Synthesis of novel phosphinamide phosphoramidate conjugates with possible applications in catalysis

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INTRODUCTION

This work aims to extend the chemistry of phosphinamides ortho lithiated and phosphoramidates, leading to the new derivatives **6a-e** and **7a-e** in order to investigate their usefulness as ligands di-, tri- and tetradentate towards Y^{3+} and lanthanides (La^{3+}, Sm^{3+} and Eu^{3+}), as well as the application in catalysis[1].

RESULTS AND DISCUSSION

The intermediates mono- and di-imines **4** and **5** were synthesized by refluxing the aminoalkylphosphoramidates **1** with appropriate amounts of the mono- and di-formilated phosphinamides **2** and **3** in methanol[2] **(Figure 1)**. Curiously the reaction failed for **4b** and **5b** (n=3).

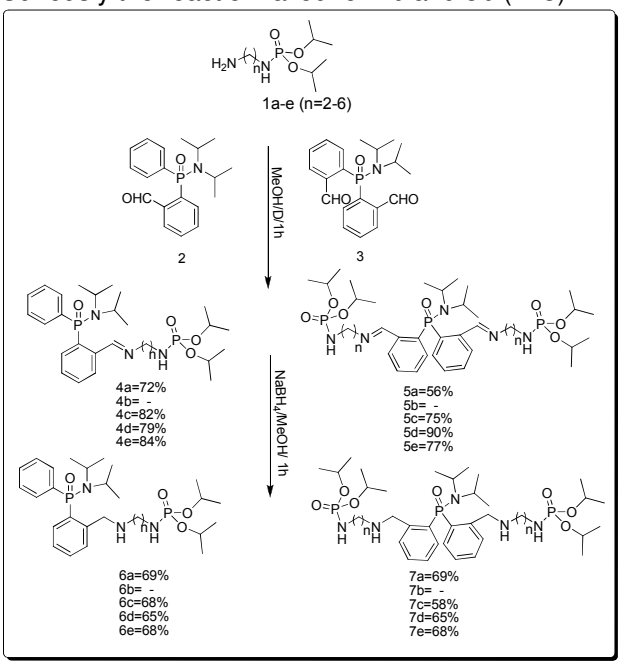

Figure 1. Synthetic route to new phosphinamide phosphoramidate conjugates (**6a-e** and **7a-e**).

The mono and diimines were subsequently reduced with $NaBH_4$/methanol at room temperature[3], generating the corresponding new amines **6** and **7** in yields ranging from 65-69% and 58-69%, respectively. Table 1 resumes the principal NMR assignments for the synthesized amines **6** and **7**.

Table 1. ^{1}H- and ^{31}P-NMR assignments for **6** and **7** ($CDCl_3$).

	NMR (δ in ppm, *J* in Hz)	
	^{31}P	^{1}H
6a	34,29 (s, 1 P) 8,06 (s, 1P)	7,68 (m, 2H), 7,56-7,24 (m, 6H), 4,53 (m, 2H), 4,00 (m, 1H) 3,89 (m, 1H) 3,72 (m, 1H) 3,44 (m, 2H), 2,99 (m, 2H), 2,57 (m, 2H), 1,31-1,07 (m, 18H).
6c	34,46 (s, 1 P) 8,11 (s, 1 P)	7,74-7,62 (m, 2H), 7,52-7,33 (m, 6H), 7,22 (m 1H), 4,59-4,46 (m, 2H), 4,03 (m, 1H) 3,71 (m, 1H) 3,53-3,30 (m, 2H) 2,79 (m, 2H), 2,43 (m, 2H), 1,41 (m, 4H), 1,28-1,14 (m, 22H).
6d	34,55 (s, 1 P) 8,02 (s, 1 P)	7,76-7,69 (m, 2H), 7,56-7,41 (m, 7H) 4,65-4,51 (m, 2H), 4,11 (d, 1H, J= 12,88) 3,76 (d, 1H, J= 13,04) 3,56-3,38 (m, 2H) 2,94-2,81 (m, 2H), 2,55-2,40 (m, 4H), 2,16-2,03 (m, 4H), 1,54-1,38 (m, 4H), 1,34-1,18 (m, 27H).
6e	34,52 (s, 1 P) 8,00 (s, 1 P)	7,68-7,61 (m, 2H), 7,49-7,34 (m, 6H) 4,57-4,46 (m, 2H), 4,03 (d, 1H, J= 12,73) 3,69 (d, 1H, J= 12,87) 3,40 (m, 3H) 2,85-2,73 (m, 3H), 2,45-2,32 (m, 3H), 1,40 (m, 6H), 1,25-1,19 (m, 25 H), 1,13-1,11 (m, 5H).
7a	28,90 (s, 1 P) 8,62 (s, 2 P)	7,80-7,51 (m, 8H), 4,75 (m, 2H), 4,37 (m, 4H), 3,92 (m, 1H), 3,66 (m, 1H) 2,74 (m, 4H) 2,27 (m, 1H), 1,97 (m, 1H), 1,22-1,12 (m, 45H).
7c	38,84 (s, 1 P) 8,23 (s, 2 P)	7,85 (m, 1H), 7,49 (m, 4H), 7,24 (m, 3H), 4,57 (m, 4H), 4,12 (m, 2H), 3,70 (m, 2H), 3,44 (m, 2H) 3,21 (m, 2H) 2,84 (m, 4H), 2,50 (m, 5H), 1,46 (m, 8H) 1,33-1,21 (m, 44H).
7d	38,62 (s, 1 P) 8,15 (s, 2 P)	7,49 (m, 4H), 7,24 (m, 4H), 4,57 (m, 4H), 4,12 (m, 2H), 3,72 (m, 2H), 3,43 (m, 2H) 2,82 (m, 4H) 2,48 (m, 6H), 1,44 (m, 10H) 1,33-1,21 (m, 40H).
7e	38,76 (s, 1 P) 8,75 (s, 2 P)	7,42 (m, 4H), 7,18 (m, 4H), 4,54 (m, 4H), 3,69 (d, 2H) 3,39 (m, 2H) 2,81 (m, 4H) 2,45 (m, 8H), 1,40 (m, 12H) 1,29-1,25 (m, 44H).

CONCLUSION

Eight new molecules were synthesized in this work (**6a,c,d,e** and **7a,c,d,e**). The compounds were fully characterized by IR spectroscopy, ^{31}P-NMR, ^{1}H-NMR and ^{13}C-NMR and HRMS. Complexation tests with ligands **6** and **7** and Zn^{+2}, Y^{+3} and Cu^{+2} are in progress.

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