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Allyl–palladium complexes with fluorinated benzene thiolate ligands. Examination of the electronic effects in the Pd-catalyzed allylic alkylation reaction with the catalytic system $[(\eta^3\text{-}C_3H_5)Pd(\mu\text{-}SR_f)]_2/PR_3$

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Abstract

The bimetallic complexes $[(\eta^3\text{-}C_3H_5)Pd(\mu\text{-}SR_f)]_2$ [$R_f = C_6F_5$, (**1**); C_6F_4H-4, (**2**); C_6H_4F-2, (**3**); C_6H_4F-3, (**4**) and C_6H_4F-4, (**5**)] in the presence of *para*-substituted phosphines $P(C_6H_4X\text{-}4)_3$ [$X = OCH_3$, CH_3, H, F, Cl, and CF_3] are efficient catalytic systems in the allylic alkylation couplings of (*E*)-3-acetoxy-1,3-diphenyl-1-propene and dimethyl malonate. Results concerning the electronic effects of both sulfur and phosphorus substituents in this reaction are discussed.

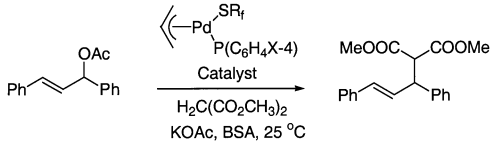
Keywords: Allyl palladium complexes; Allylic alkylation; Fluorothiolate complexes; Electronic effects; Catalysis

1. Introduction

The allylic alkylation reaction is without a doubt one of the most important reactions in organic chemistry for the formation of C–C bonds, and the topic has been the subject of several recent high profile reports [1]. Although impressive yields and turnovers are attained, it can be envisaged that tuning of the ligands sterically and/or electronically will not be a trivial exercise.

Sulfur containing complexes have not been widely used in catalysis due in part to the assumed tendency of sulfur to act as catalyst poison. This is certainly not the case and recently sulfur-containing species have found application in different catalytic processes such as Heck reaction, hydroformylation, etc. [2].

The chemistry of aromatic sterically hindered thiols has been extensively studied in recent years due to the importance that some of its complexes may play as models for active sites in metalloproteins [3]. This is particularly true in the case of nitrogenase, thought to be the key catalyst in the reduction of dinitrogen to ammonia [4]. Among the sterically hindered thiolate ligands, fluorinated benzenethiols have occupied an important place, due to their ability to stabilize unusual geometries, oxidation states and intra- or intermolecular interactions [5]. Some complexes have also been used as highly active catalysts in hydroformylation and polymerization reactions [6] and identified as active intermediates in desulfurization processes [7]. The success of the fluorinated thiols over other sterically hindered thiols lays in the facility with which steric and electronic properties can be tuned by changing fluorine substitution in the aromatic ring [8]. Thus, we wish to report here that $[(\eta^3\text{-}C_3H_5)Pd(\mu\text{-}SR_f)]_2/PR_3$ is an efficient system in the allylic couplings of (*E*)-3-acetoxy-1,3-diphenyl-1-propene and dimethyl malonate (Scheme 1).



Scheme 1.

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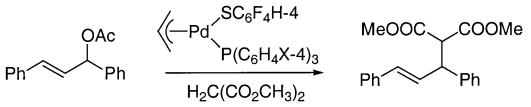
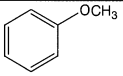
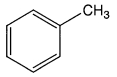
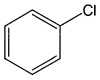
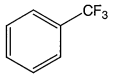
Table 1
Allylic couplings of (*E*)-3-acetoxy-1,3-diphenyl-1-propene and dimethyl malonate using the system $[(\eta^3\text{-}C_3H_5)Pd(\mu\text{-}SR_f)]_2/PR_3$ as catalyst. Effect of the *para*-substituent phosphine vs. % yield



Entry	X	χ_i	% Conversion[a]
1		10.5	96.1
2		11.5	94.2
3		13.3	88.2
4		15.7	66.8
5		16.8	63.5
6		20.2	21.6

