Addendum

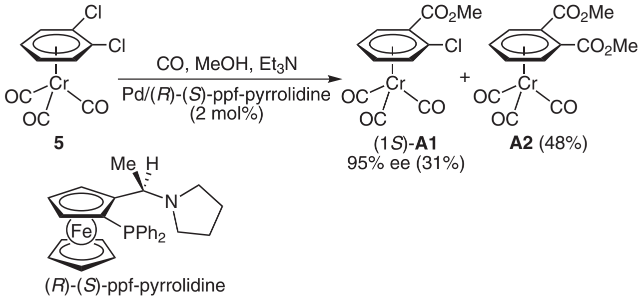
Transition-Metal-Catalyzed Enantioselective Synthesis of Compounds with Non-Centrochirality

Masamichi Ogasawara,* Susumu Watanabe *Synthesis* **2009**, 1761.

After publication of the above review article, the authors became aware that the majority of research works on 'the catalytic asymmetric synthesis of planar-chiral chromium(0)–(η^6-arene) complexes' were erroneously omitted. The sections 2.1a–c given below should be added after the Section 2.1 in the review article. The authors apologize for the oversight.

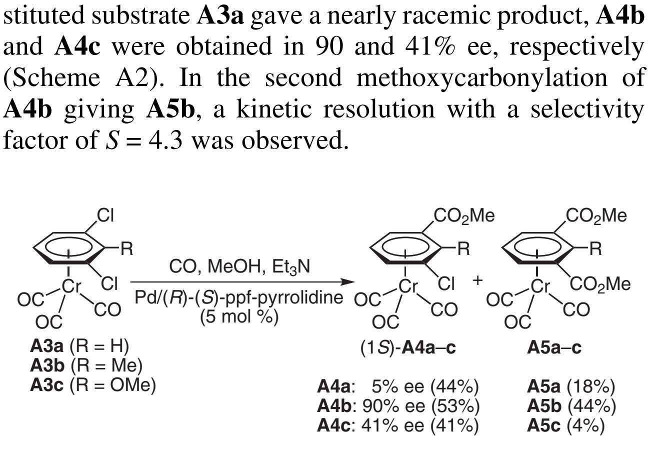
2.1a Synthesis of Planar-Chiral Chromium(0)-(η^6-arene) Complexes by Palladium-Catalyzed Methoxycarbonylation

Palladium-catalyzed methoxycarbonylation was applied to the preparation of planar-chiral chromium(0)-arene complexes by Schmaltz and co-workers. A palladium complex coordinated with (*R*)-(*S*)-ppf-pyrrolidine was effective in desymmetrizing **5**, and the monoester (1*S*)-**A1** was obtained in 95% ee (31% yield) together with 48% of the achiral diester **A2** (Scheme A1).[A1a] Although the ee value of the initially formed **A1** was not so high (ca. 60% ee), (1*S*)-**A1** of higher optical purity could be obtained because the minor enantiomer (1*R*)-**A1** was consumed more rapidly than its antipode in the second methoxycarbonylation leading to **A2**.



Scheme A1

The same catalytic system was also applied to the desymmetrization of the tricarbonyl(η^6-1,3-dichloroarene)chromium(0) complexes **A3**.[A1b] A substituent at the 2-position in the η^6-arene moiety affected some enantioselectivity in the palladium-catalyzed reaction. Although the 2-unsubstituted substrate **A3a** gave a nearly racemic product, **A4b** and **A4c** were obtained in 90 and 41% ee, respectively (Scheme A2). In the second methoxycarbonylation of **A4b** giving **A5b**, a kinetic resolution with a selectivity factor of *S* = 4.3 was observed.

