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Catalytic Reductive Coupling of 9-Bromofluorene

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The reductive homocoupling of 9-bromofluorene is catalyzed by 0.1 mol % $Ru_3(CO)_{12}$ in refluxing xylene, with a TON in excess of 3000. A stoichiometric reaction affords the novel cluster $Ru_4(\mu_3\text{-OMe})(\mu_3\text{-OH})(\mu\text{-Br})_2(CO)_{10}$, which is found to be even more catalytically active. Further reaction of this cluster with bromofluorene gives another novel cluster, $Ru_4(\mu_4\text{-O})(\mu\text{-Br})_6(CO)_8$, which is inactive.

Introduction

C−C bond formation is one of the most fundamental reactions in organic synthesis. A very important strategy in C−C bond formation is the coupling of sp^3 carbon centers, and a useful methodology is that of catalytic coupling involving a Grignard reagent.[1] The direct coupling of alkyl halides is much less common.[2] In the course of an attempt at the preparation of a fluorenyl ruthenium complex via the reaction of $Ru_3(CO)_{12}$, **1**, and 9-bromofluorene, **RBr**, we stumbled upon the catalytic coupling of the latter to form bifluorenyl, **RR**. Such a reductive coupling of 9-bromofluorene to 9,9′-bifluorenyl has been reported to be effected by a variety of reducing agents,[3] but none of these methods were catalytic. We wish to present in this paper our studies on this intriguing reaction.

Results and Discussion

When equimolar amounts of $Ru_3(CO)_{12}$, **1**, and 9-bromofluorene, **RBr**, were refluxed in *p*-xylene, three compounds were isolated from the mixture (Scheme 1). The cluster **3-OH** reacted further with equimolar amounts of **RBr** to afford, besides **RR**, another novel cluster, $[Ru_4(\mu_4\text{-O})(\mu\text{-Br})_6(CO)_8]$, **5**. All the compounds have been completely characterized, including by single-crystal X-ray structural studies.

The isolation of **RR** in such high yield suggested that a catalytic C−C coupling reaction involving an sp^3 carbon has occurred. Indeed, the reaction did not yield **RR** in the absence of **1** under the same conditions (Table 1, run 13), and **1** was active even at 0.01 mol % albeit with a low product yield (entry 5). The catalysis also worked for substituted bromofluorenes such as 2-nitro-9-bromofluorene (entry 6), but not when substitution was at the 9-position such as 9-phenyl-9-bromofluorene, presumably because of steric hindrance. We have also ruled out the involvement of metallic ruthenium, which did not exhibit any catalytic activity.[4] Consistent with the expectation that **2** was a side product from the reaction of **1** with the solvent,[5] we have found it to be catalytically inactive (entry 7). Cluster **5** also showed no activity after 2.5 h but gave a very low conversion of **RBr** to **RR** after refluxing for 56 h (entry 12). On the other hand, **3-OH** was catalytically more active than **1** (entries 8 and 9), although bearing in mind one of “Halpern's rules”,[6] this did not constitute definitive evidence that it was an intermediate in the catalytic cycle.

The most likely origin of the hydroxyl group in **3-OH** was adventitious water present in the solvent or on the surface of the glass reaction vessel, as carrying out the reaction in the presence of water resulted in a doubling of the yield of **3-OH**. When the reaction was conducted under scrupulously dry conditions,[8] the quantity of **3-OH** obtained was barely above the (^{1}H NMR) detection limit; the yield could not be determined reliably, although the yield of **RR** was still relatively high (69%). When the reaction was carried out in methanol or *tert*-butyl alcohol, the cluster $[Ru_4(\mu_3\text{-OMe})_2(\mu\text{-Br})_2(CO)_{10}]$, **3-OMe**, or $[Ru_4(\mu_3\text{-OBu}^t)_2(\mu\text{-Br})_2(CO)_{10}]$, **3-OBu^t**, was obtained, respectively (Scheme 2). These results thus strongly indicated that the hydroxyl group was from water in the solvent and also that the methoxy group in **3-OH** may have come from methanol. One possible source for the latter would be residual methanol used in the recrystallization of commercial samples of **RBr**; NMR evidence suggested that methanol was indeed present in

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(1) (a) Kamikawa, T.; Hayashi, T. *Tetrahedron Lett.* **1997**, *38*, 7087. (b) Billington, C. In *Comprehensive Organic Synthesis*; Trost, B. M, Fleming, I., Eds.; Pergamon: Oxford, 1991; Chapter 2.1, Vol. 3. (b) Li, C. J.; Chan, T. H. *Organic Reactions in Aqueous Media*; Wiley: New York, 1997; p 64. (c) Einhorn, C.; Luche, J. L. *J. Organomet. Chem.* **1985**, *322*, 177. (d) Katritzky, A. R.; Allin, S. M. *Synth. Commun***.** **1995**, *25*, 2781. (e) Roth, M.; Damm, W.; Geise, B. *Tetrahedron Lett.* **1996**, *37*, 351.

(2) (a) Puckette, T. A. PCT Int. Appl. 1990, 42 pp. (b) Ma, J.; Chan, T. H. *Tetrahedron Lett.* **1998**, *39*, 2499.

(3) (a) Khurana, J. M.; Chauhan, S.; Maikap. G. C. *Org. Biomol. Chem.* **2003**, *1*, 1737. (b) Eisch, J. J.; Gitua, J. N. *Eur. J. Inorg. Chem.* **2002**, *12*, 3091. (c) Larsen, A. S.; Wang, K.; Lockwood, M. A.; Rice, G. L.; Won, T.; Lovell, S.; Sadlek, M.; Turecek, F.; Mayer, J. M. *J. Am. Chem. Soc.* **2002**, *124*, 10112. (d) Bausch, J. M.; Li, W. *Synth. Commun.* **1996**, *26*, 1401. (e) Eisch, J. J.; Shi, X.; Lasota, J. *Z. Naturforsch. B* **1995**, *50*, 342. (f) Ashby, E. C.; Park, W. S.; Goel, A. B.; Su, W. Y. *J. Org. Chem.* **1985**, *50*, 5184.