[a] Reaction conditions: $[(\eta^3\text{-}C_3H_5)Pd(\mu\text{-}SR_f)]_2/PR_3$ 1:2 molar ratio, the amounts of bimetallic species and phosphine where calculated to yield 3 mg of the monometallic species $[(\eta^3\text{-}C_3H_5)Pd(\mu\text{-}SR_f)(PR_3)]$. (*E*)-3-acetoxy-1,3-diphenyl-1-propene (50.4 mg, 0.2 mmol), dimethyl malonate (68 μL, 0.6 mmol), BSA (148 μL, 0.6 mmol), and KOAc (1 mg) 4 hours reaction time.

The results concerning the electronic effects of both the S and P substituents over these reactions are discussed.

2. Experimental

2.1. General

All manipulations were carried out using standard Schlenk and glovebox techniques under purified Ar. Solvents were degassed and dried using standard procedures. The following were purchased and used without further purification, dimethyl malonate, bis-(trimethylsilyl)acetamide (BSA), fluorinated thiols and phosphines (Aldrich Chemical Co.). The complexes $[(\eta^3\text{-}C_3H_5)Pd(\mu\text{-}SR_f)]_2$ [9] and $[(\eta^3\text{-}C_3H_5)Pd(SR_f)(PR_3)]$ [9] were synthesized as previously described. The ^{1}H-NMR spectra were recorded on a Varian Unity Inova 400 spectrometer. Chemical shifts are reported in ppm down-field of TMS using the solvent as internal standard ($CDCl_3$, δ 7.26 or C_6D_6, δ 7.16). ^{13}C- and ^{31}P-NMR spectra were recorded with complete proton decoupling and are reported in ppm downfield of TMS with the solvent as internal standard ($CDCl_3$, δ 77.0 or C_6D_6, δ 128.4) and external 85% H_3PO_4, respectively. GC analyses were carried out on a HP 5890A chromatograph with a flame ionization detector (FID) and on a HP 5890 Series II with an 5971A mass selective detector gas chromatographs, and a HP-1 capillary column (25.0 m) from Hewlett Packard.

2.2. Allylic alkylation using $[(\eta^3\text{-}C_3H_5)Pd(SR_f)(P(C_6H_4X\text{-}4)_3)]$ [9]

To a solution of $[(\eta^3\text{-}C_3H_5)Pd(SR_f)(P(C_6H_4X\text{-}4)_3)]$ [X = OCH_3, CH_3, H, F, Cl, and CF_3] (3 mg) in CH_2Cl_2 (2 ml), (*E*)-3-acetoxy-1,3-diphenyl-1-propene (50.4 mg, 0.2 mmol), dimethyl malonate (68 μl, 0.6 mmol), BSA (148 μl, 0.6 mmol), and KOAc (1 mg) were added, and the resulting reaction mixture stirred at room temperature (r.t.) for 4 h. After this time, the resulting solution was diluted with ether, washed with water and brine, and then dried over $MgSO_4$. The solvent was evaporated under vacuum to yield an oily residue, which slowly crystallized. Yield >99% of *rac*-PhCH{CH-$(CO_2Me)_2$}CH=CHPh.

