Selenium-Ligated Palladium (II) Complexes as Highly Active Catalysts for Carbon-Carbon Coupling Reactions: the Heck Reaction

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Reactivity comparison between the selenide-based Pd catalysts 1-3 and analogous Pd catalysts 4-9 derived from sulfide and phosphine ligands.

Yield, turnover number (TON), turnover frequency (TOF) and the reaction conditions for the Heck reaction of aryl bromides using the selenide-based Pd catalyst **1-3** described in this work and analogous Pd catalysts **4-9** derived from sulfide and phosphine ligands¹⁻⁶ are compiled in Tables A and B. Only those data that are for the reactions of the same or very similar substrates and performed under comparable conditions are listed.

Selenide-based Pd catalysts:

Sulfide-based Pd catalysts:

Phosphine-based Pd catalysts:

Table A. Comparison of Catalysts in the Heck Reaction of Aryl Bromides with n-Butyl Acrylate

Catalyst (mol % Pd)	ArX	base	solvent	additive	temp	time	% yield	TON	TOF(h ⁻¹)	Reference
1 (7.0×10^{-4})	PhBr	Na ₂ CO ₃	DMA	none	140 °C	24h	34.4	49,100	2,056	this work
1 (3.5×10^{-4})	PhBr	Na ₂ CO ₃	DMA	none	140 °C	70h	78.1	223,000	3,186	this work
4 (1.0×10^{-3})	PhBr	NaOAc	DMA	Bu ₄ NBr (20 mol%)	120 °C	24h	45	450	19	1
2 (1.35×10^{-3})	PhBr	Na ₂ CO ₃	DMA	none	140 °C	24h	71	52,600	2,192	this work
2 (7.5×10^{-4})	PhBr	Na ₂ CO ₃	DMA	none	140 °C	48h	65.6	87,500	1,823	this work
2 (7.5×10^{-4})	PhBr	Na ₂ CO ₃	DMA	none	140 °C	70h	89	119,000	1,700	this work
5 (2.0×10^{-3})	PhBr	NaOAc	DMA	Bu ₄ NBr (100 mol%)	140 °C	28h	47 (Me) ^a	23,500	839	2
7a (2)	PhBr	NaOAc	DMA	none	140 °C	48h	96	48	1	4
7b (4.0×10^{-3})	PhBr	NaOAc	DMA	none	130 °C	175h	84.5	21,100	121	5
3 (7.0×10^{-4})	PhBr	Na ₂ CO ₃	DMA	none	140 °C	24h	50.4	72,100	3,404	this work
3 (3.5×10^{-4})	PhBr	Na ₂ CO ₃	DMA	none	140 °C	48h	61	174,000	3,625	this work
3 (3.5×10^{-4})	PhBr	Na ₂ CO ₃	DMA	none	140 °C	70h	85	243,000	3,471	this work
9 (7.0×10^{-4})	PhBr	Na ₂ CO ₃	NMP	none	140 °C	63h	93 (Me) ^a	132,900	2,110	6
2 (1.35×10^{-3})	4-MeO-PhBr	Na ₂ CO ₃	DMA	none	140 °C	24h	47.6	35,300	1,471	this work
5 (2.0×10^{-3})	4-MeO-PhBr	NaOAc	DMA	Bu ₄ NBr (20 mol%)	170 °C	6h	61	30,500	5,083	2
7a (1)	4-MeO-PhBr	NaOAc	DMA	none	140 °C	48h	87	87	2	4
7b (4.0×10^{-3})	4-MeO-PhBr	NaOAc	DMA	none	130 °C	175h	67.6	16,900	97	5
2 (1.35×10^{-3})	4-OHC-PhBr	Na ₂ CO ₃	DMA	none	140 °C	24h	90.7	67,200	2,800	this work
2 (4.0×10^{-5})	4-OHC-PhBr	Na ₂ CO ₃	DMA	none	140 °C	70h	67.8	1,700,000	24,285	this work
5 (2.0×10^{-3})	4-OHC-PhBr	NEt ₃	DMA	none	140 °C	56h	43 (Me) ^a	21,500	384	2
5 (2.0×10^{-3})	4-OHC-PhBr	NaOAc	DMA	Bu ₄ NBr (20 mol%)	140 °C	2.5h	66 (Me) ^a	33,000	13,200	2
7b (1.0×10^{-5})	4-OHC-PhBr	NaOAc	DMA	none	150 °C	96h	37.2	3,720,000	38,750	5
3 (7.0×10^{-4})	4-OHC-PhBr	Na ₂ CO ₃	DMA	none	140 °C	24h	90.9	130,000	5,417	this work
6b (2.0×10^{-3})	4-OHC-PhBr	NEt ₃	DMA	Bu ₄ NBr (20 mol%)	140 °C	24h	27 (Me) ^a	13,500	563	2
9 (7.0×10^{-4})	4-OHC-PhBr	Na ₂ CO ₃	NMP	none	140 °C	63h	79 (Me) ^a	113,000	1,794	6

^a Methyl acrylate was used for the reaction.**Table B.** Comparison of Catalysts in the Heck Reaction of Aryl Bromides with Styrene

Catalyst (mol % Pd)	ArX	base	solvent	additive	temp	time	% yield	TON	TOF(h ⁻¹)	Reference
2 (2×10^{-3})	PhBr	NaOAc	DMA	none	140 °C	20h	97.3	48,700	2,435	this work
5 (2×10^{-3})	PhBr	NaOAc	DMA	Bu ₄ NBr (100 mol%)	140 °C	28h	56	28,000	1,000	2
7a (0.1)	PhBr	NaOAc	DMA	none	140 °C	26h	77	770	30	4
2 (3.9×10^{-3})	4-MeO-PhBr	NaOAc	DMA	none	140 °C	21h	50.8	13,000	619	this work
7a (0.1)	4-MeO-PhBr	NaOAc	DMA	none	140 °C	30h	69	690	23	4
2 (9×10^{-4})	4-OHC-PhBr	NaOAc	DMA	none	140 °C	24h	92.5	130,000	5,417	this work
5 (2×10^{-3})	4-OHC-PhBr	NEt ₃	DMA	Bu ₄ NBr (20 mol%)	140 °C	90h	10	5,000	56	2

References

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