Catalysis Letters Vol. 109 Nos. 3–4, July 2006 (© 2006)
DOI: 10.1007/s10562-006-0074-2

Effect of substitution of [Pd(PPh_3)$_4$] by related compounds as catalysts in reactions of organic syntheses

Roberto S. Barbiéri,[a,b,*] C.R. Bellato,[c] A.K.C. Dias,[a] and A.C. Massabni[d]

[a]Universidade Vale do Rio Verde - UNINCOR, Três Corações, MG 36570–000, Brazil
[b]Faculdade de Minas - FAMINAS, Muriaé, MG 36880–000, Brazil
[c]Universidade Federal de Viçosa - UFV, Viçosa, MG 36570–000, Brazil
[d]Universidade Estadual Paulista - UNESP, Araraquara, SP 14800–900, Brazil

Received 6 March 2004; accepted 4 March 2006

The effect of substitution of [Pd(PPh_3)$_4$], which is unstable in air, by complexes of the type[MCl_2L_2] ($M = Pd, Pt; L = AsPh_3, SbPh_3$), [$PdL_4$]($L = PPh_3, AsPh_3, SbPh_3$) and [$NiX_2(PPh_3)_2$] on the syntheses of thioethers, acetylenes and ketones is described.

KEY WORDS: homogeneous catalysts; palladium complexes; platinum complexes; nickel complexes.

1. Introduction

Nickel, palladium or platinum complexes with triphenylphosphine (PPh_3) have been used as homogeneous catalysts in organic syntheses. The complex that seems to be the most used in laboratory scale is [Pd(PPh_3)$_4$] [1]. This zerovalent palladium compound decomposes immediately when exposed to air and requires the use of inert atmosphere techniques for its preparation and manipulation. In this work, we wish to describe the catalytic effect of some related compounds in organic syntheses. It is shown that it is possible to substitute [Pd(PPh_3)$_4$] by other compounds, more stable in air, which do not require special conditions for their syntheses and storage.

2. Experimental

2.1. Materials

Analytical grade chemicals were used in all reactions. Solvents were purified by usual procedures described in the literature.

2.2. Physical measurements and analysis

IR spectra were recorded as KBr disks at room temperature, using a Perkin Elmer 576 IR spectrophotomer. ^{1}H-n.m.r. spectra were recorded on a Bruker DRX 400 MHz Advance Spectrometer. CG analysis was performed on a Varian Aerograph 1400 chromatograph. Elemental analysis of carbon and hydrogen were carried out and the metal contents were determined by thermogravimetric analysis using a Perkin Elmer TGS-2 thermobalance.

2.3. Syntheses of the complexes

The complexes [$MCl_2(EPh_3)_2$] (M = Pd, Pt; E = P, As, Sb); [M(EPh_3)$_4$] (M = Pd, E = P, As, Sb; M = Pt, E = P, As); [Pt($SbPh_3$)$_3$] and [$NiX_2(PPh_3)_2$] ($X = Cl^-$, Br^-, I^-, $NO_3{}^-$, NCS^-) were prepared from $Na_2[PdCl_4]$, $H_2[PtCl_6]$ and NiX_2 by methods described in the literature [2–8], and characterized by IR spectra and elemental analysis of carbon and hydrogen and thermogravimetric determination of the metals [9–11].

2.4. Syntheses of thioethers

Method adapted from Migita et al. [12,13]: *p*-thiocresol (0.249 g, 2 mmol), iodobenzene (0.22 mL, 2 mmol), sodium *t*-butoxide (0.385 g, 4 mmol) and 2 mmol [$PdCl_2L_2$] or [PdL_4] (L = PPh_3, $AsPh_3$, $SbPh_3$) were added to EtOH (20 mL) and the reaction mixture was stirred thoroughly under reflux for 3 h. The solvent was removed by evaporation and the main product of the reaction phenyl-*p*-tolyl sulfide was extracted with *n*-pentane. The solution obtained was washed with water, *n*-pentane was evaporated and the residue, a brownish oil, was dried at 100 °C for 30 min.