2.3. Allylic alkylation using $[(\eta^3\text{-}C_3H_5)Pd(\mu\text{-}SR_f)]_2/PR_3$

To a solution (1 ml, CH_2Cl_2) of $[(\eta^3\text{-}C_3H_5)Pd(\mu\text{-}SR_f)]_2$ [R = C_6HF_4-4 (**2**)] (one equivalent), $[P(C_6H_4X\text{-}4)_3]$ [X = OCH_3, CH_3, H, F, Cl, and CF_3] (two equivalents) in CH_2Cl_2 (1 ml) were added (the amounts of the bimetallic species and phosphine were calculated to yield 3 mg of the monometallic species $[(\eta^3\text{-}C_3H_5)Pd(SR_f)(PR_3)]$, for instance 1.5 mg of the bimetallic complex and 1.5 mg of $[P(C_6H_4X\text{-}4)_3]$ (X = F). The reaction was allowed to proceed for 5 min at r.t. After this time (*E*)-3-acetoxy-1,3-diphenyl-1-propene (50.4 mg, 0.2 mmol), dimethyl malonate (68 μl, 0.6 mmol), BSA (148 μl, 0.6 mmol), and KOAc (1 mg) were added, and the resulting reaction mixture stirred at r.t. for 4 h. After the prescribed reaction time, the resulting solution was diluted with ether, washed with water and brine, and then dried over $MgSO_4$. The solvent was evaporated under vacuum to yield an oily residue, which slowly crystallized. Yield >99% of *rac*-PhCH{CH(CO_2-Me)$_2$}CH=CHPh.

3. Results and discussion

Conditions were found where temperature, reaction time and amount of catalyst are optimal. Using the optimized reaction conditions, experiments with the monometallic complexes $[(\eta^3\text{-}C_3H_5)Pd(\mu\text{-}SR_f)(P(C_6H_4\text{-}X\text{-}4)_3)]$ were performed. The phosphines selected allow

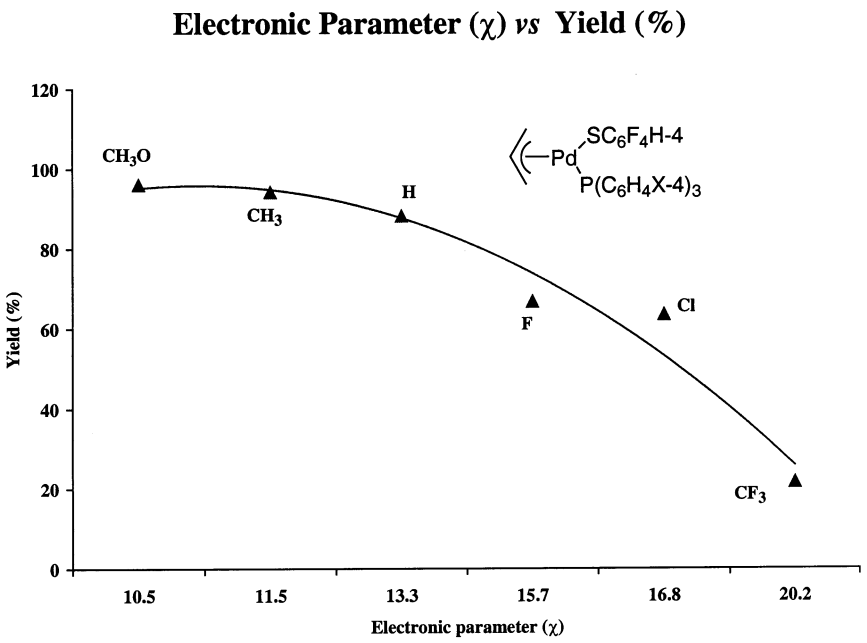


Fig. 1. Correlation between the electronic parameter (χ) of the triarylphosphine and the % yield of the allylic alkylation coupling reactions.

us the fine-tuning of the electronic effects without including any steric contribution. Similarly, the easy access to different commercially-available fluorinated thiols allow us to also examine the electronic effects of the thiolate ligands. The substrate (*E*)-3-acetoxy-1,3-diphenyl-1-propene was considered as the more appropriate allylic precursor for this study, since the added complication of regioselectivity would be zero. In a common experiment, the reactions were allowed to proceed for 4 h; chromatographic analysis of the samples after the prescribed reaction time showed complete conversions in all examined cases.

The fact that the identity of the catalytic precursor is known prompted us to explore the possibility to further simplify our experimental procedure, such that we could avoid the isolation of the monometallic catalytic precursor. Thus, ^{31}P-NMR experiments were carried out where a specific amount of the dimeric complexes $[(\eta^3\text{-}C_3H_5)Pd(\mu\text{-}SR_f)]_2$ was reacted in a 1:2 molar ratio with the corresponding *para*-substituted phosphines and compared with authentic samples of the monomers [9].

