

Use of aluminium as an electron pool. Reductive coupling of iodobenzenes promoted by electron transfer in an Ni/Pb/Al multi redox system

Hideo Tanaka, Shin-ichi Sumida, Noriko Kobayashi, Naoki Komatsu and Sigeru Torii*

Department of Applied Chemistry, Faculty of Engineering, Okayama University, Okayama 700 (Japan)

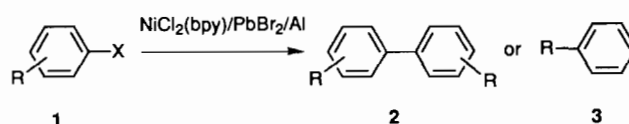
(Received January 12, 1994)

Abstract

Reductive coupling of iodobenzenes was achieved successfully by use of a stoichiometric amount of aluminium metal as an electron source and catalytic amounts of $\text{NiCl}_2(\text{bpy})$ ($\text{bpy} = 2,2'$ -bipyridyl) and lead(II) bromide as electron transfer catalysts in methanol containing potassium iodide.

Key words: Reductive coupling of iodobenzenes; Aluminium complexes; Nickel complexes; Lead complexes; Electron transfer catalyst; Multi metal redox system

Aluminium metal is an ideal reducing agent since it is cheap, easy to handle, and able to release enough electrons ($3 e^-/\text{atom}$) [1]. However, the use of aluminium metal in modern organic chemistry is rather limited owing to lack of an efficient electron transfer process between aluminium metal and organic substances. Recently, combinations of aluminium metal and a catalytic amount of metal salt have attracted much attention due to their potentiality as a powerful reductant for various synthetic purposes, that is, aluminium metal acts as an electron pool (source) and the metal salt shares an electron transfer catalyst. The chemical behavior of the bimetal redox systems is highly dependent on the nature of the metal salts and proper choice of the metal salts may achieve various reductive transformations. For instance, Barbier-type allylation of carbonyl compounds (SnCl_2/Al ; PbBr_2/Al ; BiCl_3/Al) [2], imines (PbBr_2/Al ; TiCl_4/Al) [3], and acetals (PbBr_2/Al) [4], reductive dimerization of imines (PbBr_2/Al) [5], and others [6] have been performed successfully using the bimetal redox systems. In a previous paper, we disclosed a new three metal redox system, involving $\text{NiCl}_2(\text{bpy})$ ($\text{bpy} = 2,2'$ -bipyridyl), lead(II) bromide, and aluminium metal, which can promote reductive coupling of vinyl halides [7]. Herein, we disclose reductive dimerization of iodobenzenes **1** as an expansion of the scope of the multi metal redox system (Scheme 1).



Scheme 1.

The reaction procedure is simple; thus, a mixture of 4-*tert*-butylphenyl iodide (**1a**) ($\text{R} = p\text{-tert-Bu}$), $\text{NiCl}_2(\text{bpy})$, lead(II) bromide and aluminium (1/0.1/0.1/1.5 mmol each) in methanol containing potassium iodide (1.5 mmol) was stirred at room temperature until most of the aluminium metal was consumed (9 h). Usual workup of the mixture afforded 4,4'-di-*tert*-butylbiphenyl (**2a**) in 95% yield (entry 1 in Table 1). The presence of both $\text{NiCl}_2(\text{bpy})$ and lead(II) bromide is essential for the reductive coupling of **1a** since the absence of $\text{NiCl}_2(\text{bpy})$ or lead(II) bromide resulted in almost complete recovery of the starting material **1a** (entries 2 and 3). The effect of potassium iodide is also remarkable. Although the reaction proceeded smoothly in the absence of potassium iodide, a mixture of the biphenyl **2a** (44%) and the corresponding hydrogenation product **3a** (39%) was obtained (entry 4). In addition, the proper choice of solvent is important. Among the solvents examined thus far, only methanol can be used successfully for this purpose, whereas *N,N*-dimethylformamide (DMF), tetrahydrofuran (THF) and methylene dichloride (CH_2Cl_2) are not effective at all for the reductive coupling (entries 5–7).

*Author to whom correspondence should be addressed.