(4) Ruthenium metal was precipitated with zinc from an aqueous solution of $RuCl_3$.

(5) (a) Johnson, B. F. G.; Johnston, R. D.; Lewis, J. *J. Chem. Soc., Chem. Commun.* **1967**, 1057. (b) Anson, C. E.; Bailey, P. J.; Conole, G.; Johnson, B. F. G.; Lewis, J.; McPartlin, M.; Powell, H. R. *J. Chem. Soc., Chem. Commun.* **1989**, 442. (c) Farrugia, L. *Acta Crystallogr., Sect. C* **1988**, *44*, 997. (d) Braga, D.; Grepioni, F.; Parisini, E.; Dyson, P. J.; Blake, A. J.; Johnson, B. F. G. *J. Chem. Soc., Dalton Trans.* **1993**, 2951. (e) Mason, R.; Robinson, W. R. *J. Chem. Soc., Chem. Commun.* **1968**, 468.

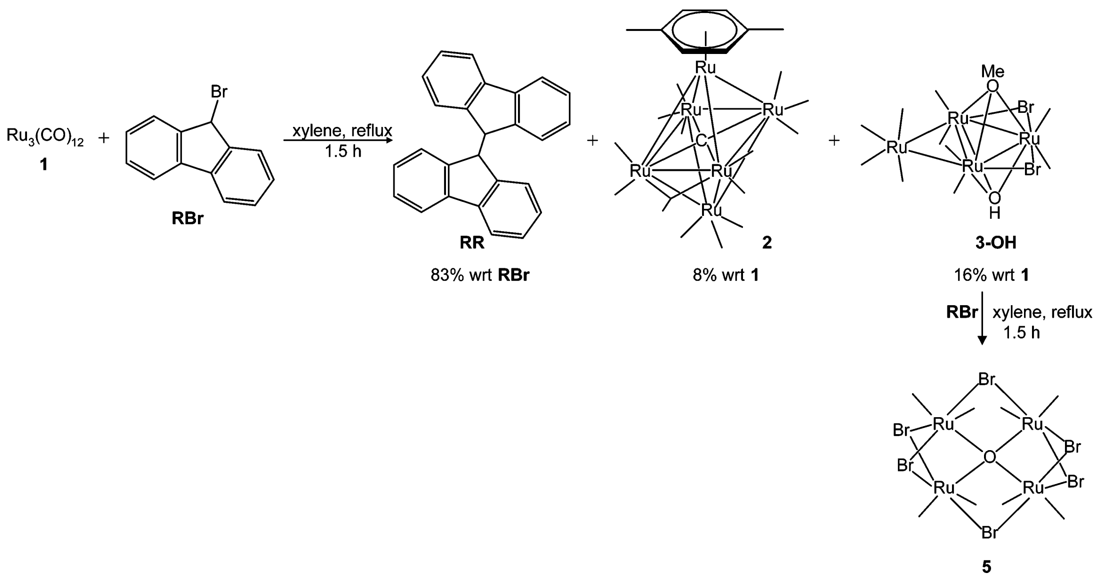
(6) A lesson from a recent paper: Hagen, C. M.; Vieille-Petit, L.; Laurenczy, G.; Süss-Fink, G.; Finke, R. G. *Organometallics* **2005**, *24*, 1819.

(7) Romanelli, M. N.; Teodori, E.; Scapecchi, S.; Dei, S. *Eur. J. Med. Chem.* **1992**, *27*, 53.

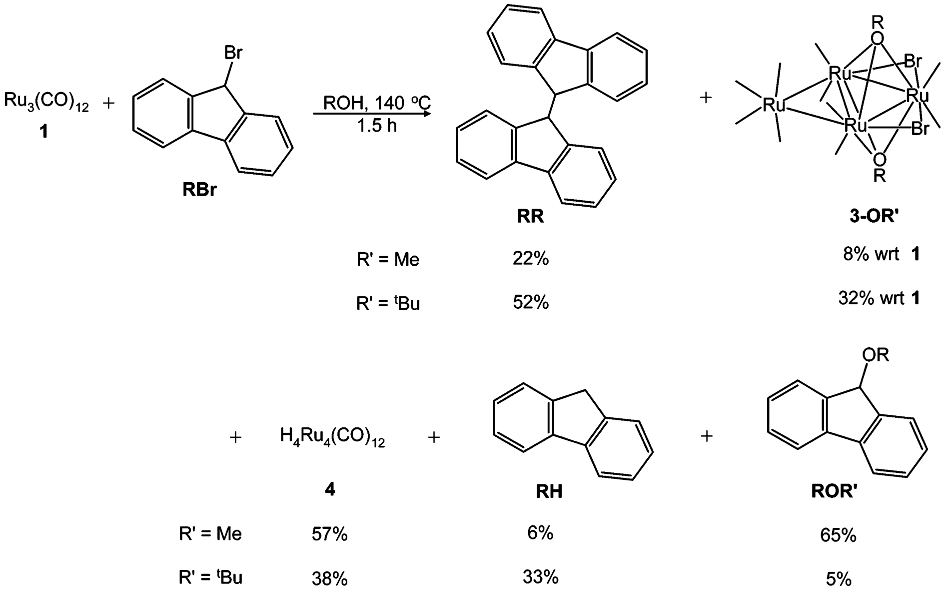
(8) Using freshly distilled toluene at 1.5 h and 140 °C. The reaction vessel was dried overnight in an oven at 120 °C, attached to a double manifold while still hot, and then cooled under an inert atmosphere.

10.1021/om050850t CCC: \$33.50

Scheme 1



Scheme 2



the commercial sample. Indeed when we recrystallized **RBr** from hexane and repeated the stoichiometric reaction, we found that much of **1** remained unreacted and the yield of **3-OH** was reduced drastically (∼4%); the yield of **RR** remained high (92%).

