Journal of Organometallic Chemistry 637–639 (2001) 318–326

www.elsevier.com/locate/jorganchem

Study on the synthesis of nonracemic C_2-symmetric 1,1′-binaphthyl-2,2′-diyl bridged ferrocene. Stereochemical result of the cross-coupling reactions controlled by Pd(II) or Pd(IV) complex intermediacy

P. Kasák, R. Mikláš, M. Putala *

Department of Organic Chemistry, Faculty of Natural Sciences, Comenius University, Mlynská dolina, SK-842 15 Bratislava, Slovak Republic

Received 4 January 2001; received in revised form 29 March 2001; accepted 29 March 2001

Abstract

Palladium catalyzed Negishi, Suzuki and Stille cross-coupling reactions of enantiopure 2,2′-diiodo-1,1′-binaphthyl with the corresponding 1,1′-dimetalloferrocenes gave the C_2-symmetric binaphthyl bridged ferrocene 1-1,1′-(1,1′-binaphthyl-2,2′-diyl)ferrocene (**1**). The latter was obtained by Stille coupling with the bis(trimethylstannyl) derivative but not with the bis(tributylstannyl) one. Products of alkyl group transfer from tin to binaphthyl were obtained as the main products in both cases. The stereochemical result of these cross-coupling reactions in the positions 2 and 2′ of 1,1′-binaphthyl depends on the reactivity of 1,1′-dimetalloferrocenes. Negishi coupling proceeds stereoconservatively (affording enantiopure product **1**). Complete racemization of binaphthyl moiety occurs during the reactions with less reactive boron and tin organometallics. Proposed different reaction pathways include C_1-symmetric palladium(II) intermediate in the former and configurationally unstable C_2-symmetric pallada(IV)cyclic intermediate in the latter cases. In contrast to the cross-coupling reactions, free radical arylation of ferrocene with enantiopure 1,1′-binaphthyl-2,2′-bisdiazonium salt gave predominantly oligomeric binaphthyl bridged ferrocenes and only traces of the partially racemized product **1**. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Binaphthyl; Cross-coupling; Ferrocene; Mechanism; Palladium complexes; Stereoconservative

1. Introduction

Nonracemic *ansa*-metallocenes, especially C_2-symmetric ones, represent a group of organometallic compounds interesting with respect to potential applications in stereoselective catalysis [1]. The bridge restricts rotation of the cyclopentadienyl rings and allows one to precisely design a chiral pocket around the catalytic center and the C_2-symmetry reduces the number of possible stereoisomers, which simplifies their synthesis and application. The majority of these nonracemic C_2-symmetric *ansa*-metallocenes are of early transition metals. Although the syntheses of several C_2-symmetric *ansa*-ferrocenes (ferrocenophanes) have been reported [2,3], only a few of them have been prepared in nonracemic forms [2].

For our study we chose 1,1′-binaphthyl-2,2′-diyl as the chiral bridge. The synthesis and X-ray study of the ferrocene derivative **1** was published [3c]. But the original synthesis was performed with a racemic substrate - via Negishi cross-coupling reaction of racemic 2,2′-diiodo-1,1′-binaphthyl (**2a**) with 1,1′-bis(chlorozincio)ferrocene (**3a**). Substitution reactions in the positions 2 and 2′ of nonracemic 1,1′-binaphthyl derivatives [4] are challenging from the stereochemical point of view since the substitution occurs in the positions where nonbonding interactions between the substituents are crucial for the configurational stability of these derivatives. Thus, it is important to investigate whether or not these substitution reactions can proceed without scrambling of enantiomeric purity. There is known just one stereoconservative cross-coupling reaction in the positions 2 and 2′ of nonracemic 1,1′-binaphthyl derivatives-methylation of 2,2′-ditriflate **2b** by methyl-

---

* Corresponding author. Fax: +421-7-6029-6690.
E-mail address: putala@fns.uniba.sk (M. Putala).

