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Synthesis of Tertiary Phosphine Oxides Mediated by $SmCp_2$ or SmI_2

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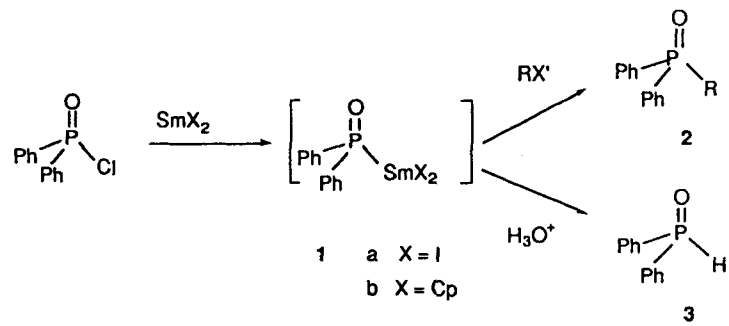
Tertiary phosphine oxides are prepared under mild conditions by sequential addition of diphenylphosphinoyl chloride to divalent samarium compounds ($SmCp_2$ and SmI_2) followed by reaction with various electrophiles such as organic halides, tosylates, epoxides or α,β-unsaturated ketones. Biscyclopentadienylsamarium ($SmCp_2$) gives better yields than SmI_2. Similar reactions, using phenylphosphonoyl dichloride, SmI_2 and subsequent addition of two equivalents of activated halides, yield the corresponding tertiary phosphine oxides.

Keywords: samarium di-iodide; divalent samarium; samarium dicyclopentadienide; phosphine oxide; Michael additions; diphenyl alkyl phosphine oxide; phenyl dialkyl phosphine oxide

In spite of the growing interest in samarium di-iodide (SmI_2), which is now used for numerous transformations,[1–3] this reagent has found few applications in phosphorus chemistry. Triphenylphosphine oxide has been reduced by SmI_2–hexamethylphosphoramide (SmI_2/HMPA) in refluxing tetrahydrofuran (THF),[4] but at room temperature only coordination of phosphine oxides to samarium is observed.[5,6] Reduction of P–P or P–C bonds by samarium or bis(pentamethylcyclopentadienyl)samarium ($SmCp_2^*$) have scarcely been reported.[7,8]

We have previously shown that P–Cl bonds in various phosphorus compounds can be transformed into P–H bonds by samarium di-iodide and that coupling reactions with activated alkyl halides give rise to tertiary phosphine oxides or sulfides.[9] In other respects, we explored the reactivity of bis(cyclopentadienyl)samarium ($SmCp_2$) and found some differences compared with the behaviour of SmI_2.[10] $SmCp_2$ especially reduces halogenated derivatives and mediates Barbier reactions under milder conditions. Another interest is in its ability to stabilize intermediates as acyl, benzyl, allyl and alkyl complexes, allowing the realization of sequential reactions instead of Barbier-type reactions.[11,12] We have now compared the reactivities of SmI_2 and $SmCp_2$ for coupling reactions involving phosphorus derivatives and found that $SmCp_2$ is superior to SmI_2 for the preparation of tertiary phosphine oxides in most cases.

Divalent reagents SmI_2 and $SmCp_2$ were first used in the reduction of diphenylphosphinoyl chloride to diphenylphosphine oxide, **3** (Scheme 1). They gave similar yields (50–60%) but reaction was more rapid for the bisyclopentadienylsamarium. Coupling reactions with benzyl chloride mediated by SmI_2 and $SmCp_2$ afford better



Scheme 1

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yields by *sequential* rather than by Barbier procedures. It is noteworthy that the Grignard procedure allows the use of reactive electrophiles in the reaction induced by divalent samarium.[11-14] Diphenylphosphinoyl chloride is added to the divalent samarium compound in THF at room temperature; at the end of the addition the colour of the reaction mixture has turned from blue to blue–green when SmI_2 is used, from purple to black with $SmCp_2$. The intermediate compound **1** is formed, and an electrophile is then introduced as indicated in Scheme 1. Benzyl chloride as well as 1-hexyl bromide and 1-heptyl iodide give better yields of phosphine oxides **2** using $SmCp_2$ and a sequential procedure rather than with samarium di-iodide. The coupling reactions with diphenylphosphinoyl chloride and various electrophiles induced by $SmCp_2$ are shown in Table 1.

