

Synthesis of a novel bridged 2-(cyclopentadienyl)-indene system using Pd-catalyzed Negishi-type cross coupling

Dirk Tews and Petra Escarpa Gaede*

Department of Chemistry, Technische Universität Berlin, Berlin, Germany

Received 10 June 2004; revised 6 October 2004; accepted 8 October 2004

Available online 22 October 2004

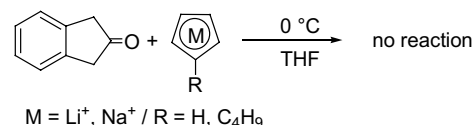
Abstract—The palladium-catalyzed Negishi-type C–C-coupling of the nonaromatic systems 2-indenyl and cyclopentadienyl were investigated. The employed catalyst played a decisive role in product formation. Instead of Pd(PPh₃)₄, the more bulky Pd(dppf)Cl₂·CH₂Cl₂ led to the desired system in distinguished yields.

© 2004 Elsevier Ltd. All rights reserved.

Palladium cross-coupling chemistry is one of the most successful areas in transition-metal catalysis and a versatile tool for carbon–carbon bond formation.¹ Depending on the reaction conditions several kinds of specifications are well established. The palladium-catalyzed cross coupling of Negishi-type is widely used for aryl- and vinyl-halides,² occasionally for heteroaromatic halides³ but no aromatic compounds like indenyl- or cyclopentadienyl-systems are rarely described previously.⁴

Our major interests are focused on bimetallic transition-metal complexes with a linking bisindenyl or bicyclopentadienyl ligand, substituted with an additional silyl bridge in 1,1'-position.⁵ Due to symmetry of these bridging systems only homodinuclear compounds could be synthesized from these polycyclic systems. To form heterobimetallic compounds, a selective stepwise deprotonation of the cyclic systems followed by metathesis reaction with appropriate metal halides is required. This can be achieved by using asymmetric organic backbones as bridging ligands, such as 2-(cyclopentadienyl)-indenyl species.

Attempts to synthesize **1** by a nucleophilic addition of LiCp^tBu or NaCp to 2-indanone failed for the desired product (Scheme 1). The alternative classical Grignard



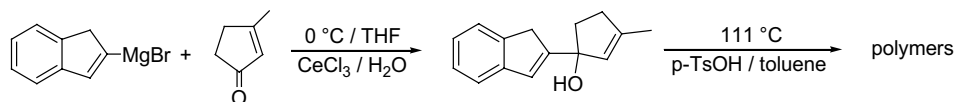
Scheme 1.

reaction of indenyl magnesium bromide and methylcyclopentenone leads only to the isolation of the starting materials. In the case of using CeCl₃ as an additive to that Grignard reaction, the tertiary alcohol was performed but dehydration with 4-toluene sulfonic acid gave only polymer products due to Diels–Alder cycloaddition (Scheme 2).

A satisfactory synthetic approach for 2-(cyclopentadienyl)-indene **1** was developed by using a palladium-catalyzed Negishi-type cross-coupling reaction of 2-bromoindene and a ^tbutylcyclopentadienyl zinc complex generated in situ. The ^tbutyl group on the cyclopentadienyl ring is essential as a bulky group blocking its neighbour positions for the introduction of the silyl bridge in the next reaction step. It directs the incoming silyl group to the neighbour position of the indenyl ring, otherwise the silyl group will react exclusively in the 3-position to give polymer products only. Additionally the ^tbutyl group improves the stability of **1** towards Diels–Alder dimerization reactions. Attempts to use trialkyl silyl groups, instead of the ^tbutyl substituent, were not very satisfactory due to unwanted bond cleavage during metallation reactions later on.

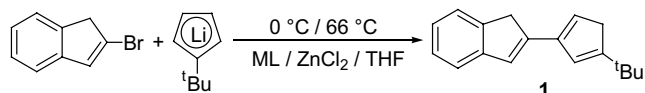
Keywords: Indene; Cyclopentadienyl; Palladium catalysis; Negishi reaction; Silyl bridges.

* Corresponding author. Tel.: +49 3031423740; fax: +49 3031421106; e-mail: escarpa@chem.tu-berlin.de



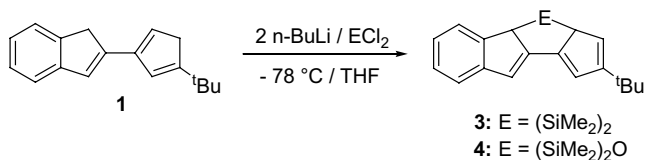
Scheme 2.

