Intracluster transmetalation of cuprates with stannanes

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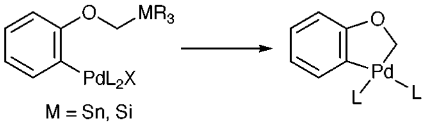
Alkylarylcuprates with intramolecularly tethered stannanes undergo an intracluster Cu^I/Sn^{IV} transmetalation to yield arylstannanes.

Transmetalation of diorganocuprates with alkenyltrialkylstannanes allows for the selective synthesis of mixed organocuprates with concomitant formation of stable tetraalkylstannanes [eqn. (1)].[1] This method has been successfully extended to the

$$R^1SnR^2_3 + R^3_2CuLi \longrightarrow R^1R^3CuLi + R^3SnR^2_3 \qquad (1)$$

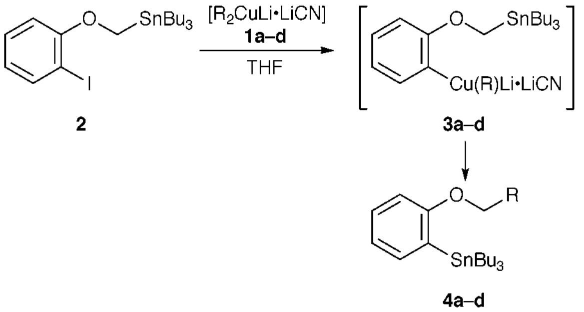
preparation of allyl cuprates.[2] However, despite the synthetic importance of this reaction[1–3] little is known about its mechanism.

We have been able to isolate the Pd/Sn and Pd/Si transmetalation steps of the Stille and Hiyama coupling reactions, respectively, by performing the reaction intramolecularly in a system which was unable to reductively eliminate because of the instability of the resulting organic product [eqn. (2)].[4] We decided to use a similar approach to study the Cu/Sn transmetalation.



M = Sn, Si (2)

Recently, Sakamoto demonstrated that mixed arylmethylcuprates can be obtained from iodobenzenes by iodine–copper exchange reaction with [LiCuMe$_2$·LiCN] (**1a**).[5,6] Therefore, we chose to study the reactivity of arylcuprates **3**, synthesised by reaction of aryl iodide **2** with **1** (Scheme 1 and Table 1). Upon warming of the solution of **3a**[7] from −78 to 23 °C, arylstannane **4a** was cleanly formed in high yield by an apparent intramolecular Cu/Sn transmetalation.[8,9]† A similar reaction was observed with cuprates **3b–d** formed *in situ* from aryl iodide **2** by reaction with the corresponding homocuprates **1b–d**, although yields were lower due to the slower iodine/copper exchange reaction as compared with that of **1a**. Stannane **4a** was also obtained by reaction of **2** with [LiCuMe$_2$·LiI], although the reaction was not so clean. Reaction of **2** with either MeLi or BuLi (2 equiv. each) failed to give any of the rearranged products **4a** or **4b**, instead yielding **5** after hydrolysis.

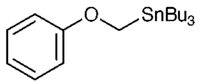


Scheme 1

Table 1 Reaction of stannane **2** with cuprates **1a–d**

1 (equiv.)	R	Product	Isolated yield (%)
1a (1.1)	Me	**4a**	96
1a (2.0)	Me	**4a**	38
1b (1.6)	Bu	**4b**	40
1b (2.0)	Bu	**4b**	50
1c (1.5)	Bu^t	**4c**	37
1c (2.0)	Bu^t	**4c**	26
1d (1.2)	Ph	**4d**	43

Arylstannanes **4** presumably arise by Cu/Sn transmetalation, followed by reaction of the resulting cuprate with RI formed in the first iodine/copper exchange process. Although a direct intramolecular process on **3** appears to be forbidden due to endocyclic restriction,[10] the following experiment also excludes a simple intermolecular pathway. Thus, treatment of a mixture of stannane **5** and iodobenzene with **1a** failed to give any of ethers **6a**,**b** and phenyltributylstannane.[11] Similarly, no Cu^I/Sn^{IV} exchange was observed between **5** and [LiCuPh$_2$·LiCN] (**1d**).



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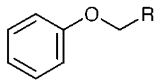
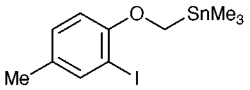


6a R = Me
6b R = Ph



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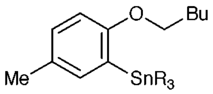
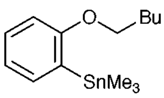


8a R = Me
8b R = Bu



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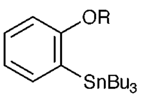
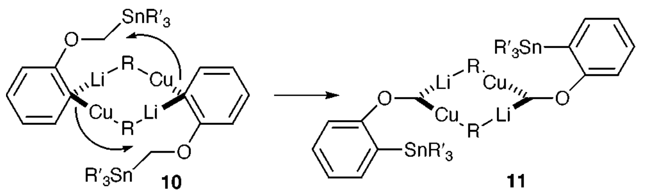


12 R = H
13 R = CH$_2$OH

On the other hand, treatment of a 1 : 1 mixture of **2** and **7** with [Bu$_2$CuLi·LiCN] led to a mixture of the four possible products **4b**, **8a**, **8b** and **9**.[12] Although apparently puzzling, this crossover experiment can be readily explained if the usual dimeric structure of the cuprates is taken into account (Scheme 2).[13] Thus, reaction of cuprates **1** with the aryl iodides would furnish



Scheme 2

dimer alkylarylcuprates **10**,[14] which could suffer a selective intracluster transmetalation to afford mixed cuprate **11**. Evidence for the formation of species **11** was obtained by the isolation of stannane **12**[15] in the reactions of **1b** with **2**, presumably as a result of the hydrolysis of hemiketal **13** resulting from the oxidation of cuprate **11** ($R = R' = Bu$) by oxygen. Final coupling of cuprates **11** with RI (R = Me, Bu, Bu^t, Ph) formed in the first iodine/copper exchange reaction accounts for the formation of products **4a–d** (Scheme 1).