The reactions in alcohol also afforded the known cluster **4**, fluorene (**RH**), as well as the ethers 9-alkoxyfluorene, **ROR′**. As given in entries 10 and 11, **3-OMe** showed significant activity in catalyzing the coupling of **RBr** but over a period of 16 h, while **4** exhibited much poorer efficiency compared to **1** or **3-OH**. However, an important implication of the reactions in Scheme 2 is that **1** also catalyzes hydrogenation and alkoxylation of **RBr**. The cluster [$Ru_4(CO)_{10}Cl_2(OPh)_2$] has been shown to be an intermediate in the hydrogen transfer from alcohols to CX_4 catalyzed by **1**,[12b] and so the formation of **RH** may be attributed to a similar reaction. We are currently exploring the potential of catalytic alkoxylation of alkyl halides with **1**.[9]

Table 1. Catalytic Runs for the Reductive Homocoupling of RBr at 140 °C

run	substrate:catalyst mole ratio	catalyst	reaction time (h)	yield (% of **RR**)	TON	TOF (h^{-1})
1	100:1	**1**	1.5	79[a]	78	52
2	1000:1	**1**	1.5	83[a]	838	559
3[b]	1000:1	**1**	1.5	5	50	33
4	1000:1	**1**	2.5	91	910	364
5	10000:1	**1**	2.5	31	3100	1240
6[c]	1000:1	**1**	18	49	490	27
7	1000:1	**2**	20	0	0	0
8	1000:1	**3-OH**	1.5	88	880	587
9	10000:1	**3-OH**	1.5	85	8500	5667
10	1000:1	**3-OMe**	16	78[a]	780	49
11	1000:1	**4**	8.5	87	870	102
12	1000:1	**5**	56	15[a]	150	3
13	control		7	0	0	0

[a] Based on isolated yields. [b] Reaction temperature at 90 °C. [c] For **RBr** = 2-nitro-9-bromofluorene. Product identified by ^{1}H NMR (d_6-DMSO): δ 5.35 (s, C−H), 6.9−8.3 (m, aromatic). Lit. values:[7] ^{1}H NMR (d_6-DMSO): δ 5.45 (s, C−H), 6.8−8.4 (m, aromatic).

The amount of bromine incorporated into the cluster **3-OH** or **5** cannot possibly be sufficient to account for all the bromine lost from **RBr**. As already observed, **3-OH** is a catalytically active species, while **5** appeared to be a side product representing

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[9] Bogdal, D.; Pielichowski, J.; Jaskot, K. *Org. Prep. Proc. Int.* **1998**, *30*, 427.

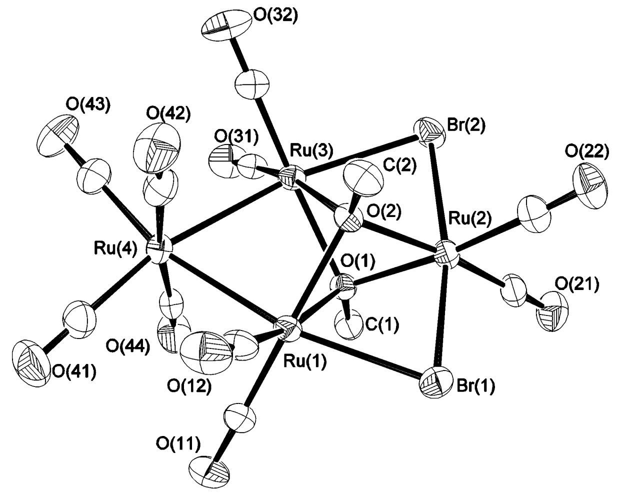


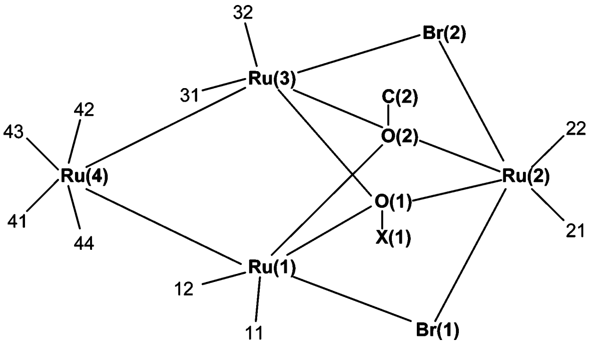
Figure 1. ORTEP diagram (50% thermal ellipsoids drawn, hydrogen atoms omitted) for **3-OMe**.

a dead-end for the catalytic cycle. We have performed detailed GC and ^{1}H NMR analyses of the reaction mixture for a 0.1 mol % run and found that 4-bromotoluene was produced in the reaction; integration of the NMR signals showed that it was produced in equimolar ratio with bifluorenyl. More importantly, no 2- or 3-bromotoluene or benzyl bromide was observed among the products. This selective formation of 4-bromotoluene ruled out the possibilities (i) that elemental bromine was produced, which subsequently reacted with the toluene, as well as (ii) of a radical mechanism. A more likely pathway involved prior coordination or C−H activation of the toluene;[10] prior coordination to a metal center would sterically favor the 4-position.

Crystallographic Discussion. As mentioned above, the structures of **3-OH** and **3-OMe** have been confirmed by single-crystal X-ray structural studies. The ORTEP plot for **3-OMe** is given in Figure 1, and a common atomic numbering scheme with selected bond parameters for both clusters **3** are given in Table 2.

The molecule of **3-OH** possesses crystallographic mirror symmetry. Known clusters with the same structural type as **3** include $[Ru_4(\mu_3\text{-OAr})_2(\mu\text{-Cl})(\mu\text{-OAr})(CO)_{10}]$, $[Ru_4(\mu_3\text{-OAr})_2(\mu\text{-OAr})_2(CO)_{10}]$ (where Ar = C_6H_4OMe-4- or -2-naphthyl),[11] and $[Ru_4(\mu_3\text{-OR})_2(\mu\text{-Cl})_2(CO)_{10}]$ (where R = Et or Ph),[12] and some of these have been demonstrated to have interesting catalytic potential.[6,12b,15] As in those clusters, **3** are 68-valence-electron, electron-precise clusters with two metal−metal bonds; the distances for the other Ru···Ru vectors, ranging from 3.0628(5) to 3.1529(5) Å, indicate nonbonding interactions. The presence of both the capping moieties is also supported by observation of a singlet resonance at 4.64 ppm and a broad resonance at 2.39 ppm corresponding to the methoxy and hydroxyl groups, respectively, in **3-OH**, and a single methoxy resonance at 4.64 ppm in **3-OMe**. The O−CH_3 bond distances (1.442(5) Å in **3-OMe** to 1.463(9) Å in **3-OH**) are typical of C−O single bonds.[13] The bromine bridges are also unsymmetrical, being closer to the ruthenium with no metal−metal bonds than to the metal−metal-bonded ruthenium atom (2.4993(5) vs 2.6599(6) Å for **3-OH**; 2.5014(6) and 2.5053(6) Å vs 2.6867(6) and 2.6583(6) Å for **3-OMe**.)

