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## COMMUNICATION

## 1,5-Migration of rhodium via C-H bond activation in catalytic decyanative silvlation of nitriles†

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Unprecedented aryl-to-aryl 1,5-rhodium migration is involved in decyanative silvlation of aryl cyanides bearing a tethered arene. The 1.5-migration proceeds through remote C-H bond activation. 1,5-Migration also occurs in other rhodium-catalyzed reactions, including borylation and oxidative Mizoroki-Heck reactions.

1,4-Migration of transition metals has emerged as a unique and powerful organometallic process applicable to catalytic reactions.<sup>1</sup> The migration process proceeds through formal intramolecular C-H activation, enabling site-specific generation of organometallic species that are otherwise difficult to access. To date, a number of catalytic reactions involving 1,4-migration of a metal center have been developed with palladium<sup>2-6</sup> and rhodium<sup>7,8</sup> catalysts (Scheme 1a). Extension of the 1,4-migration process to one-atomextended systems would enable remote functionalization via C-H activation, thus significantly increasing the utility of the process (Scheme 1b). However, the greater distance between the metal center and the C-H bond and the relative difficulty in forming a sixmembered metallacyclic intermediate (or transition state) render such a 1,5-migration process far less favorable than 1,4-migration. Indeed, there have been only two catalytic reactions involving 1,5-palladium migration. One requires a well-designed and highly elaborate tricyclic system, 9a,b and the other uses triphenylsilane derivatives.<sup>9c</sup> In the case of rhodium, no 1,5-migration has been reported, to the best of our knowledge. In this communication, we report the first catalytic reactions involving 1,5-migration of rhodium, using relatively simple substrates.



Scheme 1 (a) 1,4- and (b) 1,5-migration of palladium and rhodium via C-H bond activation.

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In the course of our investigation of rhodium-catalyzed decyanative silvlation of aryl cyanides,<sup>10</sup> we tested 2-phenoxybenzonitrile derivatives as possible substrates. The reaction of 2-(4-methoxyphenoxy)benzonitrile (1a) with hexamethyldisilane (2) in the presence of a catalytic amount of [RhCl(cod)]<sub>2</sub> afforded two silvlated products in a ratio of 73/27. 2D NMR spectroscopy, including NOESY, COSY, HMOC and HMBC, as well as independent synthesis of authentic compounds unambiguously established that the major product was the expected silvlated compound 3a, and the minor one was its positional isomer 4a (entry 1, Table 1).<sup>11</sup> The formation of **4a** clearly indicates that a putative arylrhodium intermediate generated by the cleavage of a C-CN bond<sup>12</sup> underwent unprecedented 1.5-migration. This intriguing result prompted us to investigate the rhodiumcatalyzed decyanative silvlation of biaryl ether-based nitriles in more detail. Addition of ligands and bases significantly decreased the conversion in the silvlation reaction, rather than affecting the 3/4 ratio.<sup>11</sup> The product distribution proved to be highly dependent on the electronic environment of the C-H bond to be activated, as in the case of 1,4-palladium migration reactions.<sup>3</sup> With substrates bearing electron-donating groups, such as  $1a (R^2 = OMe)$  and 1b

 Table 1
 Rh-catalyzed decyanative silvlation of 2-aryloxybenzonitriles<sup>a</sup>

