiv. of phenol in basic conditions, followed by addition of 0.5 equiv. of ethylene glycol generated the intermediate bisphosphite, which was subsequently oxidized to give **4** in fair yield (35%). The new bisphosphate ligands were readily characterized by the usual spectroscopies and gave satisfactory high-resolution mass spectrometry analyses. The crystal structure of **3** was also unequivocally determined by X-ray diffraction analyses.[11]



Scheme 1 Synthesis of bisphosphates **3** and **4**.

We initially decided to probe the catalytic performance of the above phosphates in the zinc-catalyzed hydrosilylation. The optimization of this reaction was carried out with

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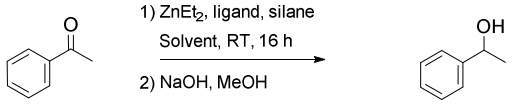
(**5a**) as the model substrate (Table 1). At first, **5a** and diethoxymethylsilane (DEMS) as the hydride source were placed in reaction into a CH_2Cl_2 solution of diethylzinc (5 mol%) and TPP (5 mol%). After stirring overnight at RT and basic cleavage on the silyl ether intermediate, only 15% of 1-phenylethanol (**6a**) were obtained (Table 1, entry 1). Gratifyingly, conversions were raised to 32% and 97% in toluene and acetonitrile, respectively, and full conversion of acetophenone was even reached with this catalytic system in THF (Table 1, entries 2-4). In addition, ligands **3** and **4** gave also a near-quantitative consumption of **5a** with DEMS in THF (Table 1, entries 5 and 6). Several alternative hydrosilanes were then tested in THF with the combination of diethylzinc and TPP. Although no conversion was detected with triethylsilane (Table 1, entry 7), polymethylhydrosiloxane (PMHS), phenylsilane, and diphenylsilane worked as well as DEMS in this transformation (Table 1, entries 8-10). Finally, decreasing the zinc catalyst loading to 2.5 mol% in the presence of either 2.5 or 5 mol% of TPP proved to be detrimental to the reaction (Table 1, entries 11 and 12).

Table 1 Optimization study for the hydrosilylation of acetophenone[a]



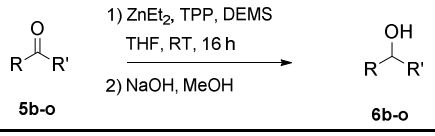
5a **6a**

Entry	Silane (equiv.)[b]	Ligand[c]	Solvent	Conv. [%][d]
1	DEMS (1.2)	TPP	CH_2Cl_2	15
2	DEMS (1.2)	TPP	toluene	32
3	DEMS (1.2)	TPP	MeCN	97
4	DEMS (1.2)	TPP	THF	>99 (72)
5	DEMS (1.2)	**3**	THF	>99
6	DEMS (1.2)	**4**	THF	>99
7	Et_3SiH (1.2)	TPP	THF	0
8	Ph_2SiH_2 (1.2)	TPP	THF	99
9	$PhSiH_3$ (1.2)	TPP	THF	>99 (74)
10	PMHS (1.5)	TPP	THF	>99 (84)
11[e]	PMHS (1.5)	TPP	THF	40
12[f]	PMHS (1.5)	TPP	THF	34