This method allows the preparation of phosphine oxides **2** under mild conditions with moderate to good yields. Reactions are easier with RX' where R is a primary alkyl group; iodide, bromide, tosylate or triflate can be used as leaving groups (entries 1–6, Table 1). Reactions are more difficult when R is a secondary alkyl group. 2-Propyl iodide and 2-octyl iodide lead to the corresponding phosphine oxides (Table 1, entries 7 and 8) but all attempts to react the phosphorus intermediate with cyclohexyl iodide or tosylate failed (Table 1, entry 9). Phenyl iodide or β-bromostyrene gives no coupling product. We examined the reactivity of an α-bromoketone and obtained selectively the β-ketophosphine oxide **2** (R = t-BuCOCH$_2$) without any product arising from attack on the keto group (Table 1, entry 12). When epoxypropane is added to the samarium species **1**, opening of the epoxide ring on the less-substituted side is observed, yielding the β-hydroxyphosphine oxide **4** (Table 1, entry 13 and Scheme 2).

Reaction of 2-hexen-4-one with the intermediate species **1** gives the γ-ketophosphine oxide **5** (Scheme 3) resulting from an 1,4-addition on the α,β-unsaturated ketone. The phosphine oxide is obtained smoothly after 1 h at room temperature. For this Michael reaction, $SmCp_2$ and SmI_2 give the γ-ketophosphine oxide with similar yields. Reactivity and yield compare well with known procedures involving $[R_2PO^-]M^+$ (M = Na, MgX).[15]

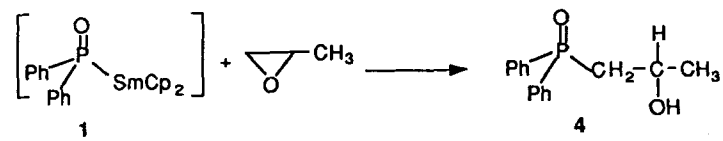
Two equivalents of SmX_2 are required for the formation of **2**. The first step is probably the reduction of the diphenylphosphinoyl chloride to give a phosphinoyl radical ($Ph_2PO^\cdot$) which is then reduced by a second samarium(II) complex to the samarium intermediate **1**. Little is known about the structure of such anions. Metallophosphine oxide complexes of niobium and tantalum have been prepared but their structure was not extensively studied.[16] Diorganothioxophosphorus transition-metal complexes exist with an η^2 structure **6**,[17] and analogous sodium salts have a phosphite structure **7**.[18] Similar η^1 or η^2 structures can

Table 1 Preparation of phosphine oxides **2**, **4** and **5** mediated by $SmCp_2$

Entry	R	X	Temp. (°C)	Yield (%)[a]
1	$PhCH_2$	Cl	25	80
2	$CH_2{=}CHCH_2$	Br	25	87
3	n-C_6H_{13}	Br	66	55
4	n-C_7H_{15}	I	25	56
5	n-$C_{12}H_{25}$	OTs	66	67
6	n-C_5H_{11}	OTf	25	74
7	i-C_3H_7	I	66	50
8	$CH_3CHC_6H_{13}$	OTs[b]	66	66
9	Cyclohexyl	I, OTs	66	0
10	Ph	I	25	0
11	PhCH=CH	Br	25	0
12	t-BuCOCH$_2$	Br	25	44
	Reagents			
13	*dl*-Epoxypropane + **1**		25	57
14	2-Hexen-4-one + **1**		25	65[c]

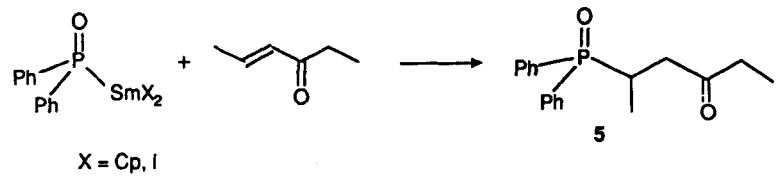
Abbreviations: Ts, tosyl; Tf, triflyl (trifluoromethanesulphonyl).