R <sup>1</sup>	CN O 1a-g	R <sup>2</sup> + Me₃Si—Si№ 5 <b>2</b> (2 equiv	$(he_{3}) = \frac{[RhCl(cod)]_{2}}{(he_{3})} (f_{2}) = \frac{(he_{3})}{(he_{3})} (f_{2}) = \frac{(he_{3})}{(he_{3})} (f_{2}) = \frac{(he_{3})}{(he_{3})} (f_{2}) = \frac{(he_{3})}{(he_{3})} (f_{3}) (f_{3}) = \frac{(he_{3})}{(he_{3})} (f_{3}) (f_{3}) = \frac{(he_{3})}{(he_{3})} (f_{3}) (f_{3}) = \frac{(he_{3})}{(he_{3$	5 mol%) me
	R <sup>1</sup>	SiMe <sub>3</sub> O J 3a-g	+ R <sup>1</sup> 4a-g	$R^2$
Entry	$R^1$	R <sup>2</sup>	$\mathrm{Yield}^{b}(\%)$	<b>3</b> / <b>4</b> <sup>c</sup>
1	Н	4-OMe	78	73/27
2	Н	4-Me	70	$80/20^{d}$
3	Н	4-CO <sub>2</sub> Me	80	64/36
4	Н	$4-CF_3$	58	50/50
5	Н	3,4,5-F <sub>3</sub>	89	23/77
6	OMe	3,4,5-F <sub>3</sub>	35	23/77
7	$CF_3$	3,4,5-F <sub>3</sub>	85	12/88

<sup>a</sup> Reaction conditions: 1 (0.50 mmol), 2 (1.0 mmol), [RhCl(cod)]<sub>2</sub> (0.025 mmol), and ethylcyclohexane (0.50 mL) in a screw-capped vial under N<sub>2</sub> at 160 °C for 15 h unless otherwise noted. <sup>b</sup> Isolated combined yield of 3 and 4 based on 1. <sup>c</sup> Ratio of 3/4 determined by <sup>1</sup>H NMR unless otherwise noted. <sup>d</sup> Determined by GC.

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 $(R^2 = Me)$ , a normal decyanative silvlation product **3** was formed preferentially (entries 1 and 2). Conversely, the more electronwithdrawing the substituent  $R^2$  becomes, the more 1,5-migration product **4** is formed (entries 3–5). Predominant formation of the 1,5-migration product was achieved by using a highly electrondeficient 3,4,5-trifluorophenyl group (entry 5). The electronic properties of the benzonitrile moiety of biaryl ether **1** also influenced the reactivity and selectivity. Introduction of a trifluoromethyl group *para* to the cyano group further promoted 1,5-migration to furnish **3g/4g** in a ratio of 12/88 (entry 7).

The nature of the linker between the two arenes exerted a profound effect. The rhodium-catalyzed reaction of the methylenelinked substrate **1h** with **2** produced decyanative silylation products with decreased selectivity for the 1,5-migration product **4h** (eqn (1)) compared with those obtained with **1e** as the substrate (entry 5, Table 1).<sup>13</sup>



The many examples of facile alkyl to aryl 1,4-metal migration<sup>4,7</sup> led us to examine alkyl cyanide **5** (Fig. 1), but neither normal nor migrated silylation occurred under these conditions.<sup>14</sup> Nitriles **6** and **7** simply afforded normal silylation products, and no 1,6- or 1,7-migration<sup>15</sup> took place. Interestingly, when biaryl cyanide **8** was used under rhodium-catalyzed conditions, no silylation *via* 1,4-migration was observed.<sup>16</sup>

There are several scenarios that could dictate the product ratios (Scheme 2). One is the case in which 1,5-migration ( $\mathbf{A} \rightarrow \mathbf{B}$ , step a) is in a rapid equilibrium, and the rate difference between the silylation of arylrhodium **A** (step b) and that of the migrated arylrhodium **B** (step c) determines the ratio of 3/4 (Curtin– Hammett scenario); if this were the case, isomeric aryl cyanides 1**a** and 1**i** would result in a similar product distribution. However, these two substrates afforded silylated products in a completely different ratio (eqn (2) *vs.* entry 1 in Table 1). These observations indicate that 1,5-migration is irreversible, and the migration rate is one of the factors controlling the product distribution, in addition to the rates of steps b and c. Although the exact mechanism of the 1,5-migration remains elusive, plausible processes are oxidative addition/reductive elimination of a C–H bond<sup>17</sup> and concerted



Fig. 1 Unsuitable substrates.



