



Technology Offer

N-substituted pyridiniumphosphines, processes for their preparation and their use

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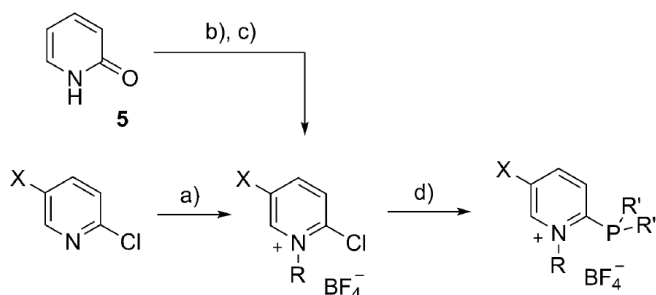
We offer a new family of cationic ligands, namely N-alkyl/aryl pyridiniumphosphines. The ligands can be synthesized through a short, scalable, and highly modular route. Evaluation of their electronic properties evidenced weak σ -donor and quite strong π -acceptor character when used as ancillary ligands.

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 π -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 pyridiniumphosphines, has been synthesized through a short, scalable, and highly modular route.



1; X = H
2; X = F
3; X = CF₃
4; X = OMe

6; X = H; R = Me
7; X = H; R = Ph
8; X = F; R = Me
9; X = CF₃; R = Me
10; X = CF₃; R = Et
11; X = OMe; R = Me

12; X = H; R = Me; R' = Ph
13; X = H; R = Me; R' = Cy
14; X = H; R = Ph; R' = Ph
15; X = F; R = Me; R' = Ph
16; X = CF₃; R = Me; R' = Ph
17; X = F; R = Me; R' = Cy
18; X = OMe; R = Me; R' = Cy
19; X = CF₃; R = Et;
R' = 3,5-(CF₃)₂C₆H₃

Scheme 1. Synthesis of pyridinium-substituted phosphines.

Reagents and conditions (yields):

- a) Me₃OBF₄ or Et₃OBF₄, CH₂Cl₂, RT; **6** (91 %); **8** (99 %); **9** (99 %); **10** (98 %); **11** (89 %);
b) **5** (1.2 equiv), iodobenzene (1 equiv), CuBr (10 mol %), Cs₂CO₃ (2.1 equiv), DMSO, 60 °C, (95 %);
c) oxalyl chloride (3 equiv), Cl(CH₂)₂Cl, and then NaBF₄ (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 σ -donor and quite strong π -acceptor character when used as ancillary ligands.

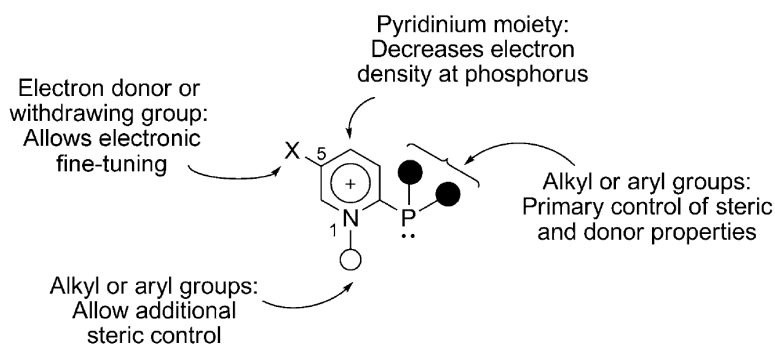
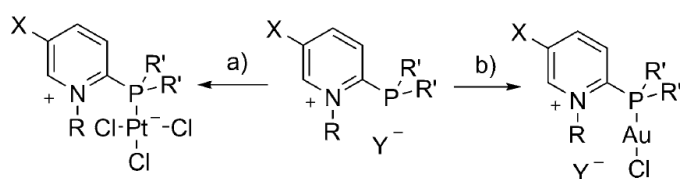


Figure 1. Structural features of pyridinium-substituted phosphines and their impact on the donor properties of the resulting ligand

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



28; X = H; R = Me; R' = Ph
29; X = CF₃; R = Me; R' = Ph

30; X = H; Y = BF₄; R = Me; R' = Ph
31; X = H; Y = BF₄; R = Ph; R' = Ph
32; X = F; Y = BF₄; R = Me; R' = Ph
33; X = CF₃; Y = BF₄; R = Me; R' = Ph
34; X = CF₃; Y = SbF₆; R = Et;
R' = 3,5-(CF₃)₂C₆H₃

Scheme 2. Synthesis of Pt and Au complexes

Reagent and conditions (yields):
a) K₂PtCl₄ (1.0 equiv), CH₃CN, RT; **28** (80%); **29** (40%);
b) (Me₂S)AuCl (1.0 equiv), CH₂Cl₂, RT; **30** (97%); **31** (69%); **32** (98%); **33** (98%); **34** (51%)

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

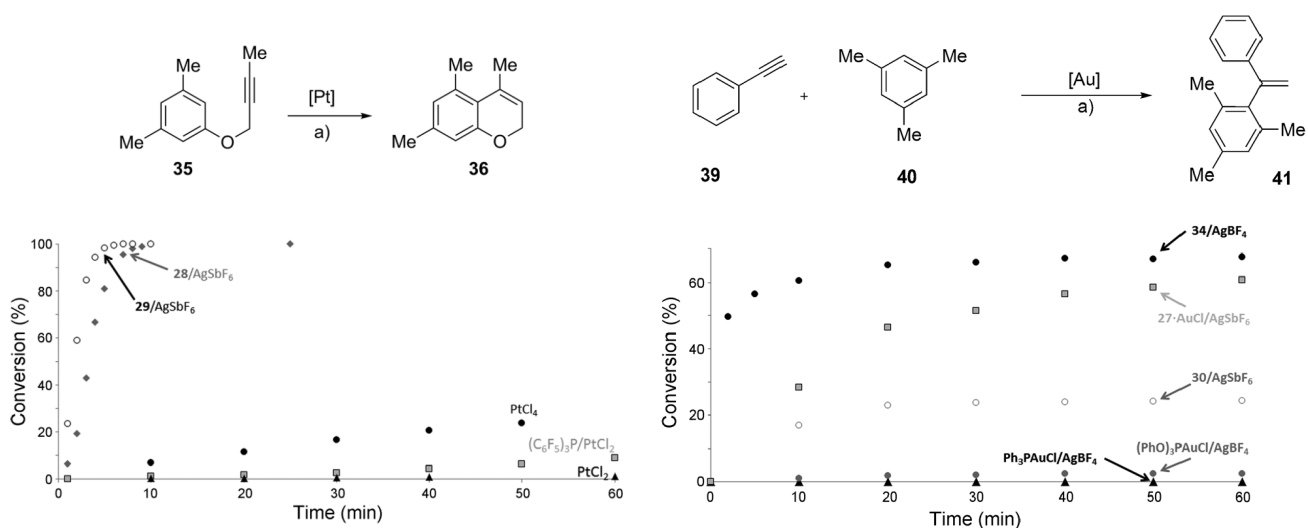




Figure 2. Ligand effect on the Pt-catalyzed hydroarylation of propargyl aryl ether **35** to chromene **36**.
Reagents and conditions: **35** (0.05m), Pt precatalysts (2 mol%), AgSbF₆ (2 mol%), (CH₂)₂Cl₂, 80°C.

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) Aul precatalysts (5 mol%), AgBF₄ or AgSbF₆ (5 mol%), (CH₂)₂Cl₂, 60°C.

Literature

Hendrik Tinnermann, Christian Wille, Manuel Alcarazo: "Synthesis, Structure, and Applications of Pyridiniophosphines", *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.