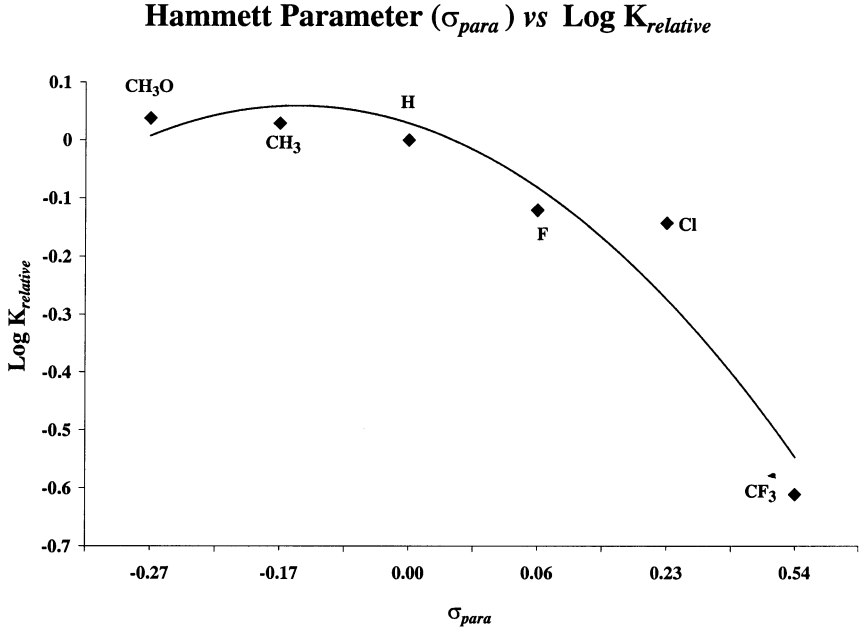


Fig. 2. Hammett correlation between reaction rates and the *para*-substituent in the triarylphosphine.

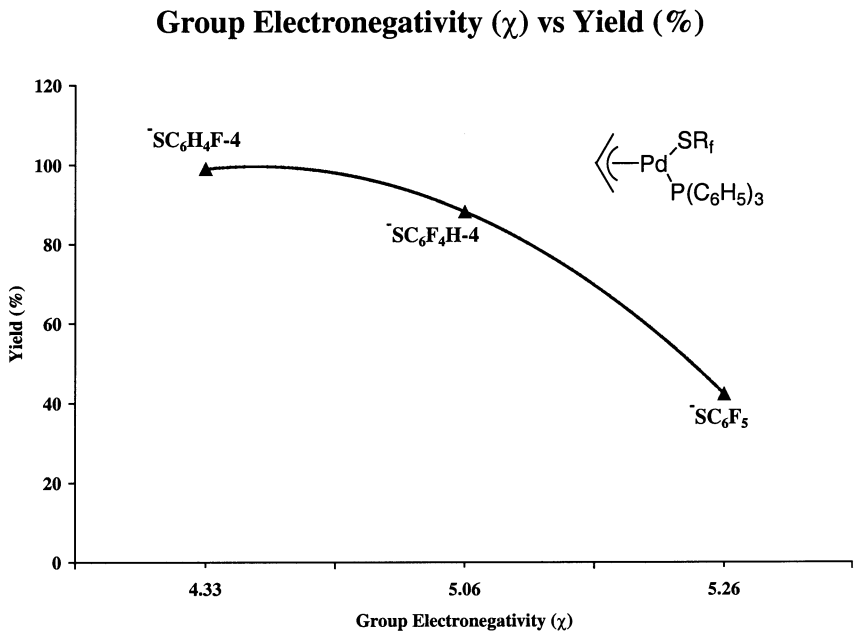


Fig. 3. Correlation between the group electronegativity of the fluorinated thiol and the % yield of the allylic alkylation coupling reactions.

The resulting mixtures showed the fast and quantitative formation of the monometallic species as the unique products.