Scheme 2 Mechanistic consideration.

metal/hydride migration,<sup>18</sup> in both of which more electrondeficient (or acidic) C–H bonds are expected to react faster.<sup>19–21</sup>

The 1,5-migration of rhodium was also observed in a related decyanative borylation reaction (eqn (3)),<sup>22</sup> in which the migrated product **10** was formed to a greater extent than in the silylation reaction.



Importantly, the 1,5-rhodium migration process is not limited to an arylrhodium intermediate generated from aryl cyanides. We also observed a 1,5-migration product in a rhodium-catalyzed oxidative Mizoroki–Heck reaction of arylboronic acid **11** with alkene **12** (eqn (4)).<sup>23</sup>



In summary, we have demonstrated that unprecedented 1,5-rhodium migration occurs using substrates with a simple skeleton. The process enables generation of difficult-to-access arylrhodium species *via* remote C–H activation. We anticipate that 1,5-rhodium migration will be used as extensively as 1,4-rhodium migration in designing catalytic reaction after further optimization.<sup>24</sup>

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## Notes and references

- Reviews: (a) S. Ma and Z. Gu, Angew. Chem., Int. Ed., 2005, 44, 7512; (b) F. Shi and R. C. Larock, Top. Curr. Chem., 2010, 292, 123.
- 2 Selected examples of vinyl to aryl 1,4-migration of palladium: (*a*) Q. Tian and R. C. Larock, *Org. Lett.*, 2000, **2**, 3329; (*b*) J. Zhao and R. C. Larock, *J. Org. Chem.*, 2006, **71**, 5340.
- 3 Selected examples of aryl to aryl 1,4-migration of palladium: (a) M. A. Campo and R. C. Larock, J. Am. Chem. Soc., 2002, 124, 14326; (b) G. Karig, M.-T. Moon, N. Thasana and T. Gallagher, Org. Lett., 2002, 4, 3115; (c) M. A. Campo, Q. Huang, T. Yao, Q. Tian and R. C. Larock, J. Am. Chem. Soc., 2003, 125, 11506; (d) Q. Huang, M. A. Campo, T. Yao, Q. Tian and R. C. Larock, J. Org. Chem., 2004, 69, 8251; (e) D. Masselot, J. P. H. Charmant and T. Gallagher, J. Am. Chem. Soc., 2005, 128, 694; (f) M. A. Campo, H. Zhang, T. Yao, A. Ibdah, R. D. McCulla, Q. Huang, J. Zhao, W. S. Jenks and R. C. Larock, J. Am. Chem. Soc., 2007, 129, 6298.
- 4 Selected examples of alkyl to aryl 1,4-migration of palladium:
  (a) G. Bocelli, M. Catellani and G. P. Chiusoli, J. Organomet. Chem., 1984, 279, 225; (b) L. Wang, Y. Pan, X. Jiang and H. Hu, Tetrahedron Lett., 2000, 41, 725; (c) Q. Huang, A. Fazio, G. Dai, M. A. Campo and R. C. Larock, J. Am. Chem. Soc., 2004, 126, 7460.
- Selected examples of aryl to alkyl 1,4-migration of palladium:
   (a) G. Dyker, Chem. Ber., 1994, 127, 739;
   (b) O. Baudoin, A. Herrbach and F. Guéritte, Angew. Chem., Int. Ed., 2003, 42, 5736;
   (c) T. E. Barder, S. D. Walker, J. R. Martinelli and S. L. Buchwald, J. Am. Chem. Soc., 2005, 127, 4685;
   (d) J. Hitce, P. Retailleau and O. Baudoin, Chem.-Eur. J., 2007, 13, 792;
   (e) S. R. Taylor, A. T. Ung and S. G. Pyne, Tetrahedron, 2007, 63, 10889;
   (f) T. Kesharwani and R. C. Larock, Tetrahedron, 2008, 64, 6090.
- 6 Other examples of 1,4-migration of palladium: (a) J. Zhao, M. Campo and R. C. Larock, Angew. Chem., Int. Ed., 2005, 44, 1873; (b) J. Zhao, D. Yue, M. A. Campo and R. C. Larock, J. Am. Chem. Soc., 2007, 129, 5288; (c) T. Kesharwani, A. K. Verma, D. Emrich, J. A. Ward and R. C. Larock, Org. Lett., 2009, 11, 2591.
- 7 Selected examples of alkyl to aryl 1,4-rhodium migration: (a) K. Oguma, M. Miura, T. Satoh and M. Nomura, J. Am. Chem. Soc., 2000, 122, 10464; (b) T. Matsuda, M. Shigeno, M. Makino and M. Murakami, Org. Lett., 2006, 8, 3379; (c) T. Matsuda, M. Shigeno and M. Murakami, J. Am. Chem. Soc., 2007, 129, 12086; (d) J. Panteleev, F. Menard and M. Lautens, Adv. Synth. Catal., 2008, 350, 2893; (e) T. Seiser, O. A. Roth and N. Cramer, Angew. Chem., Int. Ed., 2009, 48, 6320; (f) M. Shigeno, T. Yamamoto and M. Murakami, Chem.-Eur. J., 2009, 15, 12929; (g) T. Seiser, G. Cathomen and N. Cramer, Synlett, 2010, 1699; (h) T. Seiser and N. Cramer, Angew. Chem., Int. Ed., 2010, 49, 10163; (i) N. Cramer and T. Seiser, Synlett, 2011, 449; (j) T. Matsuda, Y. Suda and A. Takahashi, Chem. Commun., 2012, 48, 2988.
- 8 Selected examples of vinyl to aryl 1,4-rhodium migration: (a) T. Hayashi, K. Inoue, N. Taniguchi and M. Ogasawara, J. Am. Chem. Soc., 2001, 123, 9918; (b) T. Miura, T. Sasaki, H. Nakazawa

