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Palladium (II) complexes of (diisopropylphosphino)-ferrocenes: improved catalysts for the Heck reaction

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Abstract

Palladium (II) chloride complexes of (diisopropylphosphino)ferrocenes act as efficient catalyst precursors for the Heck reaction, providing yields well in excess of the corresponding (diphenylphosphino)ferrocene analogues such as the archetypal [$PdCl_2$(dppf)]. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: ferrocenes; phosphines; ligands; Heck reaction

As the only known one-step method for the arylation of olefins, the Heck reaction has been the subject of much research interest [1,2]. The traditional catalyst mixture of palladium (II) acetate and hindered tertiary amine in the presence of triarylphosphine suffers from a number of drawbacks, including catalyst decomposition and lack of regioselectivity. Bidentate phosphine ligands have been shown to provide increased regioselectivity by virtue of their chelate effect and the possibility of phosphine dissociation preceding oxidative addition of the olefin to the palladium during the rate determining step of the catalytic cycle [3]. Furthermore, the rate of reductive elimination from bidentate phosphine complexes of palladium has been shown to be dependent upon the bite angle [4,5]. The steric properties of a number of bidentate phosphine ligands have therefore been compared in order to optimise reaction conditions and yield with respect to their chelate effect [3,5].

While the chemistry of 1,1'-bis-(diphenylphosphino)ferrocene (dppf, **1**) [6] is well documented [7], its analogue 1,1'-bis-(diisopropylphosphino)ferrocene (disoppf, **2**) [8] has been used relatively little. Nevertheless, disoppf has been shown to be highly effective in hydrogenation catalysis in

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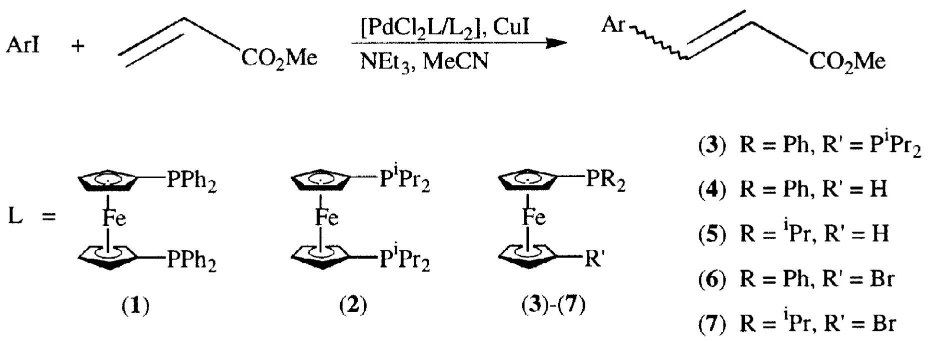
conjunction with iridium [9] and rhodium [10], when compared with dppf, because of its different steric and electronic properties.

During our continuing studies in the synthesis of ferrocenylphosphines we prepared a number of isopropylphosphine ligands **2**, **3** [8], **5** [11] and **7** [11]. In order to assess their synthetic utility we sought to compare their efficacy in homogeneous catalysis with that of some previously reported phenylphosphine ligands **1**, **4** [12] and **6** [11]. The palladium (II) chloride complex of disoppf **2** (single crystal X-ray structure depicted in Fig.1) was prepared, and we report herein a new synthetic application of this complex as a catalyst precursor for the Heck reaction (Scheme 1). A comparison of disoppf with a series of other ferrocenylphosphines is also presented, and the results are summarised in Table 1.



(3) R = Ph, R' = P^iPr_2
(4) R = Ph, R' = H
(5) R = ^iPr, R' = H
(6) R = Ph, R' = Br
(7) R = ^iPr, R' = Br

Scheme 1
Heck reaction of aryl iodides (Ar = phenyl, ferrocenyl) with methyl acrylate catalysed by palladium-ferrocenylphosphines

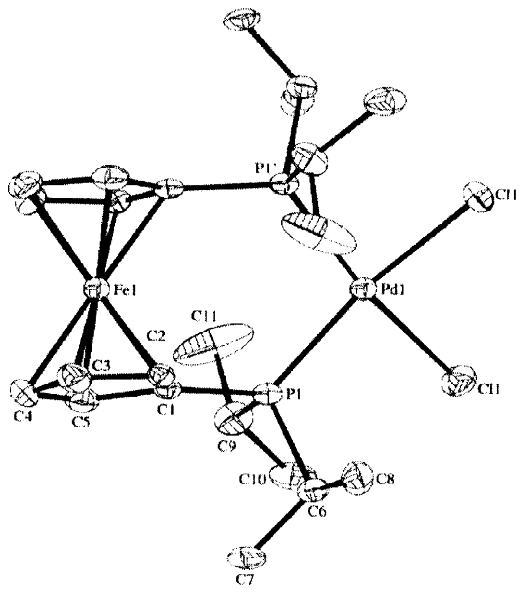


Figure 1
Single crystal X-ray structure of $[PdCl_2(disoppf)]$. Selected bond lengths and angles:- Pd-P 2.2982Å (13), Pd-Cl 2.3595Å (12), P-Pd-P 103.43° (6), P-Pd-Cl 171.28° (4), Cl-Pd-Cl 87.72° (6).