PII: S0022-328X(01)00926-3

magnesium halides [5]. In addition, a few other relative stereoconservative substitutions of nonracemic 1,1′-binaphthyl 2,2′-dielectrophiles (**2a**, **2b**) catalyzed by transition metal complexes were reported [6].

A wide variety of methods to attach aryl groups directly to ferrocene have been elaborated:

- cross-coupling reactions of metalloferrocenes (Li [7], Mg [7], Zn [8], Hg [9], Sn [10], B [11]) with haloarenes, or haloferrocenes with arylboronic acids [12];
- oxidative coupling of metalloarenes and metalloferrocenes or Ullmann coupling [13];
- reaction of lithioferrocenes with heteroarenes [14];
- arylation of ferrocene with arenediazonium salts [15], aryldiazanes (in the presence of $AlCl_3$ or Ag_2O) [16], or chlorobenzene (catalyzed by intramolecular ferrocenylphosphane palladium complex) [17];
- photolysis of haloferrocenes or diferrocenylmercury in the presence of arenes [18];
- photolysis and thermal decomposition of dicarbonyl(η^5-cyclopentadienyl)(η^1-arenecarbonyl)iron (Ar–CO–Fp) [8h];
- synthesis of arylcyclopentadienyl ligand followed by metallation [19].

However, the yields of arylferrocenes are moderate at best (10–60%), and only a few cross-coupling reactions exceed the given range.

The choice of synthetic methods for our study was limited also by availability of 1,1′-binaphthyl-2,2′-diyl precursors in an enantiopure form. The following 2,2′-dielectrophiles are readily accessible:

- ditriflate **2b** from commercially available enantiopure 1,1′-binaphthyl-2,2′-diol (BINOL) [20], or in one additional step starting from 2-naphthol [21] and simple resolution of BINOL [22];
- dibromide **2c** and diiodide **2a** in three steps from 2-naphthol [23], including simple resolution of 2,2′-diamine [23];
- also bisdiazonium salt **2d** can be considered; it is formed as an intermediate in the synthesis of dihalides **2a** and **2c** [23].

The synthesis of suitable nonracemic 2,2′-dimetallo-1,1′-binaphthyls has not been reported [4].

2. Results and discussion

2.1. Synthesis of racemic 1

In agreement with the general trend in the reactivity of aryl electrophiles in cross-coupling reactions (OTf < Br < I), we found that the ditriflate **2b**, the most easily accessible of 1,1′-binaphthyl 2,2′-dielectrophiles **2**, is the least reactive one (in a cross-coupling reaction with dizinc **3a**). The product **1** was not obtained, even a variety of different reaction conditions, catalysts (nickel and palladium complexes with dppf, dppe and PPh_3), solvents (THF, PhMe, NMP) were tried. The unreacted ditriflate **2b** was recovered almost quantitatively. Small amounts of biferrocenyl **5a** (5%) were obtained as the only product.

The original synthesis of racemic **1** from diiodide **2a** with dizinc **3a** in the presence of $Pd(dppf)Cl_2$ [3c] was reported to give 37% yield accompanied with oligomeric compounds 4 and a small amount of the biferrocenyl **5**. A similar result was obtained in the synthesis of the analogous 1,1′-(1,1′-biphenyl-2,2′-diyl)ferrocene [3b] from 2,2′-diiodo-1,1′-biphenyl and **3a** (20% yield + oligomers; formation of **5a** was not noticed). We found the result of the former reaction (**2a** with **3a**) close to the reported one (35% 1 + 4 + 1.5% **5a**; Table 1, entry 2). Attempts to increase the yield of **1** by further optimization were not successful.

