

## Technology Offer

**N-substituted pyridiniophosphines, processes for their preparation and their use**

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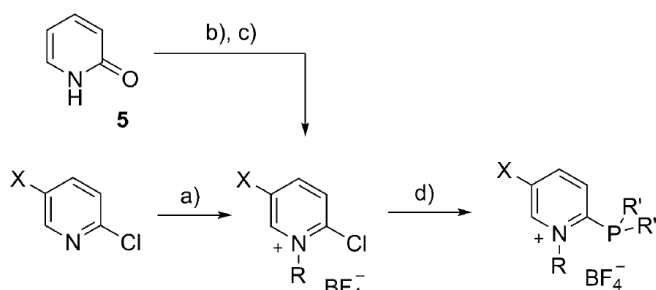
**We offer a new family of cationic ligands, namely N-alkyl/aryl pyridiniophosphines. The ligands can be synthesized through a short, scalable, and highly modular route. Evaluation of their electronic properties evidenced weak  $\sigma$ -donor and quite strong  $\pi$ -acceptor character when used as ancillary ligands.**

**Background**

In coordination chemistry, typical ancillary ligands are anionic or neutral species. Cationic ones are exceptions and, when used, the positively charged groups are normally attached to the periphery and not close to the donating atom. Recently a growing number of studies indicate that cationic ligands depict excellent  $\pi$ -acceptor character that can exceed that of phosphites or polyfluorinated phosphines. This property has been used to increase the Lewis acidity of the metals they coordinate.

**Technology**

A new family of cationic ligands, N-alkyl/aryl pyridiniophosphines, has been synthesized through a short, scalable, and highly modular route.

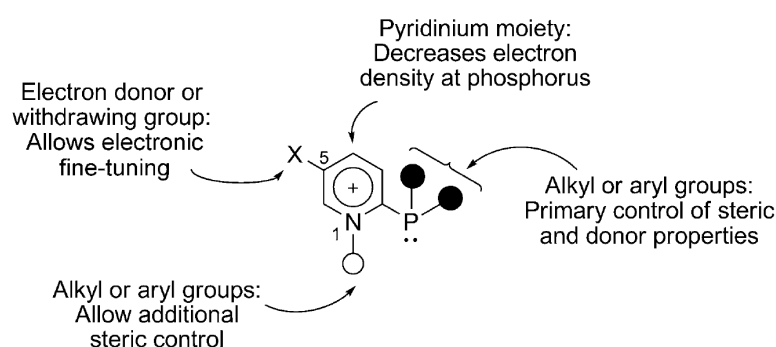


- |                        |                                  |  |
|------------------------|----------------------------------|--|
| 1; X = H               | 6; X = H; R = Me                 | 12; X = H; R = Me; R' = Ph   |
| 2; X = F               | 7; X = H; R = Ph                 | 13; X = H; R = Me; R' = Cy   |
| 3; X = CF <sub>3</sub> | 8; X = F; R = Me                 | 14; X = H; R = Ph; R' = Ph   |
| 4; X = OMe             | 9; X = CF <sub>3</sub> ; R = Me  | 15; X = F; R = Me; R' = Ph   |
|                        | 10; X = CF <sub>3</sub> ; R = Et | 16; X = CF <sub>3</sub> ; R = Me; R' = Ph                              |
|                        | 11; X = OMe; R = Me              | 17; X = F; R = Me; R' = Cy   |
|                        |                                  | 18; X = OMe; R = Me; R' = Cy   |
|                        |                                  | 19; X = CF <sub>3</sub> ; R = Et;                                      |
|                        |                                  | R' = 3,5-(CF <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> |

**Scheme 1. Synthesis of pyridinium-substituted phosphines.**
**Reagents and conditions (yields):**

- a) Me<sub>3</sub>OBF<sub>4</sub> or Et<sub>3</sub>OBF<sub>4</sub>, CH<sub>2</sub>Cl<sub>2</sub>, RT; **6** (91%); **8** (99%); **9** (99%); **10** (98%); **11** (89%);  
 b) **5** (1.2 equiv), iodobenzene (1 equiv), CuBr (10 mol%), Cs<sub>2</sub>CO<sub>3</sub> (2.1 equiv), DMSO, 60°C, (95%);  
 c) oxalyl chloride (3 equiv), Cl(CH<sub>2</sub>)<sub>2</sub>Cl, and then NaBF<sub>4</sub> (4 equiv), (71%);  
 d) diaryl/dialkylphosphine (2 equiv), THF, 65°C; 1–3 days; **12** (70%), **13** (80%); **14** (71%); **15** (43%); **16** (60%); **17** (77%); **18** (89%); **19** (30%).

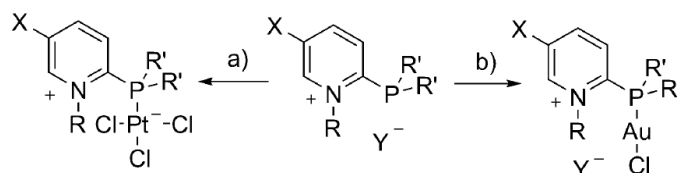
Evaluation of their electronic properties evidenced weak  $\sigma$ -donor and quite strong  $\pi$ -acceptor character when used as ancillary ligands.