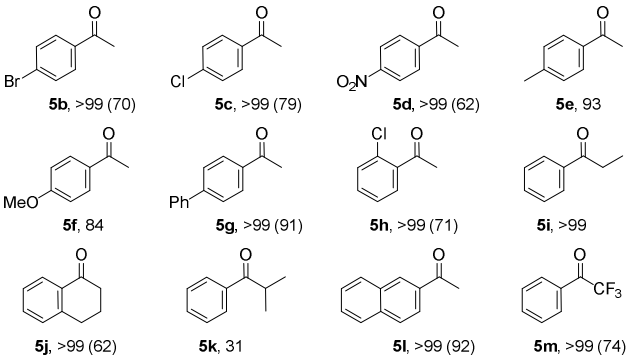
[a] Reaction conditions unless otherwise stated: acetophenone (1 mmol), solvent (2 mL), silane, $ZnEt_2$ (5 mol%), ligand (5 mol%), RT, 16 h. [b] PMHS = polymethylhydrosiloxane, DEMS = diethoxymethylsilane. [c] TPP = $(PhO)_3P{=}O$. [d] Conversion determined by ^1H NMR spectroscopy after basic hydrolysis, in parenthesis, isolated yield after purification by column chromatography. [e] $ZnEt_2$ (2.5 mol%), TPP (2.5 mol%). [f] $ZnEt_2$ (2.5 mol%), TPP (5 mol%).

The scope and limitations of this new catalytic system were then investigated on a series of representative ketones (Table 2). TPP was used as the donor for diethylzinc and THF as the solvent of choice. In the first trials, when the non-toxic PMHS was privileged the results were rather disappointing,[12] hence DEMS as a relatively cheap reducing agent was subsequently retained. The *para*-substituted acetophenone derivatives **5b**-**5g** were efficiently hydrosilylated under the reaction conditions, with the exception of the electron-rich ketone **5f** that showed a reduced conversion of 84%, but overall the electronic effects on the reactivity were limited. For more encumbered substrates, no steric limitations were encountered in the reduction of **5h**-**5j**, whereas a severe drop in the conversion (31%) was observed in the case of isobutyrophenone (**5k**). 2-Acetonaphthone (**5l**), the activated ketone **5m**, and benzophenone (**5n**) also underwent clean reduction giving the products with high yields. At last, the aliphatic ketone **5o** was nicely converted to the alcohol provided that bisphosphate **3** was used instead of TPP.

Table 2 Scope of zinc-catalyzed hydrosilylation of ketones using TPP[a]



5b-o **6b-o**



5b, >99 (70) **5c**, >99 (79) **5d**, >99 (62) **5e**, 93

5f, 84 **5g**, >99 (91) **5h**, >99 (71) **5i**, >99

5j, >99 (62) **5k**, 31 **5l**, >99 (92) **5m**, >99 (74)

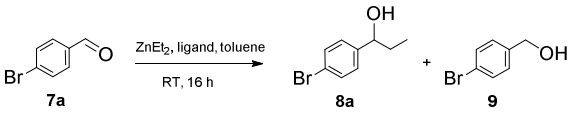
5n, >99 (91) **5o**, 69 >99 (75)[b]

[a] Typical conditions: ketone (1 mmol), THF (2 mL), DEMS (1.5 mmol), $ZnEt_2$ (5 mol%), TPP (5 mol%), RT, 16 h. Conversion determined by ^1H NMR spectroscopy after basic hydrolysis, and in parenthesis, isolated yield in alcohols **6** after purification by column chromatography. [b] 5 mol% of **3** were used.

In view of the good results obtained with the phosphates in hydrosilylation, we next decided to apply the combination between zinc(II) species and such phosphorylated Lewis bases to addition reactions of dialkylzinc to aldehydes. In the screening for optimal reaction conditions, 4-bromobenzaldehyde (**7a**) as the model substrate was first treated for 16 h at RT with a twofold amount of diethylzinc in toluene in the presence of 10 mol% of TPP (Table 3, entry 1). After reaction, adduct **8a** was weakly present at 36% because of incomplete conversion of the aldehyde (55%) and the release of undesired benzyl alcohol **9** (19%). Replacement of TPP by ligand **3** or **4** significantly reduced the formation of **9** (5-6%), but still the conversions were rather low with at most 43% of **8a** in the medium (Table 3, entries 2-5). Only when the reaction was run for a longer period of time (72 h), that alcohol **8a** was present up to 77% in the crude mixture (Table 3, entry 6). Anyway, as 1,2-addition reactions of organozinc reagents to aldehydes can also be mediated by titanium complexes, through either trans-metallation or enhancement of the electrophilicity of the carbonyl moiety,[7b] further catalytic trials were conducted with the help of titanium(IV) isopropoxide (Table 3, entries 7-12). To our delight, when using 1.2 equiv. of $Ti(O\textit{i}\text{-}Pr)_4$ along with 2 equiv. of $ZnEt_2$ and catalytic amounts of any of the phosphate