It has to be mentioned that this reaction (**2a** with **3a**) is quite sensitive to the conditions. The best results were obtained from dizinc **3a** prepared by dilithiation of ferrocene in the presence of TMEDA, if the latter was used as received from the supplier (without additional drying; entry 2). Thorough drying led to a decreased yield of **1** and an increased amount of biferrocenyl **5a** (entry 3). When we used 1,1′-dibromoferrocene instead of ferrocene/TMEDA in the reaction with *n*-butyllithium for the synthesis of 1,1′-dilithioferrocene, the results were more reproducible but the yield of **1** was lower (entry 4). The fact that the method of the preparation of **3a** can influence significantly the efficiency of the cross-coupling of **3a** with aryl electrophiles was also observed in the synthesis of 1,1′-bis(anthracen-9-yl)ferrocene **3h** (35–40% starting from $FcBr_2$ vs. 5% from FcH/TMEDA).

In order to avoid precautions required for the synthesis and handling of **3a** we also examined cross-coupling reactions with less sensitive 1,1′-metalloferrocenes. Conditions reported for an efficient synthesis of diarylferrocenes from diboronic acid **3b** and iodoarenes [11a] (DME/aqueous NaOH/$Pd(dppf)Cl_2$) in our case yielded only traces of the desired product **1** and significant hydrodehalogenation of diiodide **2a** (entry 5). Modification of the solvent mixed with water, base or ligand did not improve the result remarkably. This observation is in accordance with previous attempts to synthesize 2,2′-diaryl-1,1′-binaphthyls via Suzuki reaction from racemic dibromide **2c** [24], where the reaction stops in the first step, affording predominantly the monoarylated product (48–70%, partialy hydrodebrominated) and only traces of the diarylated product (< 3%). We found that hydrodehalogenation of **2a** does not occur in aprotic solvents. From trial combinations of solvents (THF, dioxane, DME, PhMe), catalysts precursors ($Ni(dppf)Cl_2$/BuLi or Zn; $Pd(dppf)Cl_2$; $Pd(dba)_2$ with dppf, dppe, PPh_3, CuI, without ligand; palladacycle **8**), and bases (K_2CO_3, K_3PO_4, KF, AcONa), the best result was obtained in the case of THF/$Pd(dba)_2$/K_3PO_4; the yield of **1** rose to 8% (entry 6).

The diboronic acid **3b** is sparingly soluble in aprotic organic solvents. Therefore we tried to use the more soluble diboronate **3c**. The optimized conditions were found to be the same as for **3b**, to afford the desired product **1** in 12% yield (entry 7).

In the reactions with **3b** as well as its ester **3c** the formation of **1** was accompanied by the oligomers **4**, but **5a** was not detected (with the exception of when Pd(dba)$_2$/CuI or palladacycle **8** were used as catalysts). The relatively low efficiency of the Suzuki cross-coupling reaction for our system was quite surprising because it was reported that the Suzuki reaction gives good results in the synthesis of hindered biaryl compounds [25]. Most probably in our binaphthyl system, the steric hindrance exceeded the limit, below which it is still viable (bulky 2-substituted 1-naphthyl substituent in *ortho*-position to iodine). This assumption is supported also by the fact that the yield of **1** was higher in the reactions where no phosphine ligand on palladium was used, giving a possibility to form less hindered, more catalytically active palladium species. On the other hand palladium species not stabilized with phosphine ligands were more labile. As evidenced by the precipitation of black palladium(0) powder and low conversion of diodide **2a** during these reactions. Nevertheless, this is the highest yield of 2,2′-diarylated-1,1′-binaphthyl obtained by Suzuki couplings yet.

Stille coupling of diiodide **2a** with bis(tributylstannyl) derivative **3d** did not occur under the examined conditions (reflux, various Pd-catalysts, additives and solvents; entry 8). Use of CuO as a cocatalyst to Pd(dba)$_2$/4 PPh$_3$ (in analogy to Refs. [10a,10e]; entry 9) led to a transfer of the butyl group to binaphthyl. Although the Stille cross-coupling reaction was found to be effective in the synthesis of arylferrocenes [10], it is apparently significantly sensitive to steric factors. Indeed, use of the less hindered bis(trimethylstannyl) derivative **3e** (entry 10) afforded the desired product **1** (11%) accompanied with methylation products **6c** and **7c** in addition to oligomers **4**.

