Catalytic Coupling of Aromatics and Olefins by Homogeneous Palladium(II) Compounds under Oxygen

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Summary The use of mild oxygen pressure in conjunction with homogeneous palladium(II) compounds in appropriate solvents allows coupling of aromatics and olefins to proceed catalytically with respect to the metal.

OLEFIN arylation effected by homogeneous palladium(II) compounds has been studied extensively under non-catalytic conditions.[1] In addition, the usual attempts at catalysis by palladium by the use of reoxidation catalysts have been made.[1b,2] I report here that mild oxygen pressure alone is sufficient to allow these reactions, and the oxidative coupling of olefins, to proceed catalytically in appropriate solvents. For olefin arylation, an excess of the aromatic compound can act as solvent while for oxidative coupling of olefins, chloroform can be used. A variety of soluble, labile palladium(II) compounds has been used successfully using a variety of aromatics and olefins. Examples are given in the Table. Not only are the usual reoxidation catalysts and cosolvents unnecessary, they are actually detrimental in terms of oxygen pressure required and by-products formed from side reactions of the adjuvants.

In some cases the new method allows olefin arylation to occur whereas earlier methods suppress the reaction. Ethylene, for example, reacts in benzene containing acetic acid, copper(II) acetate, and palladium(II) acetate to produce vinyl acetate. In benzene containing only palladium(II) acetate under 300 lb in^{-2} oxygen, however, no vinyl acetate is formed and a 648% yield (based on palladium) of the olefin arylation product, styrene, is obtained in 5·5 h.

This, together with a recent note[3] on biaryl formation which appeared during the preparation of this communication, appears to be the first recognition of the ability to use

Examples of catalytic coupling of aromatics and olefins by homogeneous palladium(II) *compounds under oxygen*

Run no.	Olefin[a] (mol)	Aromatic (mol)	Catalyst (mol)	Temperature (°C)	Time (h)	Oxygen (lb in^{-2})	Product[b]	Yield[c] (%)
1	Vinylcyclohexane (0·0236)	Benzene (1·13)	$Pd(OAc)_2$ (0·0025)	80	2·5	300	β-Cyclohexylstyrene	177
2	Cyclohexene (0·021)	Benzene (1·13)	$Pd(OAc)_2$ (0·0025)	80	2·5	300	1- and 4-Phenylcyclohexene	114
3	Styrene (0·025)	Chlorobenzene (0·98)	$Pd(OAc)_2$ (0·0025)	80	2·5	300	*o*-, *m*-, and *p*-Chlorostilbene	108
4	*p*-Chlorostyrene (0·025)	Benzene (1·13)	$Pd(OAc)_2$ (0·0025)	80	2·5	300	*p*-Chlorostilbene	214
5	Styrene (0·025)	Benzene (1·13)	$Pd(OAc)_2$ (0·0025)	80	2·5	300	Stilbene	248
6	Styrene (0·0132)	Benzene (0·22)	$Pd(OAc)_2$ (0·000493)	80	5·5	150	Stilbene	238
7	Styrene (0·0640)	Benzene (1·13)	$Pd(OAc)_2$ (0·0025)	80	6·0	300	Stilbene	613
8	Styrene (0·0694)	Benzene (1·13)	$Pd(OBz)_2$ (0·0025)	80	6·0	300	Stilbene	730
9	Styrene (0·0655)	Benzene (1·13)	$Pd(OPr)_2$ (0·00222)	80	5·8	300	Stilbene	370
10	Styrene (0·225)	Benzene (1·02)	$Pd(OAc)_2$ (0·0025)	100	5·0	300	Stilbene	1100
11	Ethylene (0·0346)	Benzene (1·13)	$Pd(OAc)_2$ (0·000446)	80	5·5	300	Styrene, stilbene	648 39
12	Styrene (0·0962)	None[d]	$Pd(OAc)_2$ (0·00447)	60	5·0	300	1,4-Diphenylbuta-1,3-diene[e]	187

[a] All olefin charged initially for runs 1—6 and 12. Olefin added continuously throughout runs 7—11. [b] Olefin oxidation, double bond migration, olefin–olefin oxidative coupling, and aromatization occur to varying degrees where possible. [c] Based on palladium. [d] 100 ml $CHCl_3$ used as solvent. [e] 64% *cis,trans*- and 36% *trans,trans*-isomers.

oxygen and appropriate solvents alone to perform catalytically certain reactions which usually reduce palladium-(II) to the metal. While the mechanisms of the catalytic and non-catalytic reactions may differ, the coupled products are the same.

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