TABLE 1. Dimerization of **1a** (R = *p*-tert-Bu) in an NiCl₂(bpy)/PbBr₂/Al system^a

Entry	Solvent	NiCl ₂ (bpy) (equiv.)	PbBr ₂ (equiv.)	KI (equiv.)	Time (h)	Yield (%) ^b	
						2a	3a
1	MeOH	0.1	0.1	1.5	9	95	
2	MeOH		0.1	1.5	15	^c	
3	MeOH	0.1		1.5	15	^c	
4	MeOH	0.1	0.1		4.5	44	39
5	DMF	0.1	0.1	1.5	26	trace ^c	
6	THF	0.1	0.1	1.5	27.5	^c	
7	CH ₂ Cl ₂	0.1	0.1	1.5	27.5	^c	

^aCarried out in the same manner as described in the text unless otherwise noted. ^bIsolated yield. ^cMost of **1a** (83–95%) was recovered.

The reductive coupling of various bromo- and iodobenzenes **1** was carried out in a similar manner to that described above (Table 2). Non-substituted and *p*-substituted phenyl iodides **1** (X = I) underwent reductive coupling to afford the corresponding biaryls **2** in 61–91% yields, respectively (entries 1–4), whereas the reductive coupling of bromobenzenes **1** (X = Br) occurred less effectively under similar conditions to afford only 6–10% yields of biaryls **2** together with the recovered starting materials **1** (65–78%) (entries 5–7). On the other hand, *ortho*-substituted aryl iodides **1**, e.g. *o*-methoxyphenyl iodide (**1h**), suffered hydrogenation to give the monomeric products **3**, exclusively.

Although the reaction mechanism of the NiCl₂(bpy)/PbBr₂/Al-promoted reductive coupling of iodobenzenes **1** (X = I) is not clear at present, it is evident that each of the components is indispensable and may play a significant role in the release of electrons from alu-

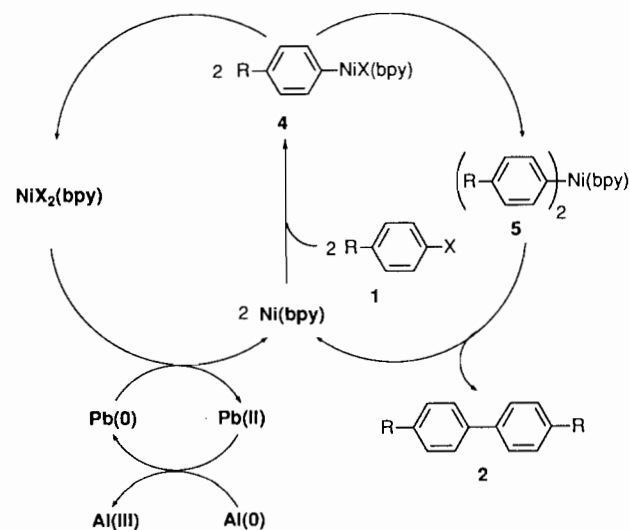
TABLE 2. Dimerization of **1** (X = I, Br) in an NiCl₂(bpy)/PbBr₂/Al system^a

Entry	Ar-X	Time (h)	Yield (%) ^b	
			2	3
1	1a R = tert-Bu, X = I	9	95	
2	1b R = OMe, X = I	18	99	
3	1c R = H, X = I	22	68	
4	1d R = Cl, X = I	16	61	
5	1e R = OMe, X = Br	23	8	
6	1f R = Me, X = Br	9	6	
7	1g R = Cl, X = Br	9	10	
8	1h	22.5		98

^aCarried out with NiCl₂(bpy) (0.1 equiv.), PbBr₂ (0.1 equiv.), Al (1.5 equiv.) and KI (1.5 equiv.) in MeOH at 20–25 °C. ^bIsolated yields after column chromatography (SiO₂; hexane/EtOAc).

minium and the transfer into the substrates. In previous papers [8], it has been reported that an NiCl₂(PR₃)₂/Zn combination (R = phenyl or alkyl) can promote the same reactions, and a plausible reaction mechanism involving disproportionation of σ -aryl nickel complexes **4**, leading to biaryl nickel **5** and nickel(II) halides, and subsequent reductive elimination affording biaryls **2** has been proposed. These enabled us to assume an analogous scheme for the electron transfer system between aluminium and iodobenzenes **1** as illustrated in Scheme 2. The initial stage of the reaction might involve a two electron reduction of nickel(II) to nickel(0) in which Pb(II)/Pb(0) redox seems to play a role as a catalyst for the electron transfer between nickel(II) and aluminium(0) since no appreciable reaction was observed in the absence of lead(II) bromide (see entry 3 in Table 1). The regeneration of nickel(0) would be similarly performed by the Pb(II)/Pb(0) promoted electron release from aluminium metal.