Using 2-mercaptobenzothiazole (0.335 g, 2 mmol), iodobenzene, butyl lithium (1.70 mL of a 15% m/v *n*-hexane solution, 4 mmol) and [$PdCl_2L_2$] or [PdL_4], following the procedure described above, phenylbenzothiazole-2-sulfide was obtained.

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*To whom correspondence should be addressed.

1011-372X/06/0700–0171/0

2.5. Syntheses of acetylenes

Procedure 1 – adapted from Sonogashira et al. [14]: iodobenzene (1.10 mL, 10 mmol) or butyl iodide (1.20 mL, 10 mmol), 1 mmol of [MCl$_2$(PPh$_3$)$_2$] (M = Ni, Pd) and CuI (0.100 g, 0.050 mmol) were added to pyridine (30 mL) and dry acetylene was bubbled into the reaction mixture for 6 h. The solvent was removed under reduced pressure, water was added to the residue and the respective acetylene (diphenylacetylene or 5-decyne) was extracted with benzene. The benzene solution was passed through a silica column to remove the catalyst.

Procedure 2 – adapted from Cassar [15]: acetylene was bubbled in a mixture of iodobenzene or butyl iodide, [MCl$_2$(PPh$_3$)$_2$] and sodium methoxide (0.680 g, 12 mmol) in dimethylformamide (20 mL) at 60 °C under stirring. The solvent was evaporated and the respective acetylene was extracted with ethylether.

2.6. Syntheses of ketones

Method adapted from Tamaru et al. [16,17] and Negishi et al. [18]: a mixture of Zn–Cu (0.150 g, 2.3 mmol) and iodobenzene (0.17 mL, 1.5 mmol) or isobutyl iodide (0.18 mL, 1.5 mmol) in benzene (3.0 mL) and dimethylformamide (0.20 mL) was stirred at 60 °C for 4 h. The mixture was cooled at room temperature and a solution of [NiX$_2$(PPh$_3$)$_2$] (X = Cl$^-$, Br$^-$, I$^-$, NO$_3^-$, NCS$^-$) (0.04 mmol) and benzoyl chloride (0.12 ml, 1.0 mmol) in benzene (2.0 mL) was added. After 10 min, the solvent was evaporated under reduced pressure and the ketone (benzophenone or isobutylphenylketone), was extracted with dichloromethane.

3. Results and discussion

Nucleophilic substitution reactions of aryl halides by thiolate anions, in different solvents, in a basic medium and under nitrogen atmosphere, catalyzed by [Pd(PPh$_3$)$_4$], led to the formation of aromatic thioethers, with yields of 60–100% [12,13]. We have found that *p*-thiocresol (**I**) or 2-mercaptobenzothiazole (**II**) and iodobenzene (**III**), in ethanol or hexane medium, in the presence of Na^{t}BuO or LiBu, in air and under reflux, do not react in absence of the catalyst, However, using [Pd(PPh$_3$)$_4$], under nitrogen, the yields of thioethers for the reactions of **I** with **III** is 82%, whereas for the reactions of **II** with **III**, the yield is 84%. The use of compounds of the type [PdCl$_2$L$_2$] (L = PPh$_3$, AsPh$_3$, SbPh$_3$) and [PdL$_4$] (L = AsPh$_3$, SbPh$_3$), instead of [Pd(PPh$_3$)$_4$], for the same reactions, under air, provides the syntheses of the respective thioethers, characterized by IR and ^{1}H n.m.r, with yields from 64% to 78% (table 1). Yields for the reactions, in a laboratory scale, in which [PdCl$_2$(PPh$_3$)$_2$] is used are 78% and 74%, which are 4% and 10% lower, respectively, in comparison to those in which [Pd(PPh$_3$)$_4$] was used. [PdCl$_2$(PPh$_3$)$_2$], stable in air, can be prepared in 1–2 min and can be stored for a long period of time without decomposition. Thus, [Pd(PP$_3$)$_4$] could be replaced by [PdCl$_2$(PPh$_3$)$_2$] with reduction in efficiency but with a considerable simplification of the experimental procedures and without necessity of use of inert atmosphere techniques. Platinum compounds of the types [PtCl$_2$L$_2$] (L = PPh$_3$, AsPh$_3$, SbPh$_3$) and [PtL$_n$] (n = 3, L = SbPh$_3$; n = 4, L = PPh$_3$, AsPh$_3$, SbPh$_3$), as well as Na$_2$[PdCl$_4$] and H$_2$[PtCl$_6$], which are the precursors of these complexes of palladium and platinum, do not promote the reactions described above.