Table 2. Common Atomic Numbering Scheme and Selected Bond Parameters for 3-OH and 3-OMe



	3-OH[a]	3-OMe
X	H	C
Ru(1)−Ru(4)	2.7536(6)	2.7578(5)
Ru(3)−Ru(4)	2.7536(6)	2.7463(5)
Ru(1)···Ru(3)	3.1010(8)	3.0628(5)
Ru(1)···Ru(2)	3.1417(6)	3.1529(5)
Ru(2)···Ru(3)	3.1417(6)	3.1222(5)
Ru(1)−Br(1)	2.6599(6)	2.6867(6)
Ru(2)−Br(2)	2.4993(5)	2.5014(6)
Ru(2)−Br(1)	2.4993(5)	2.5053(6)
Ru(3)−Br(2)	2.6599(6)	2.6583(6)
Ru(1)−O(2)	2.182(3)	2.172(3)
Ru(1)−O(1)	2.165(3)	2.184(3)
Ru(2)−O(1)	2.117(5)	2.130(3)
Ru(2)−O(2)	2.166(5)	2.138(3)
Ru(3)−O(1)	2.165(3)	2.180(3)
Ru(3)−O(2)	2.182(3)	2.195(3)
O(1)−X(1)		1.442(5)
O(2)−C(2)	1.463(9)	1.443(5)
Ru(3)−Ru(4)−Ru(1)	68.54(2)	67.624(12)
Ru(2)−Br(1)−Ru(1)	74.953(19)	74.692(16)
Ru(2)−Br(2)−Ru(3)	74.953(19)	74.406(16)

[a] Mirror symmetry through Ru(2), Ru(4), O(1), O(2). Symmetry transformation: *x*, −*y*+3/2, *z*.

There are three independent molecules found in the asymmetric unit of **5**; the ORTEP plot of one molecule, depicting its molecular structure, together with selected bond parameters, is given in Figure 2. The structure of **5** comprises four Ru(CO)$_2$ moieties, which are bonded to a central μ_4-O atom in a distorted tetrahedral arrangement. Some structurally related examples include $Fe_4(\mu_4\text{-O})(L)_6$ (where L = *N,N′*-diphenylformamidinate or *N,N′*-bis(biphenylformamidinate))[14] and the

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[10] Ruthenium complexes are capable of C−H activation of sp^2 C−H bonds, for examples: (a) Mitsudo, T.; Ura, Y.; Kondo, T. *J. Organomet. Chem*. **2004**, *689*, 4530. (b) Buskens, P.; Giunta, D.; Leitner, W. *Inorg. Chim. Acta* **2004**, *357*, 1969. (c) Giunta, D.; Hoelscher, M.; Lehmann, C. W.; Mynott, R.; Wirtz, C.; Leitner, W. *Adv. Synth. Catal*. **2003**, *345*, 1139. (d) Kanaya, S.; Komine, N.; Hirano, M.; Komiya, S. *Chem. Lett*. **2001**, *12*, 1284. (e) Voskoboynikov, A. Z.; Osina, M. A.; Shestakova, A. K.; Kazankova, M. A.; Trostyanskaya, I. G.; Beletskaya, I. P.; Dolgushin, F. M.; Yanovsky, A. I.; Struchkov, Y. T. *J. Organomet. Chem*. **1997**, *545−546*, 71. (f) Collman, J. P.; Fish, H. T.; Wagenknecht, P. S.; Tyvoll, D. A.; Chng, L.-L.; Eberspacher, T. A.; Brauman, J. I.; Bacon, J. W.; Pignolet, L. H. *Inorg. Chem*. **1996**, *35*, 6746. (g) Moreno, B.; Sabo-Etienne, S.; Chaudret, B.; Rodriguez, A.; Jalon, F.; Trofimenko, S. *J. Am. Chem. Soc*. **1995**, *117*, 7441. (h) Urbanos, F.; Halcrow, M. A.; Fernandez-Baeza, J.; Dahan, F.; Labroue, D.; Chaudret, B. *J. Am. Chem. Soc*. **1993**, *115*, 3484. (i) Ueda, T.; Yamanaka, H.; Adachi, T.; Yoshida, T. *Chem. Lett*. **1988**, *3*, 525.

[11] Jeynes, T. P.; Cifuentes, M. P.; Humphrey, M. G.; Koutsantonis, G. A.; Raston, C. L. *J. Organomet. Chem*. **1994**, *476*, 133.

[12] (a) Johnson, B. F. G.; Lewis, J.; Mace, J. M.; Raithby, P. R.; Vargas, M. D. *J. Organomet. Chem*. **1987**, *321*, 409. (b) Bhaduri, S.; Sapre, N.; Sharma, K.; Jones, P. G.; Carpenter, G. *J. Chem. Soc., Dalton Trans*. **1990**, 1305.

[13] Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans*. **1987**, S1.

[14] Cotton, F. A.; Daniels, L. M.; Falvello, L. R.; Matonic, J. H.; Murillo, C. A.; Wang, X.; Zhou, H. *Inorg. Chim. Acta* **1997**, *266*, 91.

[15] (a) Lugan, N.; Lavigne, G.; Soulié, J. M.; Fabre, S.; Kalck, P.; Saillard, J. Y.; Halet, J. F. *Organometallics* **1995**, *14*, 1712. (b) Lavigne, G.; Lugan, N.; Kalck, P.; Soulié, J. M.; Lerouge, O.; Saillard, J. Y.; Halet, J. F. *J. Am. Chem. Soc*. **1992**, *114*, 10669.