In conclusion, the simple operations and mild conditions are characteristic features of the present



Scheme 2.

NiCl₂(bpy)/PbBr₂/Al-promoted reductive coupling of iodobenzenes **1**, which may have large merits in organic syntheses as well as expand the scope of usage of aluminium metal as a potent reducing agent.

A typical procedure (entry 1 in Table 1). A mixture of *p*-tert-butylphenyl iodide **1a** (R = *p*-tert-Bu; 260 mg, 1 mmol), NiCl₂(bpy) (30 mg, 0.1 mmol), lead(II) bromide (38 mg, 0.1 mmol), aluminium (39 mg, 1.5 mmol) and potassium iodide (249 mg, 1.5 mmol) in methanol (5 ml) was stirred at room temperature for 9 h. The mixture was poured into 1 M hydrochloric acid and extracted with ethyl acetate. The extracts were washed with brine, dried (Na₂SO₄) and concentrated *in vacuo*. The residue was chromatographed (SiO₂, hexane/ethyl acetate) to give 4,4'-di-tert-butylbiphenyl (**2a**) (126 mg, 95%). IR (KBr): 2968, 2870, 1497, 1270, 1002, 1004, 822 cm⁻¹. ¹H NMR (CDCl₃): δ 1.38 (s, 18H), 7.48–7.57 (m, 8H).

References

- 1 M. Smith, in R.L. Augustin (ed.), *Reduction Techniques and Applications in Organic Synthesis*, Marcel Dekker, New York, 1968, pp. 95–170.
- 2 J. Nokami, S. Wakabayashi and R. Okawara, *Chem. Lett.*, (1984) 869; K. Uneyama, N. Kamaki, A. Moriya and S. Torii, *J. Org. Chem.*, **50** (1985) 5396; K. Uneyama, H. Nanbu and S. Torii, *Tetrahedron Lett.*, **27** (1986) 2395; H. Tanaka, S. Yamashita, T. Hamatani, Y. Ikemoto and S. Torii, *Syn. Commun.*, **17** (1987) 789; M. Wada, H. Ohki and K. Akiba, *J. Chem. Soc., Chem. Commun.*, (1987) 708; Z.-Y. Yang and D.J. Burton, *J. Org. Chem.*, **56** (1991) 1037.
- 3 H. Tanaka, K. Inoue, U. Pokorski, M. Taniguchi and S. Torii, *Tetrahedron Lett.*, **31** (1990) 3023.
- 4 H. Tanaka, S. Yamashita, Y. Ikemoto and S. Torii, *Tetrahedron Lett.*, **29** (1988) 1721.
- 5 H. Tanaka, H. Dhimane, H. Fujita, Y. Ikemoto and S. Torii, *Tetrahedron Lett.*, **29** (1988) 3811.
- 6 H. Tanaka, S. Yamashita, Y. Katayama and S. Torii, *Chem. Lett.*, (1986) 2043; H. Tanaka, S. Yamashita and S. Torii, *Bull. Chem. Soc. Jpn.*, **60** (1987) 1951; H. Tanaka, S. Yamashita, M. Yamanoue and S. Torii, *J. Org. Chem.*, **54** (1989) 444; H. Tanaka, M. Tanaka, A. Nakai, Y. Katayama and S. Torii, *Bull. Chem. Soc. Jpn.*, **62** (1989) 687; H. Dhimane, H. Tanaka and S. Torii, *Bull. Soc. Chim. Fr.*, **127** (1990) 283; R. Khanna and P.K. Singh, *Syn. Commun.*, **20** (1990) 1743; W.B. Wang, L.-L. Shi and Y.-Z. Huang, *Tetrahedron Lett.*, **31** (1990) 1185; B.K. Sarmah and N.C. Barua, *Tetrahedron*, **40** (1991) 8587, and refs. therein.
- 7 H. Tanaka, A. Kosaka, S. Yamashita, K. Morisaki and S. Torii, *Tetrahedron Lett.*, **30** (1989) 1261.
- 8 M. Zembayashi, K. Tamao, J. Yoshida and M. Kumada, *Tetrahedron Lett.*, (1977) 4089; K. Takagi, N. Hayama and S. Inokawa, *Bull. Chem. Soc. Jpn.*, **53** (1980) 3691; K. Takagi, N. Hayama and K. Sasaki, *Bull. Chem. Soc. Jpn.*, **57** (1984) 1887.