Cross-coupling of the diiodide **2a** with dicopper **3f** (entry 11) and dimercury **3g** (entry 12) did not proceed under any conditions. The dicopper **3f** was almost quantitatively transformed by to biferrocenyl **5a** and oligomeric ferrocenes **5b** (terferrocenyl was identified among them).

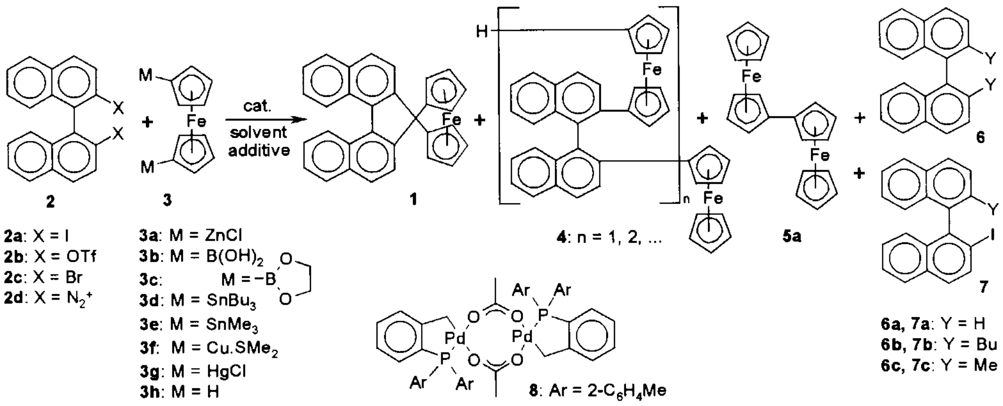
The possible application of bisdiazonium salt **2d** in the synthesis of **1** would save one step in the synthesis of the binaphthyl precursor, but for this reaction only its decomposition under catalytic conditions was observed. We applied it therefore in situ to a direct arylation of ferrocene **3h** (entry 13). This reaction gave just traces of the desired product **1** (2%). The rest of binaphthyl precursor **2d** was transformed to oligomers **4**—with a significant predominance of oligomers **4** over product **1** in comparison to the cross-coupling reactions.

We did not give special attention to oligomers **4**, since they have been already characterized [3c], their isolation is problematic (mixture, low retention factors,

Table 1
Synthesis of racemic **1**

	Precursor of			Solvent/additive	Temp./time (d)	Conv. [c] (%)	Isolated yield (%)		
	Binaphthyl	Ferrocene [a]	Catalyst [b]				**1** [d]	**5a**	**6**/**7**
1	**2b** X = OTf	**3a** M = ZnCl [e]	various Ni, Pd	various	reflux/6	5–10	–	5	–
2	**2a** X = I	**3a** [e]	Pd(dppf)Cl$_2$	THF	r.t./3	100	35	1.5	–
3	**2a**	**3a** [f]	Pd(dppf)Cl$_2$	THF	r.t./3	100	10–15	10–40	–
4	**2a**	**3a** [g]	Pd(dppf)Cl$_2$	THF	r.t./3	100	26	<2	–
5	**2a**	**3b** M = B(OH)$_2$	Pd(dppf)Cl$_2$	DME–H$_2$O/NaOH	reflux/6	85	2	–	38/9 (a)
6	**2a**	**3b**	Pd(dba)$_2$ [h]	THF/K$_3$PO$_4$	reflux/1	40	8	–	–
7	**2a**	**3c** M = B(OR)$_2$	Pd(dba)$_2$ [h]	THF/K$_3$PO$_4$	reflux/1	50	12	–	–
8	**2a**	**3d** M = SnBu$_3$	various Pd	various	reflux/3	5	–	–	–
9	**2a**	**3d**	Pd(dppf)Cl$_2$/CuO	DMF	100 °C/0.5	100	–	–	50/8 (b)
10	**2a**	**3e** M = SnMe$_3$	Pd(dba)$_2$/4 PPh$_3$	THF/LiCl	reflux/2	95	11	–	46/6 (c)
11	**2a**	**3f** M = Cu·SMe$_2$	no or various Pd	THF	r.t./1	5	–	92 [i]	–
12	**2a**	**3g** M = HgCl	Pd(dba)$_2$/4 PPh$_3$	Me$_2$CO–THF/NaI	reflux/1	5	–	–	–
13	**2d** X = N_2^+	**3h** M = H	–	50% H$_2$SO$_4$ aq.	0 °C/1	100	2	–	–