[a] Isolated yield %; see text for experimental details. [b] In this experiment, $SmCp_2$ prepared from NaCp and SmI_2 was not separated from NaI;[29] at the end of the reaction, residual 2-octyl iodide was isolated. [c] 75% yield if $SmCp_2$ is replaced by SmI_2.



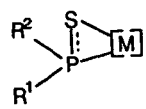
1 4

Scheme 2

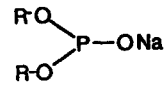


Scheme 3

be proposed for intermediate **1**. Both species may exhibit nucleophilic behaviour at phosphorus.



6



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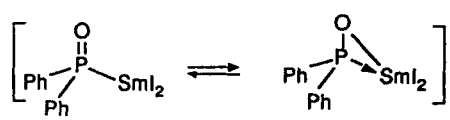
Lanthanide phosphide complexes with samarium, lutetium and lanthanum have been described but phosphinoyl complexes are not known, to the best of our knowledge.[19–22] Phosphine oxides are good ligands for lanthanide complexes and oxygen is coordinated to the metal as shown by RX and ^{31}P NMR studies. In an ytterbium complex, the bifunctional $[OPPh_2C_5H_4]^-$ ligand is coordinated by oxygen rather than by cyclopentadienyl.[23,24] We examined the intermediates **1** obtained from SmI_2 (**1a**) and from $SmCp_2$ (**1b**) by ^{31}P NMR. With SmI_2 two peaks (δ 40.9 and 19.08 ppm) were observed, while $SmCp_2$ leads to only one peak (δ 19.4 ppm). This could be explained in the case of **1a** by an equilibrium between phosphinoyl and phosphinite species (Scheme 4).

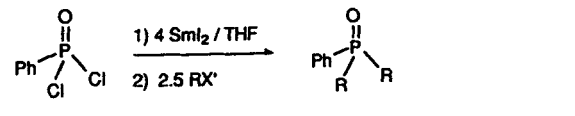
In **1b** the cyclopentadienyl ligand should stabilize the samarium-phosphorus bond as it does for samarium–carbon bonds, thereby explaining the better results obtained with $SmCp_2$ compared with SmI_2.

The reactivity of phenylphosphonoyl dichloride with SmI_2 was also explored. At room temperature, when two equivalents of SmI_2 were used (followed by addition of the halogenated derivative) a mixture of products was observed, but four equivalents of SmI_2 followed by addition of benzyl chloride or allyl chloride gave dibenzylphenylphosphine oxide **8** and diallylphenylphosphine



1a

Scheme 4



8 R = $PhCH_2$ 70% yield

9 R = CH_2=$CHCH_2$ 60% yield

Scheme 5

oxide **9** respectively (Scheme 5). The reaction with alkyl iodides or 1,5-di-iodopentane failed to give the corresponding tertiary phosphine oxides in good yields.

Recent preparations of phosphine oxides by substitution reactions based on nucleophilic phosphorus, in particular $[R_2PO^-]$, have been reported but they need very harsh bases or reducing agents.[25–27] SmI_2 and $SmCp_2$, which are used under milder conditions and are very selective reagents, may increase the interest of this synthetic route. The Michael addition using SmI_2 and α,β-unsaturated ketones is also a promising route to β-ketophosphine oxides. The structure of the intermediate phosphorus species and further developments of these reactions with other classes of electrophiles are currently under investigation, especially in the area of chiral phosphines.[28]

EXPERIMENTAL

Preparation of phosphine oxides 2

In a typical experiment, a solution of diphenylphosphinoyl chloride (2 mmol, 473 mg) in 20 ml THF is added with a syringe pump to a suspension of 5 mmol of $SmCp_2$[29] in 75 ml THF, in 15 min, under argon. At the end of the addition, the reaction mixture turns black and a solution of benzyl chloride (2.5 mmol, 316 mg) in 2 ml THF is rapidly released into it, giving a yellow colour. After one day at room temperature the mixture is

hydrolysed with 0.1 M HCl, extracted with CH_2Cl_2, and washed with water and brine. The crude product **2** (R = n-C_7H_{15}) is purified by flash chromatography on silica gel, using as eluent CH_2Cl_2/AcOEt (70:30). Yield 467 mg, 80%.