ligands (5 mol% for **3** and **4**, 10 mol% for TPP), conversion of **7a** was quantitative (Table 3, entries 9,11, and 12). In the same time, the side-reaction leading to **9** was decreased to a very low level (2%), thus demonstrating the good activity of the phosphate-based catalytic system in this titanium-promoted ethyl transfer.

Table 3 Optimization study for the addition of diethylzinc to **7a**[a]



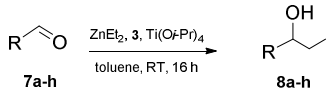
7a **8a** **9**

Entry	Ligand (mol%)	Ti(O*i*-Pr)$_4$ (equiv.)	Product distribution[b] **7a** / **8a** / **9**
1	TPP (10)	-	45 / 36 / 19
2	**3** (5)	-	52 / 43 / 5
3[c]	**3** (5)	-	75 / 19 / 6
4[d]	**3** (5)	-	60 / 35 / 5
5	**4** (5)	-	65 / 30 / 5
6[e]	**3** (5)	-	13 / 77 / 10
7	TPP (5)	0.1	45 / 52 / 3
8	TPP (5)	1.2	12 / 86 / 2
9	TPP (10)	1.2	0 / 98 / 2
10	**3** (5)	0.1	26 / 71 / 3
11	**3** (5)	1.2	0 / 98 / 2
12	**4** (5)	1.2	0 / 98 / 2

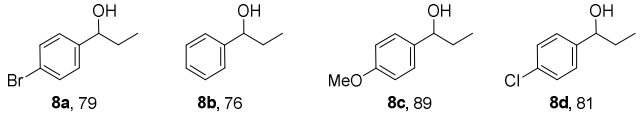
[a] Reaction conditions unless otherwise stated: 4-bromobenzaldehyde (0.5 mmol), toluene (2 mL), $ZnEt_2$ (1 mmol), ligand, RT, 16 h. [b] Determined by ^{1}H NMR spectroscopy of the crude product. [c] THF was used as solvent. [d] CH_2Cl_2 was used as solvent. [e] Reaction was run for 72 h.

In addition, we briefly investigated the generalization of this reaction using the more polar bisphosphate **3** as it was more easily separated from alcohols **8** in the purification step contrary to TPP or **4** (Table 4). All reactions were carried out according to conditions described in entry 11 of Table 3, and gave full conversions. Thus, a variety of aldehydes **7a**-**h** were alkylated with good yields to give the corresponding alcohols **8a**-**h**, irrespective of whether the substrates bore functional aromatic or aliphatic groups.

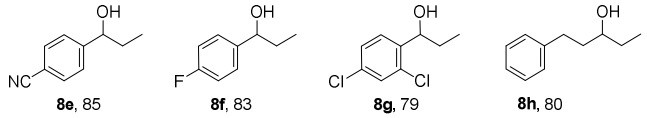
Table 4 Scope of diethylzinc addition to aldehydes using phosphate **3**[a]



7a-h **8a-h**



8a, 79 **8b**, 76 **8c**, 89 **8d**, 81



8e, 85 **8f**, 83 **8g**, 79 **8h**, 80

[a] Reaction conditions: aldehyde (0.5 mmol), toluene (2 mL), $ZnEt_2$ (1 mmol), ligand **3** (5 mol%), Ti(O*i*-Pr)$_4$ (0.6 mmol), RT, 16 h. Isolated yield after purification by column chromatography are provided.