Catalytic activity of [NiCl$_2$(PPh$_3$)$_2$] was also compared to that of [PdCl$_2$(PPh$_3$)$_2$]. By bubbling gaseous acetylene into a mixture of RI/CuI/catalyst/pyridine [14] or RI/NaOMe/catalyst/dimethylformamide [13] {catalyst = [PdCl$_2$(PPh$_3$)$_2$]} substituted acetylenes are obtained with yields of 70–100%. The same procedure for the reaction of butyl iodide (**IV**) or iodobenzene (**III**) with acetylene in the presence of [MCl$_2$(PPh$_3$)$_2$]

Table 1
Reactions of *p*-thiocresol (**I**) and 2-mercaptobenzothiazole (**II**) with iodobenzene (**III**), under reflux, in the presence of a base and palladium complexes

Thiol (mmol)	ArI (mmol)	Base (mmol)	Catalyst (mmol)	Solvent	Thioether (yield %)
I (2)	**III** (2)	Na^{t}BuO (4)	[PdCl$_2$(PPh$_3$)$_2$] (0.020)	EtOH	78
			[PdCl$_2$(AsPh$_3$)$_2$] (0.020)		78
			[PdCl$_2$(SbPh$_3$)$_2$] (0.020)		66
			[Pd(PPh$_3$)$_4$] (0.020)		82
			[Pd(AsPh$_3$)$_4$] (0.020)		64
			[Pd(SbPh$_3$)$_4$] (0.020)		67
II (2)	**III** (2)	LiBu (4)	[PdCl$_2$(PPh$_3$)$_2$] (0.020)	hexane	74
			[PdCl$_2$(AsPh$_3$)$_2$] (0.020)		71
			[PdCl$_2$(SbPh$_3$)$_2$] (0.020)		64
			[Pd(PPh$_3$)$_4$] (0.020)		84
			[Pd(AsPh$_3$)$_4$] (0.020)		74
			[Pd(SbPh$_3$)$_4$] (0.020)		72

Table 2
Preparation of diphenylacetylene (**V**) and 5-decyne ((**VI**) by the reaction of iodobenzene ((**III**) or butyl iodide (**IV**) with acetylene in the presence of [$MCl_2(PPh_3)_2$] (M = Ni, Pd), in pyridine (py) or dimethylformamide (dmf)

RI (mmol)	Catalyst (mmol)	Solvent	Product	Yield (%)
III (10)	[$NiCl_2(PPh_3)_2$] (0.010)	py	**V**	79
	[$NiCl_2(PPh_3)_2$] (0.010)	dmf		71
	[$PdCl_2(PPh_3)_2$] (0.010)	py		87
	[$PdCl_2$ $(PPh_3)_2$] (0.010)	dmf		74
IV (10)	[$NiCl_2(PPh_3)_2$] (0.010)	py	**VI**	66
	[$NiCl_2(PPh_3)_2$] (0.010)	dmf		54
	[$PdCl_2(PPh_3)_2$] (0.010)	py		68
	[$PdCl_2(PPh_3)_2$] (0.010)	dmf		61

Table 3
Reactions of benzoyl chloride (**VII**) with iodobenzene (**III**) or isobutyl iodide (**VIII**) in the presence of [$NiX_2(PPh_3)_2$] ($X = Cl^-$, Br^-, I^-, NO_3^-, NCS^-) and Cu/Zn, in benzene/dimethylformamide