^{1}H NMR (TMS as internal standard, $CDCl_3$): δ (ppm) 7–7.8 (m, 15H); 3.7 (d, ^2JPH = 14 Hz, 2H).
^{31}P NMR (85% H_3PO_4 as external standard, $CDCl_3$): δ (ppm) 29.5.
MS (electron impact, 70 eV): 291 (23) $M-1$; 201 (100); 183 (3); 77 (11).

Spectroscopic data of some other phosphine oxides

2 (*R = allyl*)
^{1}H NMR: δ (ppm) 7.3–7.7 (m, 10H); 5.7 (m, 1H); 5 (m, 2H); 3 (dd, ^2JPH = 14.5 Hz, ^3JHH = 8 Hz, 2H).
^{31}P NMR: δ (ppm) 30.0.
MS: 242 (13) M^+; 227 (1); 201 (100); 183 (3); 153 (2); 77 (21); 51 (8).

2 (*R = i-Pr*)
^{1}H NMR: δ (ppm) 7.4–7.8 (m, 10H); 2.3 (sept., ^3JHH = 7.4 Hz, 1H); 1.2 (dd, ^3JPH = 16 Hz, ^3JHH = 7.4 Hz, 6H).
^{31}P NMR: δ (ppm) 37.0.
MS: 244 (2) M^+; 201 (100); 183 (4); 155 (4); 77 (16); 47 (8).

Preparation of phosphine oxide 5

A solution of diphenylphosphinoyl chloride (2 mmol, 473 mg) in 20 ml THF is slowly added to a 0.1 M solution of SmI_2 in THF[29] (4.2 mmol, 42 ml), under argon. The solution turns green–blue at the end of the addition. 2-Hexen-4-one (3.4 mmol, 333 mg) is dropped by syringe and the reaction mixture becomes immediately yellow. After 2 h at room temperature the mixture is treated as described above and purified by flash chromatography on silica gel; eluent CH_2Cl_2/AcOEt (90:10). Yield 454 mg, 75%.

^{1}H NMR: δ (ppm) 7.3–7.9 (m, 10H); 3.1 (m, 1H); 2.6 (m, 2H); 2.3 (q, ^3J HH = 7.2 Hz, 2H); 1.05 (dd, ^3JPH = 17 Hz, ^3JHH = 7 Hz, 3H); 0.9 (t, ^3J HH = 2 Hz, 3H).
^{31}P NMR: δ (ppm) 37.5.
MS: 300(2) M^+; 285 (1); 271 (22); 258 (33); 243 (7); 230 (4); 219 (10); 202 (100); 183 (6); 155 (6); 125 (5); 77 (24); 69 (15); 47 (15).

Preparation of phosphine oxide 8

A solution of phenylphosphonyl dichloride (2.5 mmol, 487 mg) in 10 ml THF is added by a syringe pump within 15 min to a 0.1 M solution of SmI_2 in THF (10 mmol, 100 ml), under argon. The reaction mixture turns blue–green. After 10 min a solution of benzyl chloride (6.5 mmol, 822 mg) in 10 ml THF is added within 15 min. After 1 h a green–yellow suspension appears; after 10 h at room temperature the mixture is treated as described above and purified by flash chromatography on silica gel; eluent AcOEt. Yield 535 mg, 70%).

^{1}H NMR: δ (ppm) 7–7.5 (m, 15H); 3.3 (d, ^2JPH = 13.5 Hz, 4H).
^{31}P NMR: δ (ppm) 32.0.
MS: 290 (100) $M-16$; 199 (100); 183 (12); 165 (50); 152 (12); 122 (12); 91 (62); 77 (33).

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