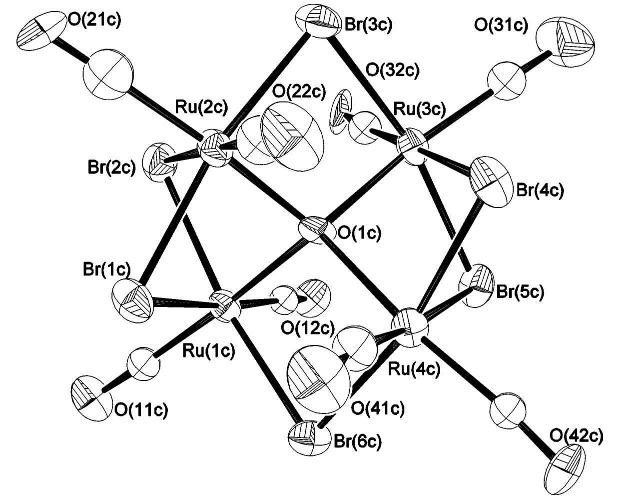

Figure 2. ORTEP diagram (50% thermal ellipsoids drawn) and selected bond lengths (Å) and angles (deg) for molecule C of cluster **5**. Ru(1C)$\cdots$Ru(2C) = 3.109(4); Ru(3C)$\cdots$Ru(4C) = 3.115(4); Ru(1C)−Br(1C) = 2.611(4); Ru(1C)−Br(2C) = 2.506(4); Ru(1C)−Br(6C) = 2.504(4); Ru(2C)−Br(1C) = 2.509(4); Ru(2C)−Br(2C) = 2.599(4); Ru(2C)−Br(3C) = 2.518(4); Ru(3C)−Br(3C) = 2.525(4); Ru(3C)−Br(4C) = 2.605(4); Ru(3C)−Br(5C) = 2.492(4); Ru(4C)−Br(4C) = 2.498(5); Ru(4C)−Br(5C) = 2.589(4); Ru(4C)−Br(6C) = 2.514(5); Ru(1C)−O(1C) = 2.16(2); Ru(2C)−O(1C) = 2.11(2); Ru(3C)−O(1C) = 2.08(2); Ru(4C)−O(1C) = 2.121(18); Ru(2C)−Br(1C)−Ru(1C) = 74.74(12); Ru(1C)−Br(2C)−Ru(2C) = 75.03(12); Ru(2C)−Br(3C)−Ru(3C) = 83.99(13); Ru(4C)−Br(4C)−Ru(3C) = 75.20(12); Ru(3C)−Br(5C)−Ru(4C) = 75.58(12); Ru(1C)−Br(6C)−Ru(4C) = 85.16(13); Ru(3C)−O(1C)−Ru(2C) = 107.3(9); Ru(3C)−O(1C)−Ru(4C) = 95.7(9); Ru(2C)−O(1C)−Ru(4C) = 130.9(10); Ru(3C)−O(1C)−Ru(1C) = 128.9(10); Ru(2C)−O(1C)−Ru(1C) = 93.5(8); Ru(4C)−O(1C)−Ru(1C) = 105.0(9).

anionic $[Ru_4(\mu_4\text{-}O)(\mu\text{-}Cl)_4(CO)_{10}]^{2-}$.[15] The $Ru(CO)_2$ units are doubly bridged by bromine atoms in pairs, so that they are in a twisted bowtie arrangement. The $Ru(CO)_2$ unit on each of the wings of this bowtie is in turn bridged by another bromine atom to an $Ru(CO)_2$ unit on the other wing. This final set of two bridges imparts helical chirality to the molecule. The closest Ru$\cdots$Ru contacts are between the pair of ruthenium atoms that are connected by the double bromine bridges, and these are all beyond 3 Å in length (ranging from 3.098(4) to 3.137(4) Å) and hence are clearly nonbonding, as is consistent with the total valence electron count of 72, for which no metal−metal bond is expected.

The bromine bridges which are *trans* to another bromine atom on one side and *trans* to a carbonyl on the other are all unsymmetrical; the Ru−Br bond *trans* to a carbonyl is always longer than that *trans* to a bromine (ranges of 2.586(4) to 2.613(4) Å and 2.492(4) to 2.514(4) Å, respectively). The observed range of Ru−Br bond lengths *trans* to a carbonyl is also in accord with that in the compound $[Ru(CO)_3Br_2]_2$, which also has bromine atoms *trans* to carbonyls, for which the observed Ru−Br bond lengths were 2.543(4) and 2.571(4) Å.[16] In comparison, for those that are *trans* to bromine atoms on both sides (the single bridges Br(3) and Br(6)) the largest difference in their Ru−Br distances is $\sim 4\sigma$. This probably reflects the *trans* influence of the carbonyl ligand. In accord with this, the range of Ru−Br bond distances associated with the single, symmetrical bromine bridges is 2.488(5) to 2.527(4) Å, which overlaps with the range observed above for an Ru−Br bond *trans* to bromine.

Concluding Remarks

We have thus found that $Ru_3(CO)_{12}$ is a very efficient catalytic precursor for the C−C bond coupling of 9-bromofluorenes to bifluorenyls. C−H activation of the aromatic solvent is probably involved, but it certainly effectively transfers the halogen to it. The potential of this concept, of using an aromatic solvent as a halogen acceptor for such catalytic reductive coupling of alkyl halides, is worth further exploration.