Thus the present study demonstrates that transmetalation of stannanes with cuprates can proceed in an intracluster manner. This is also the first example of transmetalation of alkylstannanes with organocuprates. Similar transformations could be conceived with organostannanes bonded to the lithium atoms of cuprate dimers through the appropriate directing groups.

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Notes and references

† *Preparation* of **4a**: MeLi (1.6 M solution in hexanes, 0.93 ml, 1.49 mmol) was added into a suspension of CuCN (66 mg, 0.74 mmol) in THF (4 ml) at −78 °C. After stirring at −78 °C for 3 h, the light yellow solution was treated with a solution of **2** (350 mg, 0.67 mmol) in THF (5 ml). The resulting mixture was allowed to reach 23 °C over 17 h. A saturated $NH_4Cl–NH_3$ buffered solution (pH = 8, 50 ml) and Et_2O (100 ml) were then added. After the usual extractive workup and chromatography (SiO_2, hexanes) **4a** was obtained as a colorless oil (264 mg, 96%); $\delta_H(CDCl_3$, 200 MHz) 7.37 (dd, *J* 6.6, 1H), 7.32–7.24 (m, 1H), 6.94 (br t, *J* 7.1, 1H), 6.78 (br d, *J* 8.1, 1H), 3.99 (q, *J* 6.9, 2H), 1.65–1.12 (m, 15H), 1.08–0.99 (m, 6H), 0.92–0.84 (m, 9H); $\delta_C(CDCl_3$, 75 MHz) 163.09, 136.99 [$^2J(^{13}C–Sn)$ 23], 130.24, 129.60, 120.7 [$^1J(^{13}C–Sn)$ 40], 109.35 [$^2J(^{13}C–Sn)$ 21], 62.92, 29.20 [$^3J(^{13}C–Sn)$ 19], 27.42 [$^2J(^{13}C–Sn)$ 58], 14.92, 13.70, 9.83 [$^1J(^{13}C–^{119}Sn)$ 333.3, $^1J(^{13}C–^{117}Sn)$ 332.6]; *m/z* (EI) 411 (M^+), 355 (100%) (Calc. for $C_{20}H_{36}OSn$: C, 58.42; H, 8.82. Found: 58.45; H, 9.15%).

1 J. R. Behling, K. A. Babiak, J. S. Ng, A. L. Campbell, R. Moretti, M. Koerner and B. H. Lipshutz, *J. Am. Chem. Soc.*, 1988, **110**, 2641. This method has been successfully extended for the preparation of allyl cuprates.

2 B. H. Lipshutz, R. Crow, S. H. Dimock, E. L. Ellsworth, R. A. J. Smith and J. R. Behling, *J. Am. Chem. Soc.*, 1990, **112**, 4063.

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5 Y. Kondo, T. Matsudaira, J. Sato, N. Murata and T. Sakamoto, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 736.

6 For the structure of organocuprates generated from CuCN: N. Krause, *Angew. Chem., Int. Ed.*, 1999, **38**, 79.

7 Formation of an arylcuprate intermediate was demonstrated by the formation of *o*-allylphenol by treatment *o*-iodophenol allyl ether with **1a** (73% yield). For a similar rearrangement: J. Barluenga, R. Sanz and F. J. Fañanás, *Tetrahedron Lett.*, 1997, **38**, 6103.

8 Best results were obtained with 1.1–1.5 equiv. of cuprate **1a**. The use of larger amounts led to lower yields of **4a**, presumably as a result of the early quenching of MeI by the excess **1a** (ref. 5).

9 The mixed cuprates could not be prepared by the direct Sn/Cu exchange from the *o*-substituted arylstannanes, probably due to steric hindrance. Thus, no reaction was observed in the reaction of **1a** or **1b** with 2-(tri-*n*-butylstannylmethoxy)phenyltri-*n*-butylstannane, while the reaction between phenyltri-*n*-butylstannane and **1b** yields tetra-*n*-butylstanne (74% isolated yield).

10 P. Beak, *Acc. Chem. Res.*, 1992, **25**, 215; M. L. Kurtzweil, D. Loo and P. Beak, *J. Am. Chem. Soc.*, 1993, **115**, 421

11 The only new stannane was methyltributylstannane, resulting from the selective transmetalation of **5** with [LiCuMePh·LiCN]. A similar reaction with [$LiCuBu_2$·LiCN] afforded Bu_4Sn.

12 Determined by ^1H NMR and GC-EI-MS analysis.

13 G. van Koten, S. L. James and J. T. B. H. Jastrzebski, *Comprehensive Organometallic Chemistry II*, Pergamon, Oxford, 1995, vol. 3, ch. 2.

14 Coordination of the ethers to the lithium atoms is omitted for clarity in Scheme 2. The arrows in **10** only indicate the group connectivity in the rearranged product **11**.

15 Variable amounts of **12** and phenol, the product of protodestannylation of **12**, were obtained when oxygen was present before the aqueous workup.

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