In conclusion, phosphotriesters are readily available and stable compounds that remain largely under-examined in the field of (organo)catalysis. Herein we have threw some light on the usefulness of these phosphates as stabilizing ligands for zinc and titanium Lewis acids through efficient hydrosilylation of ketones and 1,2-addition reactions to aldehydes. This in turn should open the way to future achievements.

Experimental section

Preparation of bisphosphates

Compound **3**: under an atmosphere of argon, to a solution of 2,2'-biphenol (**1**, 120 mg, 0.64 mmol) and chlorophosphate **2** (515 mg, 1.92 mmol) in dry CH_2Cl_2 (15 mL) was added NEt_3 (0.27 mL, 1.92 mmol). The reaction was stirred overnight at room temperature and then hydrolysed with water (20 mL). After extraction with CH_2Cl_2 (2 x 10 mL), the combined organic layers were washed with an aqueous 1 N HCl solution (20 mL) and water (20 mL). After drying over anhydrous $MgSO_4$, filtration and evaporation to dryness, the residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate (1/1) as eluent, followed by recrystallization in boiling absolute ethanol (the crystals obtained were suitable for X-ray diffraction). White solid (300 mg, 0.46 mmol, 72% yield). M.p. 215 °C. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 6.94–6.97 (m, 4 H, Ar), 7.12 (t, J_{HH} = 4.7 Hz, 2 H, Ar), 7.23–7.37 (m, 12 H, Ar), 7.39–7.43 (m, 4 H, Ar), 7.52 (d, J_{HH} = 6.2 Hz, 2 H, Ar). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, ppm): δ = 119.9 (d, J_{CP} = 2.2 Hz, 2 C, Ar), 121.4 (d, J_{CP} = 4.5 Hz, 4 C, Ar), 125.3 (2 C, Ar), 126.5 (d, J_{CP} = 2.2 Hz, 4 C, Ar), 128.0 (d, J_{CP} = 1.5 Hz, 2 C, Ar), 128.5 (d, J_{CP} = 7.5 Hz, 2 C, Ar), 129.4 (2 C, Ar), 129.8 (d, J_{CP} = 0.7 Hz, 4 C, Ar), 130.1 (d, J_{CP} = 0.7 Hz, 4 C, Ar), 132.0 (4 C, Ar), 147.6 (d, J_{CP} = 9.7 Hz, 4 C, Ar), 147.9 (d, J_{CP} = 6.7 Hz, 2 C, Ar). ^{31}P NMR (202 MHz, $CDCl_3$, ppm): δ = -4.8 (s, 2 P). IR–UATR (solid, cm^{-1}): 3058, 1473, 1434, 1308, 1179, 964, 947, 927, 756. HRMS (ESI): *m/z* calcd for $C_{36}H_{24}O_8NaP_2$ $[M+Na]^+$ 669.0838; found 669.0844. Anal. calcd for $C_{36}H_{24}O_8P_2$ (%): C 66.88, H 3.74; found (%): C 66.68, H 3.73.

Compound **4**: under an atmosphere of argon, to a solution of PCl_3 (0.5 mL, 5.7 mmol) in toluene (60 mL) at 0 °C were added phenol (1.07 g, 11.4 mmol) and then NEt_3 (4.5 mL, 32.3 mmol) dropwise. The reaction was stirred 0.5 h at 0 °C before addition of ethylene glycol (159 µL, 2.85 mmol). The reaction was stirred at room temperature for 1 h and then hydrolysed with water (40 mL). After extraction with ethyl acetate (2 x 20 mL), the combined organic layers were washed with water (2 x 20 mL), an aqueous 5% NaOCl solution (2 x 30 mL), and brine (2 x 20 mL). After drying over anhydrous $MgSO_4$, filtration and