RI (mmol)	RCOCl (mmol)	Catalyst (mmol)	Product	Yield (%)
III (1.5)	**VII** (1.0)	None	Benzophenone	19
		[$NiCl_2(PPh_3)_2$] (0.040)		83
		[$NiBr_2(PPh_3)_2$] (0.040)		65
		[$NiI_2(PPh_3)_2$] (0.040)		7
		[$Ni(NO_3)_2(PPh_3)_2$] (0.040)		<5
		[$Ni(NCS)_2(PPh_3)_2$] (0.040)		<5
VI (1.5)	**VIII** (1.0)	None	Isobutylphenylketone	23
		[$NiCl_2(PPh_3)_2$] (0.040)		85
		[$NiBr_2(PPh_3)_2$] (0.040)		76
		[$NiI_2(PPh_3)_2$] (0.040)		<5
		[$Ni(NO_3)_2(PPh_3)_2$] (0.040)		<5
		[$Ni(NCS)_2(PPh_3)_2$] (0.040)		<5

(M = Ni, Pd), results in diphenylacetylene and 5-decyne. Yields of the products were determined by CG analysis by comparison with authentic samples. Reactions in pyridine presented relatively higher yields (66–87%) than those using dimethylformamide (57–74%). The observed yields of the reactions catalyzed by [$NiCl_2(PPh_3)_2$] are slightly lower (2–8%) than that when [$PdCl_2(PPh_3)_2$] was used (table 2). It was also verified that [$Pd(PPh_3)_4$] and [$PdCl_2(PPh_3)_2$] can be substituted by [$NiCl_2(PPh_3)_2$], which is stable in air, easy to prepare, and the reagents and the process are significantly less expensive.

The effect of substitution of [$Pd(PPh_3)_4$] by nickel(II) complexes of the type [$NiX_2(PPh_3)_2$] ($X = Cl^-$, Br^-,I^-,NO_3^-,NCS^-) as potential catalysts for preparation of ketones by reactions of acyl chlorides with organic iodides, in the presence of Zn–Cu in benzene/dimethylformamide [16–18] was investigated. At 70–80°C, such reactions occur with low yields in the absence of catalysts. In the presence of catalysts, the reactions are spontaneous and are completed at room temperature. The yields of benzophenone or isobutylphenylketone, determined by CG analysis for comparation with authentic samples, for the reaction of benzoyl chloride (**VII**) with (**III**) or isobutyl iodide (**VIII**), in the absence of catalysts, are 19% and 23%, respectively. For the reactions in which complexes of the type [$NiX_2(PPh_3)_2$] ($X = I^-$,NO_3^-,NCS^-) were used the yields (7% or $<5\%$) are smaller than those for the non-catalyzed reactions. When [$NiCl_2(PPh_3)_2$] was used, the respective yields were 83% and 85% (table 3), comparable to those of similar reactions catalyzed by [$Pd(PPh_3)_4$] [16–18]. Probably, a partial dissociation of the Ni(II) complexes in solution, forming anions (I^-,NO_3^- or NCS), inhibit the reactions of iodobenzene and isobutyliodide.

4. Conclusions

The reactions described in the present paper have all been previously reported to be catalyzed by [$Pd(PPh_3)_4$] [12–18]. We have demonstrated that this catalyst can be replaced by other stable complexes of Pd(II) or Ni(II), by using common laboratory equipment without necessity of special inert atmosphere apparatus. Consequently, there would be a considerable reduction in the costs of the industrial processes, an important requirement of the chemical industry. Nevertheless, yields are lower (7–10%) than those obtained when [$Pd(PPh_3)_4$] is used as the catalyst.

Acknowledgments

We are grateful to CAPES (Coordenadoria de Aperfeiçoamento de Pessoal de Ensino Superior) and CNPq (Conselho Nacional do Desenvolvimento Científico e Tecnológico) - Brazil, for financial support.

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