Indeed, when $\text{Pd}(\text{PPh}_3)_4$ was used as a catalyst, the formation of **1** occurred after stirring at rt, albeit in very poor yields. Heating the solution in THF, toluene, dioxane or DMF did not increase the yield of **1**. It was shown by Miller and Farrell⁶ that the reactivity depends also on the Pd catalyst used in the Negishi reaction. An exchange of the catalyst to $\text{Pd}(\text{dppf})\text{Cl}_2 \cdot \text{CH}_2\text{Cl}_2$ described by Hayashi et al.,⁷ led to the novel organic system **1** in 80% yield (Scheme 3).⁸ Neither dimerization nor other side reactions were observed. Traces of 2-bromoindene were removed by sublimation. However, the palladium catalyst was not feasible to recycle.



ML = $\text{Pd}(\text{PPh}_3)_4$, $\text{Pd}(\text{dppf})\text{Cl}_2 \cdot \text{CH}_2\text{Cl}_2$

Scheme 3.



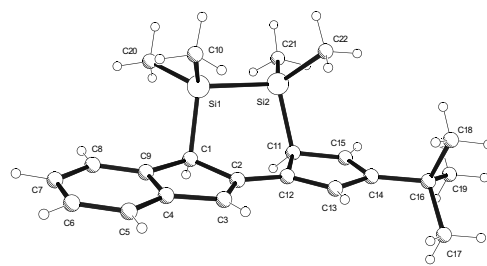
Scheme 4.

Deprotonation of **1** with 2 molar equiv of butyllithium in diethyl ether formed the dilithio compound **2**. Subsequent reactions with dichlorotetramethyldisilane or dichlorotetramethyldisiloxane gave the desired polycyclic systems **3** and **4**, respectively (Scheme 4).⁹ The size of the central ring varies from six to seven members and has a deciding influence on the stability and flexibility of the product. Attempts to introduce the dimethylsilyl bridge failed and led to polymerized products. Apparently, the sterical shield of the methyl groups in the formed five-membered silyl ring is not sufficient to prevent a nucleophilic attack on the silicon.

Crystals of **3** suitable for X-ray diffraction were obtained by recrystallization from *n*-hexane/diethyl ether. The X-ray acquisition and refinement parameters are listed in Table 1, and a plot of this system is shown in Figure 1. It offers both cyclic moieties in an ideal planar structure, which are tilted slightly against each other (with an angle of 0.56°). It is noteworthy that the silyl groups bend out of this plane due to the sp^3 -character of the carbon atoms C1 and C11, respectively. The geometry of the molecule is comparable to former de-

Table 1. Crystallographic data for **3**

Empirical formula	$\text{C}_{22}\text{H}_{30}\text{Si}_2$
Fw	350.64
Cryst syst	Monoclinic
Space group	$P 2_1/c$ (Nr. 14)
Volume (\AA^3)	2051.05(2)
a (\AA), α (deg)	13.4719(10), 90
b (\AA), β (deg)	9.8816(10), 122
c (\AA), γ (deg)	18.2888(10), 90
Z	4
D (calcd g/cm^3)	1.136
μ ($\text{MoK}\alpha$) (mm^{-1})	0.174
$F(000)$	760
$2\theta_{\text{min}}$, $2\theta_{\text{max}}$ (deg)	2.58, 50.0
Index ranges	$-13 \leq h \leq 19$ $-14 \leq k \leq 9$ $-26 \leq l \leq 24$
Cryst size	$0.65 \times 0.30 \times 0.18 \text{ mm}^3$
No. of reflns collected	11657
No. of ind reflns	3599 [$R_{\text{int}} = 0.1828$]
Residual electron density	0.306 and $-0.406 \text{ e}\text{\AA}^{-3}$
GOF on F^2	0.800
R indices [$I > 2\sigma(I)$]	$R1 = 0.0640$ $wR2 = 0.1174$
R indices (all data)	$R1 = 0.1544$ $wR2 = 0.1418$

Figure 1. Crystal structure of **3**.

scribed silyl bridged 2,2'-bisindenyl and bicyclopentadienyl compounds.⁵

Crystallographic data (excluding structure factors) for the structure in this paper, have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 240958.

Acknowledgements

We would like to thank the Deutsche Forschungsgemeinschaft (DFG) and the Graduiertenkolleg G352 for financial support.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.tetlet.2004.10.042](https://doi.org/10.1016/j.tetlet.2004.10.042).