Experimental Section

General Procedures. All reactions were performed under argon using Schlenk techniques. Solvents were purified, dried, distilled, and stored under nitrogen prior to use, except for xylene and *tert*-butyl alcohol, which were used as supplied. IR spectra were obtained on a Shimadzu Prestige-21 FTIR-8400S or a Merlin IR spectrometer. ^1H NMR spectra were recorded on a Bruker ACF300, DPX 300, or AV300 NMR spectrometer as $CDCl_3$ solutions unless otherwise stated. ^1H chemical shifts reported are referenced against the residual proton signals of the solvents. Mass spectra were obtained on a Finnigan MAT95XL-T spectrometer in a 3NBA matrix (FAB), a Finnigan MAT LCQ spectrometer with MeOH as solvent (ESI), or a Macromass VG7035 at 70 eV (EI). All elemental analyses were performed by the microanalytical laboratory at NUS. GC-MS analyses were performed on a Zebron ZB-1 gas chromatograph equipped with an HP5973 mass selective detector, using a ValcoBon CFS-A capillary column (30.0m × 530 μm) coated with poly(dimethylsiloxane) (25.0 μm). The cluster $Ru_3(CO)_{12}$, **1**, was purchased from Oxkem Ltd. and used as supplied. All other reagents are commercially available and used without further purification. Yields of organic products reported are with respect to organic substrate, and those of cluster products are with respect to the cluster precursor.

Procedure for Catalytic Runs. For the catalytic runs for which isolated yields were determined, **RBr** (76.7 mg, 0.313 mmol) and the appropriate amount of **1** were brought to reflux in xylene (10 mL) under an argon atmosphere. After the heating period, the reaction mixture was allowed to cool to room temperature, the solvent was removed under reduced pressure, and the residue obtained was chromatographed on silica gel TLC plates, eluting with hexane to afford **RR**.

For the other catalytic runs, the catalysts were prepared as stock solutions in toluene, from which the appropriate volume was withdrawn via a microsyringe and added to a toluene (10 mL) solution of **RBr** and docosane as the internal standard. The solutions were heated at 140 °C in a Carius tube, and 1 mL aliquots withdrawn for NMR analyses. Yields were determined from the integration ratios of the alkyl protons on the substrate and the product before and after the reaction.

Reaction of RBr with 1 in Xylene. A xylene solution (10 mL) of **1** (300 mg, 0.469 mmol) and **RBr** (115 mg, 0.469 mmol) was refluxed for 1.5 h. The solvent was then removed under reduced pressure, and the residue obtained was extracted with dichloromethane and chromatographed on silica gel TLC plates. Elution with hexane/CH_2Cl_2 (1:1, v/v) gave three bands.

Band 1 ($R_f = 0.95$): yellow solid, bifluorenyl, **RR** (yield = 64 mg, 83% with respect to bromofluorene). ^1H NMR (δ, $CDCl_3$): 7.78 (d, 4H, aromatic), 7.23−7.41 (m, 4H, aromatic), 6.97−7.1 (m, 8H, aromatic), 5.03 (s, 2H, CH) (lit. values[17] (δ, $CDCl_3$): 7.61 (m, 4H), 7.11(m, 12H), 4.71(s, 2H)). EI-MS: 330 $[M]^+$. X-ray crystal data: monoclinic, $P2_1/n$; $a = 5.5963(3)$ Å, $b = 17.6769(11)$ Å, $c = 17.6150(10)$ Å, $\beta = 91.296(3)°$, $V = 1742.12(17)$ Å^3, $Z = 4$ (lit. values:[18] monoclinic, space group $P2_1/n$, $a = 17.586(2)$ Å, $b = 17.764(3)$ Å, $c = 5.682(l)$ Å, $\beta = 9l.44(l)°$, $Z = 4$).

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[16] Merlino, S.; Montagnoli, G. *Acta Crystallogr.* **1968**, *B24*, 424.

[17] Rabinovitz, M.; Agranat, I.; Bergmann, E. D. *Tetrahedron Lett.* **1965**, *18*, 1265.

Band 2 (R_f = 0.66): reddish brown solid, [$Ru_6C(CO)_{14}$(*p*-xylene)], **2** (yield = 20.2 mg, 7.7% with respect to ruthenium). IR (CH_2Cl_2): ν_{CO} 2075m, 2024vs cm^{-1}. ^{1}H NMR (δ, $CDCl_3$): 5.6 (s, 4H, aromatic), 2.1(s, 6H, CH_3). FAB-MS: 1087 [M − CO]$^+$. Anal. Calcd for $C_{23}H_{10}O_{14}Ru_6$: C, 24.74; H, 0.90. Found: C, 24.33; H, 1.04.

Band 3 (R_f = 0.16): orange-yellow solid, [Ru_4(μ_3-OMe)(μ_3-OH)(μ-Br)$_2$(CO)$_{10}$], **3-OH** (yield = 50 mg, 16% with respect to ruthenium). IR (CH_2Cl_2): ν_{CO} 2096m, 2073s, 2025vs, 2016vs, 1952m cm^{-1}. ^{1}H NMR (δ, $CDCl_3$): 4.64 (s, 3H, OMe), 2.39 (s br, 1H, OH). FAB-MS: 892 [M]$^+$. Anal. Calcd for $C_{11}H_4Br_2O_{12}Ru_4$: C, 14.81; H, 0.45. Found: C, 14.75; H, 0.57.

Using a commercial sample of **RBr** that has been recrystallized from hexane and otherwise identical conditions as above yielded, after chromatographic separation, unreacted **1** (140 mg, 47%), **RR** (71.2 mg, 92% with respect to **RBr**), **2** (20 mg, 7.6%), and **3-OH** (12 mg, 3.8%).

Reaction of RBr with 1 in the Presence of Water. A solution of **1** (300 mg, 0.469 mmol) and **RBr** (115 mg, 0.469 mmol) in a solvent mixture of THF (2 mL), H_2O (2 mL), and toluene (6 mL) was heated at 140 °C in a Carius tube. The solvent was then removed under reduced pressure, and the residue obtained was dissolved in the minimum amount of dichloromethane and chromatographed on silica gel TLC plates. Elution with hexane/CH_2Cl_2 (1:1, v/v) gave two bands.

Band 1 (R_f = 0.97): yellow solid of **RR** (yield = 70 mg, 90%).

Band 2 (R_f = 0.21): orange-yellow solid of **3-OH** (yield = 100 mg, 32%).

Synthesis of 3-OMe. A solution of **1** (300 mg, 0.469 mmol) and **RBr** (115 mg, 0.469 mmol) in methanol (4 mL) was heated under argon at 140 °C in an autoclave for 2.5 h. After removal of the solvent under reduced pressure, the residue was extracted with dichloromethane and chromatographed on silica gel TLC plates. Elution with 100% hexane (50 mL) gave five bands other than a trace of unreacted **1**.