In view of these results, catalytic experiments involving the preparation in situ of the catalyst precursors were performed. The results obtained showed consistently that high yields can be obtained regardless of the procedure employed. Thus we decided to carry out the whole set of catalysis experiments by the more convenient in situ generation of the catalytic precursors, thus eliminating the preparation, isolation and purification steps for the monometallic complexes. Furthermore, since the dimeric complexes are more stable in the solid state than their monometallic counterparts [9], they can be stored for longer periods of time.

Since all previous experiments have shown quantitative yields, experiments reducing the reaction times to only 1 h were carried out in order to obtain data, which could show us a clear trend in reactivity (Table 1). The results obtained clearly indicate that the systems involving the more electron-rich phosphines are more efficient in the allylic substitution reactions. These results agreed well with the previously observed higher stability conferred to the active species by electron rich phosphines in other palladium catalyzed reactions [10].

To better visualize how the phosphines were affecting the reactions, graphics of yield against the electronic parameter of the phosphine χ [11] (Fig. 1) and relative rate against the Hammet parameters (σ_{para}) [12] (Fig. 2) were obtained. However these graphics do not show a linear trend but a behavior that can be better described as bell-shaped exhibiting a maximum value when $-CH_3$ is the *para*-substituent in the phosphine. This effect has been previously documented by Amatore et al. [13] in oxidative addition reactions to Pd(0) species. They have described this behavior to be caused by two antagonistic effects, the intrinsic reactivity of the catalytic species and their concentration. Thus when the phosphine becomes more electron rich, the active species become more nucleophilic and their intrinsic reactivity increases. However, when the phosphine becomes more electron rich, the concentration of the active species decreases because an equilibrium between the palladium(0) complexes becomes more in favor of less active intermediates. Presumably a similar explanation can be invoked in the present case, thus the arguments presented above would explain the behavior observed in our graphics.

The same behavior (Table 2) can be observed in the graphic of the group-electronegativity of the thiolates [8] versus % yield, where the more basic or less electronegative thiolate occupies the crest of the curve (Fig. 3).

In summary, $[(\eta^3\text{-}C_3H_5)Pd(\mu\text{-}SR_f)]_2/PR_3$ is a highly efficient catalytic system for the allylic alkylation couplings of (*E*)-3-acetoxy-1,3-diphenyl-1-propene and dimethyl malonate. Moreover, the present work offers a couple of possible strategies to fine-tune the electronic effects of a particular catalytic system including thiolates or phosphines.

Acknowledgements

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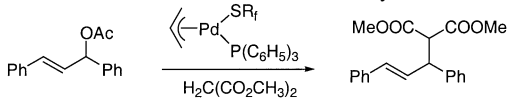
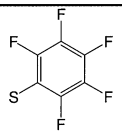
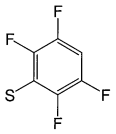
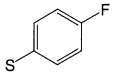
Table 2
Allylic couplings of (*E*)-3-acetoxy-1,3-diphenyl-1-propene and dimethyl malonate using the system $[(\eta^3\text{-}C_3H_5)Pd(\mu\text{-}SR_f)]_2/PR_3$ as catalyst. Effect of the fluorinated thiolate vs. % yield



Entry	SR_f	χ	% Conversion[a]
1		5.26	42.3
2		5.06	88.2
3		4.33	99

[a] Reaction conditions: $[(\eta^3\text{-}C_3H_5)Pd(\mu\text{-}SR_f)]_2/PR_3$ 1:2 molar ratio, the amounts of bimetallic species and phosphine where calculated to yield 3 mg of the monometallic species $[(\eta^3\text{-}C_3H_5)Pd(\mu\text{-}SR_f)(PR_3)]$. (*E*)-3-acetoxy-1,3-diphenyl-1-propene (50.4 mg, 0.2 mmol), dimethyl malonate (68 μL, 0.6 mmol), BSA (148 μL, 0.6 mmol), and KOAc (1 mg) 4 hours reaction time.

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