**Figure 1. Structural features of pyridinium-substituted phosphines and their impact on the donor properties of the resulting ligand**



These attributes confer a substantially enhanced  $\pi$ -acidity to the  $\text{Pt}^{\text{II}}$  and  $\text{Au}^{\text{I}}$  complexes thereof derived and, as result, they depict an improved ability to activate alkynes towards nucleophilic attack.

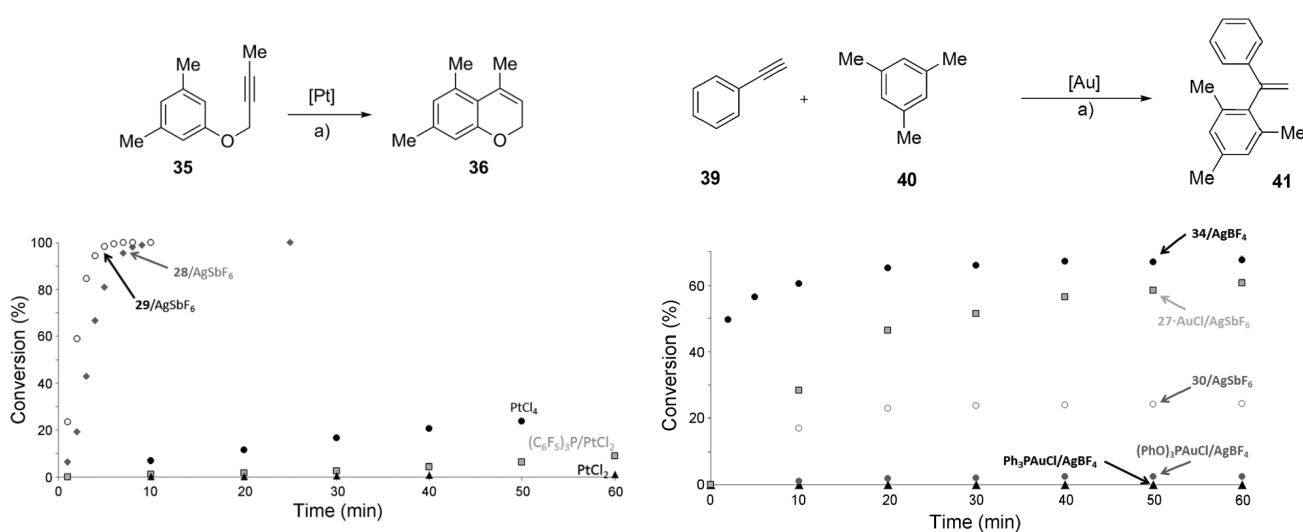


**Scheme 2. Synthesis of Pt and Au complexes**  
Reagent and conditions (yields):  
a)  $\text{K}_2\text{PtCl}_4$  (1.0 equiv),  $\text{CH}_3\text{CN}$ , RT; **28** (80%); **29** (40%);  
b)  $(\text{Me}_2\text{S})\text{AuCl}$  (1.0 equiv),  $\text{CH}_2\text{Cl}_2$ , RT; **30** (97%);  
**31** (69%); **32** (98%); **33** (98%); **34** (51%)

**28**; X = H; R = Me; R' = Ph  
**29**; X =  $\text{CF}_3$ ; R = Me; R' = Ph

**30**; X = H; Y =  $\text{BF}_4^-$ ; R = Me; R' = Ph  
**31**; X = H; Y =  $\text{BF}_4^-$ ; R = Ph; R' = Ph  
**32**; X = F; Y =  $\text{BF}_4^-$ ; R = Me; R' = Ph  
**33**; X =  $\text{CF}_3$ ; Y =  $\text{BF}_4^-$ ; R = Me; R' = Ph  
**34**; X =  $\text{CF}_3$ ; Y =  $\text{SbF}_6^-$ ; R = Et;  
R' = 3,5-( $\text{CF}_3$ ) $_2\text{C}_6\text{H}_3$

This superior performance has been demonstrated along several mechanistically diverse  $\text{Pt}^{\text{II}}$ - and  $\text{Au}^{\text{I}}$  catalyzed transformations.



**Figure 2. Ligand effect on the Pt-catalyzed hydroarylation of propargyl aryl ether **35** to chromene **36**.** Reagents and conditions: **35** (0.05m), Pt precatalysts (2 mol%),  $\text{AgSbF}_6$  (2 mol%),  $(\text{CH}_2)_2\text{Cl}_2$ , 80°C.

**Figure 3. Ligand effect on the Au-catalyzed hydroarylation of alkyne **39** with arene **40**.** Reagents and conditions: **39** (0.05m), **40** (4 equiv; 0.2m) AuI precatalysts (5 mol%),  $\text{AgBF}_4$  or  $\text{AgSbF}_6$  (5 mol%),  $(\text{CH}_2)_2\text{Cl}_2$ , 60°C.

## Literature

Hendrik Tinnemann, Christian Wille, Manuel Alcarazo: "Synthesis, Structure, and Applications of Pyridinophosphines", *Angew. Chem. Int. Ed.* 2014, 53, 8732–8736

## Patent Information

EP priority patent application filed in April 2014.  
PCT patent application filed in April 2015.