Band 1 (R_f = 0.79): yellow solid, [$H_4Ru_4(CO)_{12}$], **4** (yield = 150 mg, 57%).

IR (cyclohex): ν_{CO} 2081s, 2066vs, 2030m, 2024s, 2008w cm^{-1}. ^{1}H NMR (δ, $CDCl_3$): −17.8 (s, RuHRu) (lit. values:[19] IR (cyclohex): ν_{CO} 2081s, 2067vs, 2030m, 2024s, 2009w cm^{-1}. ^{1}H NMR (δ, $CDCl_3$): −17.98 (s, RuHRu)).

Band 2 (R_f = 0.63): colorless solid, Fluorene, **RH** (yield = 5 mg, 6%). ^{1}H NMR (δ, $CDCl_3$): 3.91 (s, 2H, CH_2), 7.30−7.38 (m, 4H, aromatic), 7.55 (d, 2H, aromatic), 7.8 (d, 2H, aromatic). These values were compared to that of an authentic sample.

Band 3 (R_f = 0.55): dark reddish orange solid, [Ru_4(μ_3-OMe)$_2$(μ-Br)$_2$(CO)$_{10}$], **3-OMe** (yield = 25.5 mg, 8%). IR (CH_2Cl_2): ν_{CO} 2100m, 2072s, 2025vs, 2020vs, 1951m cm^{-1}. ^{1}H NMR (δ, $CDCl_3$): 4.64 (s, OCH_3). FAB-MS: 906 [M]$^+$. Anal. Calcd for $C_{12}H_6Br_2O_{12}Ru_4\cdot1/4$hexane: C, 17.44; H, 1.03. Found: C, 17.24; H, 0.85%. The presence of hexane in the analytical sample was confirmed by ^{1}H NMR spectroscopy.

Band 4 (R_f = 0.32): yellow solid of **RR** (yield = 17 mg, 22%).

Band 5 (R_f = 0.21): colorless crystalline solid, 9-methoxyfluorene, **ROMe** (yield = 60 mg, 65%). ^{1}H NMR (δ, $CDCl_3$): 7.26−7.69 (m, 8H, aromatic), 5.61 (s, 1H, CH), 3.07 (s, 3H, OMe) (lit. values:[20] (δ, $CDCl_3$): 7.26−7.70 (m, 8H, aromatic), 5.62 (s, 1H, CH), 3.07 (s, 3H, OMe)).

Synthesis of 3-OBu^t. A solution (4 mL) of **1** (300 mg, 0.469 mmol) and **RBr** (115 mg, 0.469 mmol) in *tert*-butyl alcohol (4 mL) was heated under argon at 140 °C in an autoclave for 2.5 h. After removal of the solvent under reduced pressure, the residue was extracted with dichloromethane and chromatographed on silica gel TLC plates. Elution with hexane/CH_2Cl_2 (1:1, v/v) gave five bands.

Band 1 (R_f = 0.97): yellow solid of **4** (yield = 100 mg, 38%).

Band 2 (R_f = 0.89): colorless solid of **RH** (yield = 26 mg, 33%).

Band 3 (R_f = 0.81): yellow solid of **RR** (yield = 40 mg, 52%).

Band 4 (R_f = 0.36): colorless solid, 9-*tert*-butoxyfluorene, **ROBu^t** (yield = 5 mg, 4.5%). ^{1}H NMR (δ, $CDCl_3$): 7.26−7.86 (m, 8H, aromatic), 5.56 (s, 1H, CH), 1.54 (s, 9H, CH_3) (lit. values:[21] (δ, $CDCl_3$): 7.26−7.86 (m, 8H, aromatic), 5.56 (s, 1H, CH), 1.54 (s, 9H, CH_3)). EI-MS: 238(M$^+$).

Band 5 (R_f = 0.19): dark yellowish-orange microcrystals, [Ru_4(μ_3-OBu^t)$_2$(μ-Br)$_2$(CO)$_{10}$], **3-OBu^t** (yield = 107 mg, 32%). IR (CH_2Cl_2): ν_{CO} 2096m, 2073s, 2022vs, 2017vs, 1950m cm^{-1}. ^{1}H NMR (δ, $CDCl_3$): 1.19 (s, Bu^t). ESI-MS: 990 ([M]$^+$); 877 ([M − 2Bu^t]$^+$). Anal. Calcd for $C_{18}H_{18}Br_2O_{12}Ru_4\cdot1/4C_6H_{14}$: C, 23.09; H, 2.12. Found: C, 22.97; H, 2.62. The presence of hexane solvate in the sample was confirmed by ^{1}H NMR spectroscopy.

Reaction of RBr with 3-OH. A xylene solution (10 mL) of **3-OH** (36.4 mg, 0.041 mmol) and **RBr** (10 mg, 0.041 mmol) was refluxed for 1.5 h. The solvent was then removed under reduced pressure and the residue chromatographed on silica gel TLC plates. Elution with hexane/CH_2Cl_2 (1:1, v/v) gave three identifiable bands.

Band 1 (R_f = 0.98): orange-yellow solid, [Ru_4(μ_4-O)(μ-Br)$_6$(CO)$_8$], **5** (yield = 7 mg, 22% based on reacted Ru and 67% based on Br). IR (CH_2Cl_2): ν_{CO} 2072vs, 2011s, 1983w cm^{-1}. FAB-MS: 1124 [M]$^+$. Anal. Calcd for $C_8Br_6O_9Ru_4\cdot1/4C_6H_{14}$: C, 9.98. Found: C, 10.05.

Band 2 (R_f = 0.88): yellow solid of **RR** (yield = 5.7 mg, 85%).

Band 3 (R_f = 0.19): orange-yellow solid of **3-OH** (yield = 11.4 mg).

Reaction of RBr with 3-OMe. A xylene solution (7 mL) of **3-OMe** (25.6 mg, 0.028 mmol) and **RBr** (6.9 mg, 0.028 mmol) was refluxed for 1.5 h. The solvent was then removed under reduced pressure and the residue chromatographed on silica gel TLC plates. Elution with hexane/CH_2Cl_2 (1:1, v/v) gave two identifiable bands.