References and notes

- (a) Littke, A. F.; Fu, G. C. *Angew. Chem.* **2002**, *114*, 4350; (b) Carey, F. A.; Sundberg, R. J. *Org. Chem.*; VCH: Weinheim, 1995.
- (a) Negishi, E.-I. In *Metal-Catalyzed Cross-Coupling Reactions*; Diederich, F., Stang, P. J., Eds.; Wiley-VCH: Weinheim, 1998; Chapter 1; (b) Erdik, E. *Tetrahedron* **1992**, *48*, 9577–9648.
- (a) Minato, A.; Tamao, K.; Hayashi, T.; Suzuki, K.; Kumada, M. *Tetrahedron Lett.* **1980**, *21*, 845–848; (b) Hall, J. H.; Chien, J. Y.; Kauffman, J. M.; Litak, P. T.; Adams, J. K.; Henry, R. A.; Hollins, R. A. *Heterocycl. Chem.* **1992**, *29*, 1245–1273; (c) Amat, M.; Hadida, S.; Pshenichnyi, G.; Bosch, J. *J. Org. Chem.* **1997**, *62*, 3158–3175; (d) Sakamoto, T.; Nishimura, S.; Kondo, Y.; Yamanaka, H. *Synthesis* **1988**, 485–486; (e) Sandosham, J.; Undheim, K.; Rise, F. *Heterocycles* **1993**, *35*, 235–244; (f) Angiolelli, M. E.; Casalnuovo, A. L.; Selby, T. P. *Synlett* **2000**, 905–907; (g) Sonoda, M.; Inaba, A.; Itahashi, K.; Tobe, Y. *Org. Lett.* **2001**, *3*, 2419–2421.
- Schumann, H.; Stenzel, O.; Girgsdies, F. *Organometallics* **2001**, *20*, 1743.5.
- (a) Tews, D.; Escarpa Gaede, P. *Organometallics* **2001**, *20*, 3869; (b) Tews, D.; Escarpa Gaede, P. *Organometallics* **2004**, *23*, 968; (c) Tews, D.; Ph.D. Thesis, TU Berlin, **2003**.
- Miller, J. A.; Farrell, R. P. *Tetrahedron Lett.* **1998**, *39*, 6441–6444.
- Hayashi, T.; Konishi, M.; Kobori, Y.; Kumada, M.; Higuchi, T.; Hirotsu, K. *J. Am. Chem. Soc.* **1984**, *106*, 158.
- General procedure.* A solution of 2-bromindene (14.25 g, 73.5 mmol) in THF (120 mL) was treated with Pd(dppf)Cl₂·CH₂Cl₂ (1.72 g, 2.1 mmol) at rt and stirred for 1 h. The mixture was cooled to 0 °C and given to a suspension of Cp^tBuZnCl [made by dropping LiCp^tBu (16.36 g, 127.8 mmol) in THF (120 mL) into a mixture of ZnCl₂ (17.7 g, 130 mmol) in THF (50 mL) at 0 °C]. The reaction mixture was stirred for additional 2 h and heated to reflux overnight. The solvent was evaporated and the residue redissolved in diethyl ether (120 mL). The suspension was quenched carefully with 150 mL of 1 M HCl and extracted three times with diethyl ether. The collected organic layers were dried and concentrated to dryness. Subsequently, the red oil was purified by chromatography on silica with hexane/diethyl ether (5:1) as the eluent. After removing of the solvent under vacuum, 15.3 g (88%) of **1** were obtained as a yellow solid.
- Synthesis of 1,1'-[2,2'-(C₉H₆)(C₉H₁₂)](SiMe₂)₂, **3** and 1,1'-[2,2'-(C₉H₆)(C₉H₁₂)](SiMe₂)₂O, **4**.
A solution of **1** (15 g, 63.5 mmol) in diethyl ether (300 mL) was cooled to -78 °C and *n*-BuLi (52 mL, 130 mmol) was added dropwise. After stirring overnight under warming to rt, the resulted precipitate was filtered off and washed with *n*-hexane (3 × 30 mL). Drying under vacuum lead to a light yellow powder, which represents the dilithio compound **2**. Part of **2** (6.43 g, 25.9 mmol) was suspended in THF (200 mL) and dichlorotetramethyldisilane (4.8 mL, 26 mmol) was added via syringe at -78 °C. The resulting solution was stirred for two days under warming to rt. After removing the solvent, the crude product was redissolved in *n*-hexane/diethyl ether (5:1) and quickly chromatographed on silica eluting with *n*-hexane/diethyl ether (5:1). an orange oil was isolated and recrystallized from *n*-pentane at 5 °C. Compound **3** [6.8 g (75%)] were obtained as yellow crystals. In analogy of the described synthesis for **3** the desired compound **4** was produced by adding dichlorotetramethyldisiloxane (2.5 mL, 10.5 mmol) to **2** (2.55 g, 10.3 mmol) in THF (70 mL). Purification leads to 2.6 g (71%) of **4** as an orange oil.