Entry	$[PdCl_2L_2]^a$ L =	PhI (%)	$PhCH{=}CHCO_2CH_3$ (%)^b		FcI^d (%)	$FcCH{=}CHCO_2CH_3$ (%)^b	
			cis	trans		cis	trans^c
1	$Fe(\eta^5\text{-}C_5H_4PPh_2)_2$	(93)	0	(7)	92	0	4
2	$Fe(\eta^5\text{-}C_5H_4P^iPr_2)_2$	0	0	96 (100)	56	0	38
3	$Fe(\eta^5\text{-}C_5H_4PPh_2)(\eta^5\text{-}C_5H_4P^iPr_2)$	(43)	(4)	(53)	74	0	20
4	$Fe(\eta^5\text{-}C_5H_4PPh_2)(\eta^5\text{-}C_5H_5)$	(72)	(3)	(25)	88	0	12
5	$Fe(\eta^5\text{-}C_5H_4P^iPr_2)(\eta^5\text{-}C_5H_5)$	(3)	(1)	(96)	63	0	32
6	$Fe(\eta^5\text{-}C_5H_4PPh_2)(\eta^5\text{-}C_5H_4Br)$	(89)	(<1)	(10)	93	0	4
7	$Fe(\eta^5\text{-}C_5H_4P^iPr_2)(\eta^5\text{-}C_5H_4Br)$	0	3 (4)	94 (96)	66	0	30

Notes (a) Palladium complexes prepared by stirring ligands with [Pd(COD)Cl$_2$], 10 min. in CH_2Cl_2.

(b) Isolated yields. Figures in parentheses are GLC yields, based on PhI. All products gave satisfactory spectroscopic data, including ^{1}H and ^{13}C NMR and IR, and all results were supported by GLC/MS.

(c) δ_H (CDCl$_3$) = 3.78 (s, 3H, C$\underline{H}_3$), 4.17, (s, 5H, Cp), 4.42 (t, 2H, J = 1.8Hz, 2 x C$\underline{H}$), 4.50 (t, 2H, J = 1.8Hz, 2 x C$\underline{H}$), 6.04 (d, 1H, J = 16Hz, β-C$\underline{H}$), 7.59 (d, 1H, J = 16Hz,α-C$\underline{H}$); δ_C (CDCl$_3$) = 51.4 ($\underline{C}H_3$), 68.6 (2 x $\underline{C}$H), 69.6 (5 x $\underline{C}$H), 70.8 (>$\underline{C}$<), 78.6 (2 x $\underline{C}$H), 114.4 (β-$\underline{C}$=C), 145.9 (α-$\underline{C}$=C), 167.6 ($\underline{C}$=O)

(d) For preparation see ref. [13]

Table 1

Heck reaction of aryl iodides with methyl acrylate catalysed by palladium-ferrocenylphosphines

These results demonstrate a clear advantage in the use of isopropylphosphines over their phenylphosphine counterparts. The difference can be attributed to the more electron-rich isopropylphosphines in comparison to their phenylphosphine analogues providing greater electronic stabilisation to the active catalyst. The bidentate ligand disoppf **2** provides the highest regioselectivity because of the flexibility and chelate effect associated with such a system. The bite angle of [PdCl$_2$(disoppf)] (103.4°) compares favourably with that of [PdCl$_2$(dppf)] (99.1°) [5]. Interestingly, the mixed 1-(diphenylphosphino)-1'-(diisopropylphosphino)ferrocene ligand **3** provided a correspondingly intermediate set of results, lying between those of dppf **1** and disoppf **2**. The similarity in the results using ligands **4** and **5** and ligands **6** and **7** would indicate that the effect of non-participating 1'-substituents on the ferrocene backbone is negligible: indeed these ligands represent key intermediates in the synthesis of a number of heterosubstituted ferrocenylphosphines [11]. The use of iodoferrocene [13] as substrate illustrates an important method for the derivatisation of ferrocene, providing vinyl products suitable for use in redox-active polymer chemistry [14]. We are currently developing the use of Group 10 complexes of (diisopropylphosphino)ferrocenes in other areas of homogeneous catalysis.

Typical experimental procedure: [$PdCl_2$(disoppf)] (59.5mg, 0.1mmol) and copper (I) iodide (38.1mg, 0.2mmol) were suspended in a mixture of freshly distilled acetonitrile (10ml) and triethylamine (2ml). The mixture was heated to reflux under nitrogen for 5 min., during which time the colour changed from orange to black. Iodobenzene (1.11ml, 10mmol) and methyl acrylate (1.08ml, 12mmol) were added and the mixture was refluxed for a further 24h. A sample of the reaction mixture was removed for GLC analysis, and the reaction was quenched by the addition of dilute hydrochloric acid (20ml). The mixture was extracted with diethyl ether (3 x 20ml) and the combined organic extracts were washed with brine (2 x 10ml) and water (2 x 10ml), dried over anhydrous magnesium sulfate and evaporated to dryness. Purification was achieved by flash chromatography on silica using 5% diethyl ether / light petroleum.

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