Band 1 (R_f = 0.98): orange-yellow solid of **5** (yield = 7 mg, 22% based on Ru and 67% based on Br).

Band 2 (R_f = 0.88): yellow solid of **RR** (yield = 4.6 mg, 83%).

Reaction of RBr with 4. A toluene solution (10 mL) of **4** (39.5 mg, 0.053 mmol) and **RBr** (13 mg, 0.053 mmol) was heated at 140 °C in a Carius tube for 1.5 h. The solvent was then removed under reduced pressure and the residue chromatographed on silica gel TLC plates. Elution with hexane gave three bands.

Band 1 (R_f = 0.78): unreacted **4** (yield = 37 mg, 94% based on Ru).

Band 2 (R_f = 0.64): colorless solid of **RH** (yield = 4.5 mg, 51%).

Band 3 (R_f = 0.30): yellow solid of **RR** (yield = 3 mg, 34%).

Crystal Structure Determinations. Crystals were grown from dichloromethane/hexane solutions and mounted on quartz fibers. X-ray data were collected on a Bruker AXS APEX system, using Mo Kα radiation, at 223 K with the SMART suite of programs.[22] Data were processed and corrected for Lorentz and polarization effects with SAINT[23] and for absorption effects with SADABS.[24] Structural solution and refinement were carried out with the SHELXTL suite of programs.[25] Crystal and refinement data are summarized in Table 3.

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(18) Dougherty, D. A; Llort, F. M.; Mislow, K. *Tetrahedron* **1978**, *34*, 1301.

(19) Bruce, M. I.; Williams, M. L. *Inorg. Synth.* **1990**, *28*, 219.

(20) Bertani, R.; Michelin, R. A.; Mozzon, M.; Sassi, A.; Basato, M.; Biffis, A.; Martinati, G.; Zecca, M. *Inorg. Chem. Comm.* **2001**, *4*, 281.

(21) Bertani, R.; Biasiolo, M.; Darini, K.; Michelin, R. A.; Mozzon, M.; Visentin, F.; Zanotto, L. *J. Organomet. Chem.* **2002**, *642, 32*.

(22) *SMART* version 5.628; Bruker AXS Inc.: Madison, WI, 2001.

(23) *SAINT+* version 6.22a; Bruker AXS Inc.: Madison, WI, 2001.

(24) Sheldrick, G. M. *SADABS*; 1996.

(25) *SHELXT*L version 5.1; Bruker AXS Inc.: Madison, WI, 1997.

Table 3. Crystal and Refinement Data for 2, 3-OH, 3-OMe, and 5

	2	**3**-OH	**3**-OMe	**5**
empirical formula	$C_{23}H_{10}O_{14}Ru_6$	$C_{11}H_4Br_2O_{12}Ru_4$	$C_{12}H_6Br_2O_{12}Ru_4$	$C_8Br_6O_9Ru_4$
fw	1116.73	892.24	906.27	1123.82
cryst syst	monoclinic	orthorhombic	monoclinic	monoclinic
space group	$P2_1/n$	*Pnma*	$P2_1/c$	$C2$
a, Å	17.5193(7)	16.6549(12)	9.0976(3)	42.757(2)
b, Å	10.1345(4)	9.9567(7)	11.2013(4)	10.6371(6)
c, Å	18.0790(7)	12.4927(9)	22.0160(7)	14.4885(7)
α, deg	90	90	90	90
β, deg	117.371(2)	90	90.486(2)	103.427(2)
γ, deg	90	90	90	90
volume, Å^3	2850.56(19)	2071.6(3)	2243.46(13)	6409.4(6)
Z	4	4	4	12
density (calcd), Mg/m^3	2.602	2.861	2.683	3.494
absorp coeff, mm^{-1}	3.167	6.773	6.257	14.032
$F(000)$	2096	1648	1680	6072
cryst size, mm^3	0.20 × 0.13 × 0.02	0.34 × 0.32 × 0.04	28.00 × 0.18 × 0.10	0.11 × 0.08 × 0.03
θ range for data collection, deg	2.20 to 26.37	2.04 to 29.54	2.04 to 30.03	2.15 to 26.37
no. of reflns collected	21 199	27 734	19 036	25 791
no. of indep reflns	5828 [R(int) = 0.0547]	2895 [R(int) = 0.0445]	6433 [R(int) = 0.0405]	12 213 [R(int) = 0.1171]
max. and min. transmn	0.939 and 0.570	0.773 and 0.207	0.573 and 0.008	0.678 and 0.308
no. of data/restraints/params	5828/90/408	2895/0/154	6433/0/295	12 213/1/605
goodness-of-fit on F^2	1.042	1.292	1.031	0.995
final R indices [$I > 2\sigma(I)$]	R1 = 0.0460	R1 = 0.0386	R1 = 0.0375	R1 = 0.0863
	wR2 = 0.0904	wR2 = 0.0829	wR2 = 0.0752	wR2 = 0.1628
R indices (all data)	R1 = 0.0725	R1 = 0.0425	R1 = 0.0524	R1 = 0.1769
	wR2 = 0.1006	wR2 = 0.0846	wR2 = 0.0813	wR2 = 0.2006
largest diff peak and hole, e Å^{-3}	1.013 and −0.896	1.113 and −0.702	0.837 and −0.732	2.837 and −1.583

The structures were solved by direct methods to locate the heavy atoms, followed by difference maps for the light, non-hydrogen atoms. All non-hydrogen atoms were generally given anisotropic displacement parameters in the final model (except for **5** below). Cluster **2** exhibited disorder of two carbonyls on Ru(4) and one carbonyl on Ru(5). These were each modeled with two alternative sites of equal occupancies, and appropriate restraints on their anisotropic parameters and bond distances were placed.

Cluster **5** contained three molecules in the asymmetric unit. It was refined as a racemic twin. The data quality was poor, and there appeared to be disorder in molecule A, which was not modeled. All the carbon atoms were given isotropic thermal parameters, as well as the μ_4-O atom in molecule A.

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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