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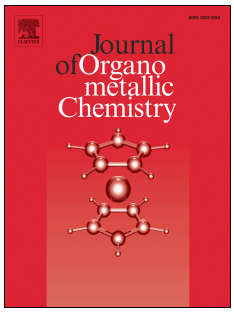

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SCS Indenediide Pincer Complexes: Zr to Pd and Pt Transmetallation

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Abstract

A new synthetic methodology based on transmetallation was developed for the preparation of SCS indenediide pincer complexes. Upon reaction of the 1,3-bis(thiophosphinoyle)indene **1** with $[Zr(NMe_2)_4]$, C_{sp3}-H activation proceeds readily to give the new complex **2**. Thermolysis at 100°C for 5 hours then affords the SCS pincer complex **3**. Complex **2** can be stored under inert atmosphere for several weeks without decomposition. It is much more stable than **3** and was thus used as precursor to study transmetallation. Zr to Pd / Pt Transmetallation occurs rapidly and cleanly at room temperature. Accordingly, the pincer complexes **4**, **5**, **7** and **8** with triphenylphosphine or chloride as co-ligand were obtained in good to excellent yields under mild conditions.

Keywords: Transmetallation, pincer complexes, zirconium, palladium, platinum

1. Introduction

Since the first report of Moulton and Shaw in 1976,[1] pincer complexes have emerged as a very useful class of complexes.[2] The central M-C bond is strengthened by the coordination of the two lateral donor groups and pincer complexes display a unique stability / reactivity balance. Besides their interest in material science[3] and pharmacology,[4] pincer complexes are extremely powerful catalysts for a myriad of important transformations.[5] In particular, spectacular achievements have been reported over the last decade taking advantage of metal-ligand cooperativity.[6]

In this respect, we recently described a new family of pincer complexes based on the indene skeleton bearing two donor groups (thiophosphinoyle $R_2P{=}S$ or phosphazene $R_2P{=}NR'$) in the 1 and 3 positions.[7] Thanks to these two coordinating groups, the very rare in-plane σ coordination is favored with early (Zr) as well as late (Pd,Pt) transition metals. The non-innocent behavior of the indenediide ligand was illustrated by stoichiometric reactions with organic and metallic electrophiles.[8] In addition, thanks to metal-ligand cooperativity, the Pd and Pt SCS indenediide complexes showed unprecedented catalytic performance in the cycloisomerization of alkynoic acids and *N*-tosylalkynylamides.[9]

All these indenediide complexes have been prepared by sequential double C-H activation of the corresponding proligands (Chart 1).[10] Although straightforward and quite efficient, this route usually requires long reaction times and/or heating, and the desired complexes are obtained in good but not excellent yields (~ 60-70%). We thus wondered about alternative strategies that may operate under milder