and M. Murakami, J. Am. Chem. Soc., 2005, 127, 1390; (c) R. Shintani, K. Okamoto and T. Hayashi, J. Am. Chem. Soc. 2005, 127, 2872; (d) H. Yamabe, A. Mizuno, H. Kusama and N. Iwasawa, J. Am. Chem. Soc., 2005, 127, 3248; (e) T. Matsuda, M. Makino and M. Murakami, Angew. Chem., Int. Ed., 2005, 44, 4608; (f) R. Shintani and T. Hayashi, Org. Lett., 2005, 7, 2071; (g) T. Miura, M. Shimada and M. Murakami, Chem.-Asian J., 2006, 1, 868; (h) R. Shintani, K. Yashio, T. Nakamura, K. Okamoto, T. Shimada and T. Hayashi, J. Am. Chem. Soc., 2006, 128, 2772; (i) R. Shintani, K. Takatsu and T. Hayashi, Angew. Chem., Int. Ed., 2007, 46, 3735; (i) R. Shintani, K. Takatsu, T. Katoh, T. Nishimura and T. Hayashi, Angew. Chem., Int. Ed., 2008, 47, 1447; (k) R. Shintani, S. Isobe, M. Takeda and T. Hayashi, Angew. Chem., Int. Ed., 2010, 49, 3795; (1) K. Sasaki, T. Nishimura, R. Shintani, E. A. B. Kantchev and T. Hayashi, Chem. Sci., 2012, 3, 1278; (m) K. Sasaki and T. Hayashi, Tetrahedron: Asymmetry, 2012, 23, 373.