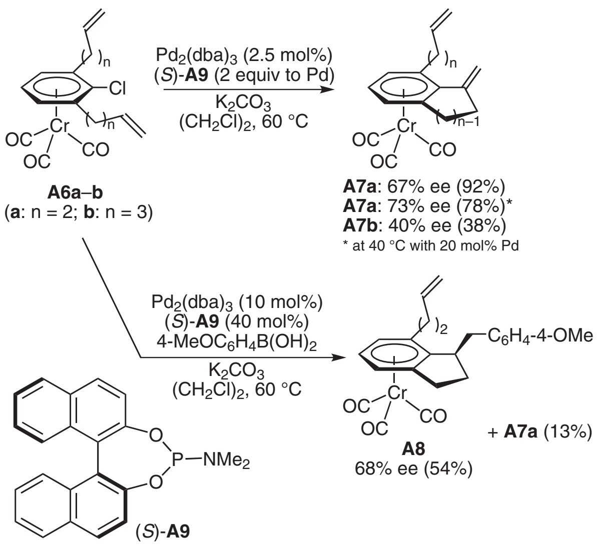


Scheme A2

2.1b Palladium-Catalyzed Intramolecular Mizoroki–Heck Reaction of Planar-Prochiral Chromium(0)-(η^6-arene) Complex

In 2005, Uemura described that a palladium complex coordinated with a phosphoramidite (*S*)-**A9** gave rise to asymmetric intramolecular Mizoroki–Heck reactions of (η^6-1,3-bisalkenyl-2-chlorobenzene)chromium(0) complexes **A6** with moderate enantioselectivity (Scheme A3).[A2] While the bis(3-butenyl) substrate **A6a** afforded the cyclized product **A7a** in 67% ee (40 °C) and 73% ee (60 °C), the bis(4-pentenyl) homologue **A7b** provided **A7b** in lower enantioselectivity of 40% ee at 60 °C.

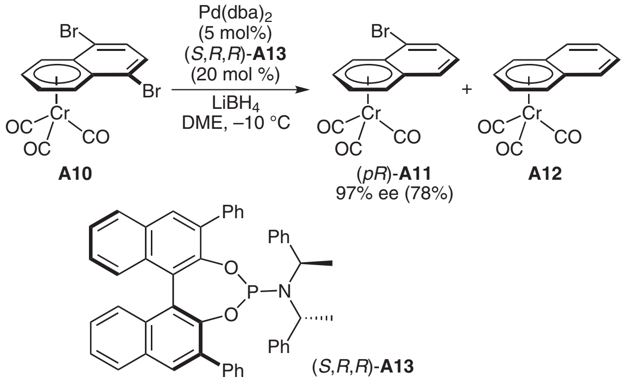
A palladium intermediate, which was generated after the carbopalladation/cyclization step in the Mizoroki–Heck reaction, could be trapped with an aryl- or alkenylboronic acid nucleophile. The Mizoroki–Heck/Suzuki–Miyaura cascade process proceeded with excellent diastereoselectivity and **A8** was obtained in 54% yield from **A6a** as a single diastereomer, for which the enantiomeric excess was 68% ee.



Scheme A3

2.1c Palladium-Catalyzed Enantioselective Hydrogenolysis of (η^6-5,8-Dibromonaphthalene)Cr(CO)$_3$

Enantioposition-selective hydrogenolysis of planar-prochiral (η^6-5,8-dibromonaphthalene)Cr(CO)$_3$ (**A10**) was accomplished with excellent enantioselectivity by Kündig and co-workers in 2006.[A3] A palladium complex coordinated with the bulky phosphoramidite (*S*,*R*,*R*)-**A13** was found to be an excellent catalyst for the asymmetric reaction, and the planar-chiral (η^6-arene)tricarbonylchromium(0) (*pR*)-**A11** was obtained in 97% ee in 78% yield under the optimized conditions (Scheme A4).



Scheme A4

References

(A1) (a) Gotov, B.; Schmalz, H.-G. *Org. Lett.* **2001**, *3*, 1753. (b) Böttcher, A.; Schmalz, H.-G. *Synlett* **2003**, 1595.

(A2) Kamikawa, K.; Harada K.; Uemura, M. *Tetrahedron: Asymmetry* **2005**, *16*, 1419.

(A3) Kündig, E. P.; Chaudhuri, P. D.; House, D.; Bernardinelli, G. *Angew. Chem. Int. Ed.* **2006**, *45*, 1092.