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PALLADIUM- AND COPPER-CATALYZED HOMOCOUPLING OF ORGANOLEAD COMPOUNDS: SYNTHESIS OF BIARYLS AND DIYNES

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Abstract: The palladium- and copper-catalyzed dimerization of aryl- and alkynyllead triacetates to form biaryls and dialkynes under mild conditions is described.

Functionalized symmetrical biaryls show specific properties as materials able to form semiconducting complexes¹ and as precursors of rigid liquid crystals.² The synthesis of biaryls from aryl halides can be achieved by transition metal catalysis in the presence of a reductant.³ Thus, the synthesis of biaryls from aryl halides is catalyzed by nickel(II) complexes, in the presence of a chemical reductant such as zinc powder^{3b-f} or upon electrochemical reduction catalyzed by palladium complexes.⁴ Here we wish to report that aryl- and alkynyllead triacetates⁵ are converted to biaryls and dialkynes^{6,7} by treatment with a catalytic amount of palladium or copper catalyst (Eq. 1).

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	RPb(OAc) ₃ —	Pd or Cu catalyst	R-R (1)	
1a	$\mathbf{R} = \mathbf{P}\mathbf{h}$	3a	$\mathbf{R} = \mathbf{P}\mathbf{h}$	
1b	$R = p - CH_3C_6H_4$	3b	$R = p - CH_3C_6H_4$	
1c	$R = p - CH_3OC_6H$	I ₄ 3c	$R = p - CH_3 OC_6 H_4$	
1d	R = 2-thienyl		R = 2-thienyl	
2	$R = PhC \equiv C$	4	$\mathbf{R} = \mathbf{PhC} \equiv \mathbf{C}$	

The results of palladium-catalyzed homocoupling of organolead compounds are summarized in Table 1. When phenyllead triacetate 1a was reacted with a catalytic amount of Pd₂(dba)₃·CHCl₃ (5 mol %) in CHCl₃ at room temperature for 10 min, biphenyl (3) was produced in 68% yield (entry 1 in Table 1). Instead of palladium as a catalyst, copper was used as a catalyst in this homocoupling. Thus phenyllead triacetate (1a) was stirred with CuI (10 mol %) in dry DMF at 50 °C for 10 min to give biphenyl (3a) which was obtained in 68% yield (entry 2 in Table 1). By palladium and copper as catalysts, p-methylphenyllead triacetate 1b was dimerized to afford 3b in 65 and 62% yields, respectively (entries 3 and 4). By the same methods, p-methoxyphenyllead triacetate 1c was coupled to afford 3e (entries 5 and 6). Alternatively, 2-thienyllead triacetate (1d) was treated with palladium and copper as catalysts to afford the coupled product 3d in 81 and 78% yields, respectively (entries 7 and 8). This method was also extended to alkynylsubstituted lead triacetate. The alkynyl-substituted lead triacetate 2 was reacted in the presence of Pd₂(dba)₃·CHCl₃ (5 mol %) and CuI (10 mol %) to give diacetylene 4 in 70 and 53% yields, respectively (entries 9 and 10).

Entry	Substrate	Method ^a	Product	Yield(%) ^b
1	1 a	А	3 a	68
2	1 a	В	3a	68
3	1b	Α	3b	65
4	1b	В	3b	62
5	1c	А	3 c	75
6	1c	В	3 c	80
7	1d	Α	3d	81
8	1d	В	3d	78
9	1e	А	4	70
10	1e	В	4	53

Table 1. Palladium- and Copper-Catalyzed Homocoupling of Organolead Compounds

^a Method A: All the reactions were run in the presence of Pd₂(dba)₃·CHCl₃ (5 mol %) in CHCl₃ at room temperature for 10 min. Method B: All the reactions were run in the presence of CuI (10 mol %) in DMF at room temperature for 10 min. ^b The yields are isolated yields.

Experimental Section

Typical procedure.

Method A: Biphenyl (3a)

To a stirred solution of phenyllead triacetate (1a) (0.20 g, 0.43 mmol) in CHCl₃ (5 mL) was added Pd₂(dba)₃·CHCl₃ (22.4 mg, 5 mol %) and the reaction mixture was stirred at room temperature for 10 min. After evaporation of the solvent, the crude product was separated by SiO₂ column chromatography (hexane Rf = 0.54) to afford biphenyl (3a) (22.7 mg, 68%). ¹H NMR (CDCl₃, 400 MHz) δ 7.39 (m, 2H), 7.47 (m, 4H), 7.62 (m, 4H). IR (KBr) 3205, 3099, 1602, 1466 cm⁻¹.

To a stirred solution of phenyllead triacetate (1a) (0.20 g, 0.43 mmol) in DMF (4 mL) was added CuI (8.25 mg, 10 mol %) and the reaction mixture was stirred at 50 °C for 10 min. H₂O (20 mL) was added and extracted with ether (20 mL X 3). The organic layer was dried over anhydrous MgSO₄ and evaporated *in vacuo*. The crude product was separated by column chromatography (hexane, Rf = 0.54) to afford biphenyl (3a) (22.6 mg, 68%).

4, 4'-Dimethylbiphenyl (**3b**) TLC, SiO₂, hexanes, Rf = 0.51. ¹H NMR (CDCl₃, 400 MHz) δ 2.39 (s, 6H), 7.24 (m, 4H), 7.47 (m, 4H). IR (KBr) 3107, 1452, 1368, 803, 720 cm⁻¹.

4, 4'-Dimethoxybiphenyl (**3c**) TLC, SiO₂, EtOAc : hexane = 1 : 30, Rf = 0.32. ¹H NMR (CDCl₃, 400 MHz) δ 4.82 (s, 6H), 6.95 (m, 4H), 7.48 (m, 4H). IR (KBr) 3145, 1609, 1478, 1301, 1042 cm⁻¹.

2, 2'-Bithiophene (**3d**) TLC, SiO₂, hexanes, Rf = 0.52. ¹H NMR (CDCl₃, 400 MHz) δ 6.99 (m, 2H), 7.17 (m, 4H). IR (KBr) 3081, 1783, 1372, 830, 695 cm⁻¹.

1, 4-Diphenylbutadiyne (4) TLC, SiO₂, hexanes, Rf = 0.43. ¹H NMR (CDCl₃, 400 MHz) δ 7.36 (m, 6H), 7.55 (m, 4H). IR (KBr) 3104, 2158, 1594, 1477, 920 cm⁻¹.

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