- 9 (a) A. J. Mota, A. Dedieu, C. Bour and J. Suffert, J. Am. Chem. Soc., 2005, 127, 7171; (b) C. Bour and J. Suffert, Org. Lett., 2005, 7, 653; (c) R. Shintani, H. Otomo, K. Ota and T. Hayashi, J. Am. Chem. Soc., 2012, 134, 7305.
- 10 (a) M. Tobisu, Y. Kita and N. Chatani, J. Am. Chem. Soc., 2006, 128, 8152; (b) M. Tobisu, Y. Kita, Y. Ano and N. Chatani, J. Am. Chem. Soc., 2008, 130, 15982; (c) M. Tobisu, R. Nakamura, Y. Kita and N. Chatani, J. Am. Chem. Soc., 2009, 131, 3174; (d) M. Tobisu, R. Nakamura, Y. Kita and N. Chatani, Bull. Korean Chem. Soc., 2010, 31, 582; (e) Y. Kita, M. Tobisu and N. Chatani, Org. Lett., 2010, 12, 1864.
- 11 See ESI<sup>†</sup> for details.
- 12 Reviews on C–CN bond activation: (a) M. Tobisu and N. Chatani, Chem. Soc. Rev., 2008, 37, 300; (b) Y. Nakao, Bull. Chem. Soc. Jpn., 2012, 85, 731.
- 13 Diphenylmethane and diphenyl ether exhibit no significant differences in ring rotation energy and Ph–X–Ph bond angles ( $X = CH_2$  and O): M. Feigel, J. Mol. Struct., 1996, **366**, 83. The decreased product ratio for 1,5-migration in **1h** may be attributed to other factors, such as an electronic or coordinating effect imposed by an oxygen atom.
- 14 Alkyl C–CN bonds can be cleaved under the influence of silylrhodium species. See ref. 10*b*–*d*.
- 15 J. Zhou, J. He, B. Wang, W. Yang and H. Ren, J. Am. Chem. Soc., 2011, 133, 6868.
- 16 The identified products are normal silylation (8%), reductive decyanation (15%) and recovered **8** (55%). See ESI† for details.
- 17 (a) D. A. Colby, R. G. Bergman and J. A. Ellman, *Chem. Rev.*, 2010, **110**, 624; (b) J. Bouffard and K. Itami, *Top. Curr. Chem.*, 2010, **292**, 231.
- 18 This is one of the major mechanisms involved in palladiummediated C-H activation: (a) D. García-Cuadrado, A. A. C. Braga, F. Maseras and A. M. Echavarren, J. Am. Chem. Soc., 2006, **128**, 1066; (b) M. Lafrance, C. N. Rowley, T. K. Woo and K. Fagnou, J. Am. Chem. Soc., 2006, **128**, 8754; (c) D. Lapointe and K. Fagnou, Chem. Lett., 2010, 1118.
- 19 Acidic C–H bonds favor the formation of 1,4-migration products in palladium catalysis. See ref. 3*f*.
- 20 Computational studies suggest that the favored mechanism in the 1,*n*-migration of palladium depends on the number *n*: (a) A. J. Mota and A. Dedieu, *Organometallics*, 2006, **25**, 3130; (b) A. J. Mota and A. Dedieu, *J. Org. Chem.*, 2007, **72**, 9669.
- 21 Selected examples of rhodium-catalyzed C-H activation, in which electron-deficient or acidic C-H bonds react preferentially: (a) Z.-M. Sun, J. Zhang, R. S. Manan and P. Zhao, J. Am. Chem. Soc., 2010, 132, 6935; (b) T. K. Hyster and T. Rovis, J. Am. Chem. Soc., 2010, 132, 10565; (c) G. Song, D. Chen, C.-L. Pan, R. H. Crabtree and X. Li, J. Org. Chem., 2010, 75, 7487; (d) N. Umeda, K. Hirano, T. Satoh, N. Shibata, H. Sato and M. Miura, J. Org. Chem., 2011, 76, 13.
- 22 M. Tobisu, H. Kinuta, Y. Kita, E. Rémond and N. Chatani, J. Am. Chem. Soc., 2012, **134**, 115.
- 23 G. Zou, J. Guo, Z. Wang, W. Huang and J. Tang, *Dalton Trans.*, 2007, 3055.
- 24 B.-H. Tan, J. Dong and N. Yoshikai, *Angew. Chem., Int. Ed.*, 2012, **51**, 9610.