

Catalytic reductive homocoupling of 9-bromofluorene

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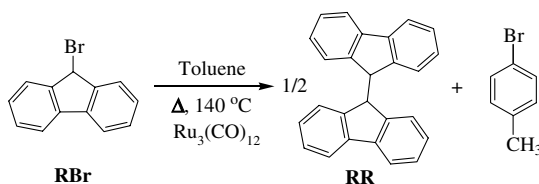
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Abstract—A number of organometallic compounds and inorganic salts, including the group 8 metal carbonyls $M_3(CO)_{12}$ and salts MCl_3 ($M = Fe, Ru, Os$), were tested for their catalytic activity in the reductive coupling of 9-bromofluorene. Among them, $FeCl_3$ was found to show excellent activity (TOF = 1960). The reaction is believed to proceed via a radical mechanism.
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The reductive homocoupling of 9-bromofluorene (**RBr**) to 9,9'-bifluorenyl (**RR**) has been reported to be effected by a variety of reducing agents in stoichiometric amounts.¹ Recently, we reported that 0.1 mol % $Ru_3(CO)_{12}$ can efficiently catalyse the reductive homocoupling of **RBr** to **RR** via transfer of the bromine to the solvent (Scheme 1).² In order to find a cheaper and better catalyst, other group 8 metal carbonyls and metal salts were tested and the results are reported herein.

A number of organometallic compounds ($Fe_3(CO)_{12}$, $Os_3(CO)_{12}$, Cp_2TiCl_2 , Cp_2ZrCl_2 , $Cp_2TiZnCl$, $Cp_2ZrZnCl$ and $(C_9H_7)Ru(CO)_2Cl$) and inorganic salts ($FeCl_3$, $RuCl_3$, $OsCl_3$, $IrCl_3$, $NiCl_2$ and $CuCl_2$) were tested for their catalytic activity in the reductive coupling of 9-bromofluorene. Of these, only the group 8 metal carbonyls $M_3(CO)_{12}$ and salts MCl_3 ($M = Fe, Ru, Os$), as well as $IrCl_3$, showed activity (Table 1).



Scheme 1.

Keywords: Reductive coupling; Catalysis; Bifluorenyl; 9-Bromofluorene.

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It is clear from Table 1 that in comparison to $Ru_3(CO)_{12}$, $RuCl_3$ had very low efficiency (entries 2 and 4, respectively). Interestingly, $IrCl_3$ also showed activity albeit the efficiency was low (entry 5). On the other hand, $Fe_3(CO)_{12}$ and $FeCl_3$ (entries 1 and 3) were as active as $Ru_3(CO)_{12}$; the activity for $FeCl_3$ was clearly the best at a 0.1 mol % catalyst loading (entries 6–10). The homocoupling of the substituted bromofluorene, 2-nitro-9-bromofluorene also occurred under $FeCl_3$ catalysis (entry 12). However, the reaction failed with 9-phenyl-9-bromofluorene, presumably because of steric reasons. The reaction also failed for compounds with bromine substitutions on the aromatic rings, for example, 2-bromofluorene and 2,7-dibromofluorene.

Both $Os_3(CO)_{12}$ and $OsCl_3$ showed moderate efficiencies (entries 8 and 10). We utilized the slower rate of reaction with $Os_3(CO)_{12}$ to monitor the progress of the reaction by 1H NMR spectroscopy and found an induction period of about 40 min. We had earlier ruled out the possibility of heterogeneous catalysis (ruthenium metal did not exhibit any catalytic activity),² and also found that an equimolar reaction between $Os_3(CO)_{12}$ and **RBr** afforded a 90% recovery of $Os_3(CO)_{12}$. This suggests that the induction period is probably related to the formation of the catalytically active tetraosmium analogue of $Ru_4(\mu_3-OMe)(\mu_3-OH)(\mu-Br)_2(CO)_{10}$, viz., $Os_4(\mu_3-OMe)(\mu_3-OH)(\mu-Br)_2(CO)_{10}$.² However, attempts to isolate intermediates from a stoichiometric reaction of **RBr** with $FeCl_3$, $Fe_3(CO)_{12}$ or $Os_3(CO)_{12}$ were unsuccessful.

Addition of a small amount of TEMPO to the $FeCl_3$ -catalysed reaction led to complete inhibition (entry 11). This is probably an indicative that the reaction

Table 1. Catalytic runs for the reductive coupling of **RBr**

Run	Substrate:catalyst mole ratio	Catalyst	Reaction time (h)	Yield (% of RR)	TON	TOF (h ⁻¹)
1	100:1	Fe ₃ (CO) ₁₂	2	98	98	49
2	100:1	Ru ₃ (CO) ₁₂	1.5	79 ^a	78	52
3	100:1	FeCl ₃	0.5	98	98	196
4	100:1	RuCl ₃	2.5	1	1	0.4
			20	37	37	1.9
5	100:1	IrCl ₃	6	30 ^a	30	5
			24	64 ^a	64	2.7
6	1000:1	Fe ₃ (CO) ₁₂	2	99	990	495
7	1000:1	Ru ₃ (CO) ₁₂	2.5	91	910	364
8	1000:1	Os ₃ (CO) ₁₂	7	80	800	114
9	1000:1	FeCl ₃	0.5	98 (96 ^a)	980	1960
10	1000:1	OsCl ₃	2	14	140	70
			5.5	21	210	38
11 ^b	1000:1	FeCl ₃	0.5	0	0	0
12 ^c	1000:1	FeCl ₃	18	83	830	46
13	10,000:1	FeCl ₃	2	16	1600	800
			6	18	1800	300

^a Isolated yields.

^b In the presence of TEMPO (0.1 mol %).

^c For **RBr** = 2-nitro-9-bromofluorene. Product identified by ¹H NMR (DMSO-*d*₆): δ 5.35 (s, C–H), 6.9–8.3 (m, aromatic). Lit. values:³ ¹H NMR (DMSO-*d*₆): δ 5.45 (s, C–H), 6.8–8.4 (m, aromatic).

follows a radical pathway, unlike in the carbonyl cluster case. In all the reactions showing activity, ¹H NMR analyses of the reaction mixtures showed that 4-bromotoluene was produced in a 2:1 ratio with respect to bifluorenyl (Scheme 1). No 2- or 3-bromotoluene, nor benzyl bromide, were observed among the products. Although the precise mechanism is not clear, it does not involve a simple halogen atom transfer.

In conclusion, we have found that in addition to the metal carbonyl Ru₃(CO)₁₂, the other group 8 carbonyls, as well as some inorganic salts, are also active in the catalytic reductive homocoupling of 9-bromofluorene to give bifluorenyl. In particular, a very cheap and environmentally friendly catalyst, FeCl₃, showed excellent activity. Its catalytic activity probably involves a radical pathway.

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Supplementary data

Experimental procedures and characterization data for the catalytic runs, and the method for determination of the induction period, are provided. Supplementary data associated with this article can be found, in the on-line version, at doi:10.1016/j.tetlet.2007.07.120.

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