

Synthesis of fluorous sulfur/carbon/sulfur pincer ligands and palladium complexes: New catalyst precursors for the Heck reaction

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Dedicated with affection to Prof. Dr. Robert J. Angelici, whose fundamental studies of complexes of sulfur donor ligands have inspired many of our own efforts over the last 30 years.

Abstract

Reactions of 1,3-C₆H₄(CH₂Br)₂ and the thiols HSCH₂CH₂R_{fn} (R_{fn} = (CF₂)_{n-1}CF₃; n = 8, 10), or the dithiol 1,3-C₆H₄(CH₂SH)₂ and ICH₂CH₂R_{fn}, in the presence of carbonate or NaOEt (70–78 °C) give the title ligands 1,3-C₆H₄(CH₂SCH₂CH₂R_{fn})₂ (**4-R_{f8}**, 58–61%; **4-R_{f10}**, 49–50%). Reactions of **4-R_{f8}** and Pd(OC(O)CF₃)₂ or (PhCN)₂Pd(Cl)₂ (80 °C) afford the title complexes (2,6,1-C₆H₃(CH₂SCH₂CH₂R_{fn})₂)Pd(X) (n/X = 8/OC(O)CF₃ (**5-R_{f8}**), 44%; 10/OC(O)CF₃, 58%; 8/Cl (**6-R_{f8}**), 45%; 10/Cl, 79%). Both **5-R_{f8}** and **6-R_{f8}** are effective catalyst precursors for the Heck reaction of iodobenzene and methyl acrylate (0.21–0.23 mol%, DMF, *i*-Pr₂NEt, 100–125 °C). However, no active catalyst can be recycled by a subsequent extraction with fluorous solvents. Rather, activity remains in the reddish DMF phase, and is quenched by the addition of mercury. Palladium nanoparticles are visible by transmission electron microscopy. These, or low valent species derived therefrom, are believed to be the active catalysts, in accord with other recent studies involving related non-fluorous and fluorous palladacycles. The CF₃C₆F₁₁/toluene partition coefficients of representative compounds are determined.

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1. Introduction

Pincer ligands and complexes have attracted wide interest as catalysts and as platforms for unusual stoichiometric chemistry [1]. Many *m*-xylene-derived bis(thioethers) 1,3-C₆H₄(CH₂SR)₂ (**I**) have been prepared and cyclopalladated, giving what are often termed SC(sp²)S pincer systems (**II**; Fig. 1) [2–9]. These have been applied in various catalytic processes, and particularly Heck reactions of alkenes and aryl halides [3–6,8,9]. Not surprisingly, recoverable

or immobilized versions of such pincer complexes have also received considerable attention [3,4,6,7a,7b–9].

We had an ongoing interest in fluorous catalysts [10], for which diverse recovery protocols have now been developed [11]. Such catalysts commonly bear substituents or “ponytails” of the formula (CH₂)_m(CF₂)_{n-1}CF₃, which can be abbreviated (CH₂)_mR_{fn} [12]. However, branched and/or oxygenated ponytails are sometimes employed [12]. Most applications involve a temperature gradient, such that homogenous conditions are realized at higher temperatures, with recovery by liquid/liquid or solid/liquid phase separations at lower temperatures.

Hence, we set out some time ago, in the initial stage of a doctoral dissertation, to prepare fluorous palladium SC(sp²)S pincer complexes, and investigate their utility as