evaporation to dryness, the residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate (2/1) as eluent. Colourless oil (520 mg, 0.99 mmol, 35% yield). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 4.43–4.46 (m, 4 H, CH_2), 7.15–7.34 (m, 20 H, Ar). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, ppm): δ = 67.1 (dd, J_{CP} = 5.7 Hz, J_{CP} = 7.7 Hz, 2 C, CH_2), 120.1 (d, J_{CP} = 4.8 Hz, 8 C, Ar), 125.6 (d, J_{CP} = 1.1 Hz, 4 C, Ar), 129.9 (8 C, Ar), 150.4 (d, J_{CP} = 7.2 Hz, 4 C, Ar). ^{31}P NMR (202 MHz, $CDCl_3$, ppm): δ = -12.0 (s, 2 P). IR–UATR (oil, cm^{-1}): 3069, 2956, 1486, 1285, 1184, 947, 933, 752. HRMS (APCI–ASAP): *m/z* calcd for $C_{26}H_{25}O_8P_2$ $[M+H]^+$ 527.1019; found 527.1019.

General procedure for hydrosilylation of ketones

In a flame-dried round-bottom flask, to a solution of TPP (16 mg, 0.05 mmol) in dry THF (2 mL) under an atmosphere of argon was added $ZnEt_2$ (50 µL, 1 M solution in *n*-hexane, 0.05 mmol). After 10 min, the ketone (1 mmol) and $(EtO)_2MeSiH$ (252 µL, 1.5 mmol) were injected and the reaction was stirred overnight at room temperature. After removal of the solvent under reduced pressure, MeOH (4 mL) and an aqueous 1 N NaOH solution (4 mL) were added and the resulting solution was stirred for 12 h. The reaction medium was quenched with an aqueous 1 N HCl solution (10 mL) and brine (10 mL), and extracted with Et_2O (3 x 10 mL). The combined organic layers were washed with an aqueous 1 N NaOH solution (10 mL) and brine (10 mL). After drying over anhydrous $MgSO_4$, filtration and evaporation to dryness, the residue was submitted to ^{1}H NMR analysis to determine the conversion. The crude product was then purified by silica gel column chromatography using petroleum ether/Et_2O mixtures. ^{1}H and ^{13}C NMR data for purified products are provided in the ESI and are in agreement with reported values.

General procedure for diethylzinc addition to aldehydes

In a flame-dried round-bottom flask, to a solution of bisphosphate **3** (16 mg, 0.025 mmol) in dry toluene (2 mL) under an atmosphere of argon were added Ti(O*i*-Pr)$_4$ (180 µL, 0.6 mmol) and $ZnEt_2$ (1 mL, 1 M solution in *n*-hexane, 1 mmol). After 10 min, the aldehyde (0.5 mmol) was injected and the reaction was stirred overnight at room temperature. The reaction medium was quenched with an aqueous 1 N HCl solution (8 mL) and extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were washed with an aqueous 1 N HCl solution (10 mL) and water (10 mL). After drying over anhydrous $MgSO_4$, filtration and evaporation to dryness, the residue was purified by silica gel column chromatography using petroleum ether/Et_2O mixtures. ^{1}H and ^{13}C NMR data for purified products are provided in the ESI and are in agreement with reported values.

Acknowledgements

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10 Synthesis of **4** only supported by ^{1}H and ^{31}P NMR analyses (δ_p = - 17.4 ppm) has already been described by reaction between ethylene glycol, $(PhO)_2P(O)Cl$, and a base. In our hands, this protocole only gave rise to mixtures of TPP (δ_p = - 17.7 ppm) and ethylene glycol by-products. See: C. Nguyen and J. Kim, *Polym. Degrad. Stab.*, 2008, **93**, 1037.
11 CCDC 1526882 contains the crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre.
12 Conversions with 1.5 mmol of PMHS were as follow: **5b**, 48%; **5c**, 85%; **5g**, >99%; **5h**, 53%; **5k**, no reaction; **5**l, 89%.