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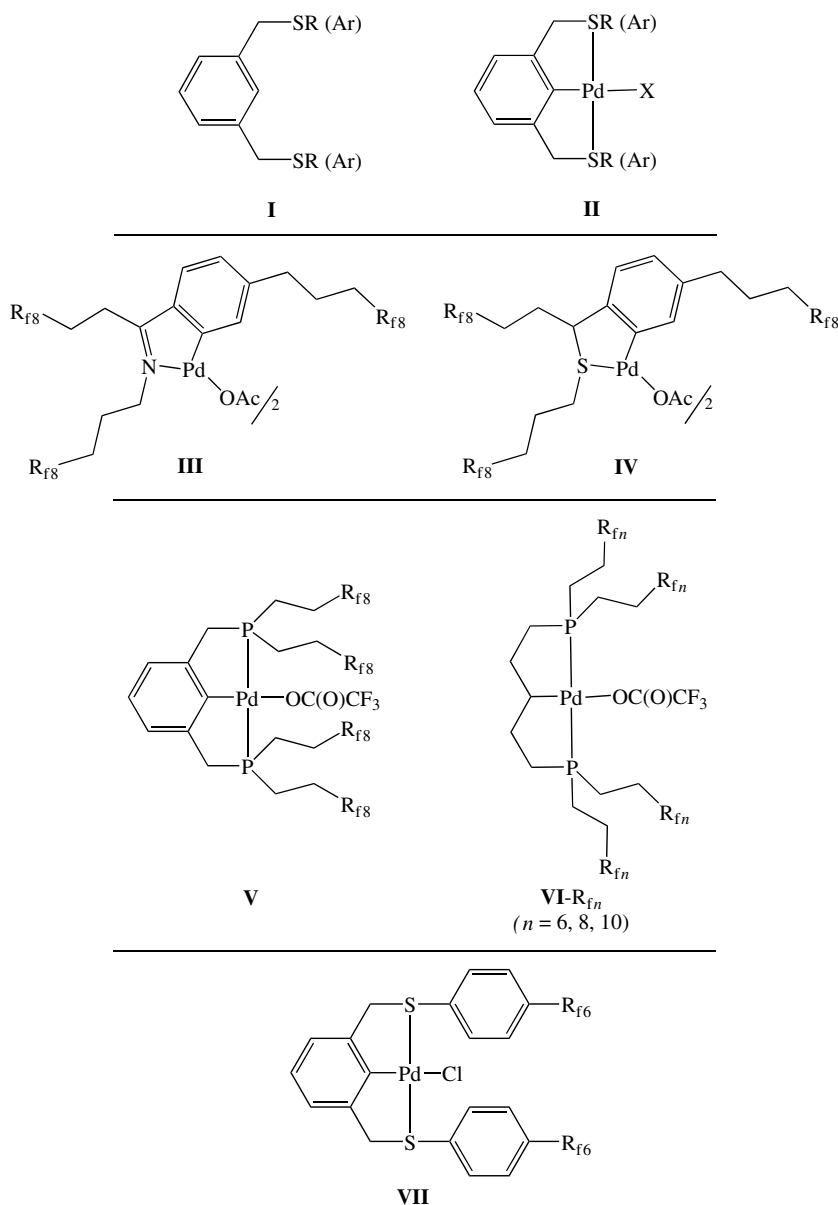


Fig. 1. $SC(sp^2)S$ pincer ligands and palladium complexes (I, II), and previously synthesized fluorous palladacycles (III–VII).

recyclable catalysts for the Heck reaction. This was in part prompted by high-quality studies involving other types of recoverable palladium $SC(sp^2)S$ pincer complexes [3,4] that provided valuable baselines for new systems. However, as the project developed, evidence accumulated that the active catalyst differed greatly from the fluorous catalyst precursor. Parallel conclusions emerged from our studies with the fluorous palladacycles III and IV (Fig. 1) [13]; only material that had never entered the catalytic cycle was recovered. More recently, in-depth mechanistic investigations using non-fluorous palladium $SC(sp^2)S$ pincer complexes have established that a pincer-free form of palladium must be the active catalyst [8,9,14].

In this paper, we describe (1) efficient syntheses of fluorous analogs of I and II, (2) the application of the latter as catalyst precursors for Heck reactions, (3) recycling

experiments, and (4) mechanistic data regarding the active catalysts that complement more extensive studies by other groups [8,9,14]. Additional details are provided elsewhere [15]. Syntheses of the fluorous $PC(sp^2)P$ and $PC(sp^3)P$ pincer complexes V and VI (Fig. 1) have been described in companion publications [16,17]. Importantly, Curran has also prepared a fluorous $SC(sp^2)S$ pincer complex (VII, Fig. 1) and shown it to be an effective precursor for the Heck reaction [6]; his results are further treated in Section 3.

2. Results

2.1. Compound synthesis and characterization

There are two obvious limiting retrosynthetic approaches to pincer ligands I for which R is an *n*-alkyl

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