[a] Two equivalents to **2**.
[b] 10 mol% to **2** (5 mol% to C–X).
[c] Based on isolated **2**.
[d] Accompanied with **4**, yield of pure **1** is given.
[e] Prepared from FcH/2.25 equivalents BuLi/2.25 equivalents of commercial TMEDA, then 2.25 equivalents ZnCl$_2$.
[f] Prepared from FcH/2.25 equivalents BuLi/2.25 equivalents dried and distilled TMEDA, then 2.25 equivalents ZnCl$_2$, thoroughly dried.
[g] Prepared from 1,1′-dibromoferrocene/three equivalents BuLi, then two equivalents ZnCl$_2$.
[h] Black precipitate of Pd(0) was formed during the reaction.
[i] Including **5b**.



Scheme 1.

bad separation) and they do not significantly contribute to the scope of the present work. Yet the formation of certain amount of oligomers **4** is understandable since the product **1**, in contrast to oligomers **4**, contains internal strain (both binaphthyl and ferrocene fragments are distorted in the molecular structure of **1** [3c]) (Scheme 1).

*2.2. Synthesis of nonracemic **1***

We examined the conservation of the stereogenic information (stereoconservativity) from the binaphthyl precursor **2** to product **1** for all synthetic approaches that succeed to give **1**. While Negishi cross-coupling reaction of (*S*)-**2a** with **3a** afforded enantiopure (*S*)-**1** (> 95% e.e., determined by HPLC), Suzuki and Stille couplings with corresponding 1,1′-dimetalloferrocenes **3b**, **3c** and **3e** yielded practically racemic **1**. Also the dimethyl derivative **6c** obtained as a main product in Stille cross-coupling with **3e** was found to be racemic. The same stereochemical result of Suzuki coupling (complete racemization of binaphthyl moiety during the reaction) was observed when this reaction was run at room temperature (as was Negishi coupling) or in the presence of the phosphine ligand (PPh_3), although the yields were lower.

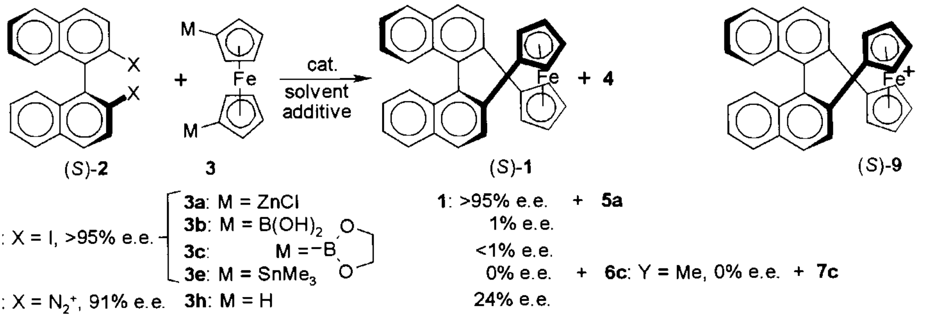
An approach using the bisdiazonium salt **2d** and ferrocene **3h** gave product **1** with partial conservation of stereogenic information from **2d**. This stereochemical result together with the observed predominance of oligomers **4** over monomer **1** in this reaction, in our opinion, supports a free radical mechanism for arylation of ferrocene by arenediazonium salts [15m]. Considering an alternative mechanism based on primary orbital interaction of diazonium salt with ferrocene iron [15k], we see no apparent reason for which partial racemization of the binaphthyl moiety occurs. The formation of the desired product **1** should be especially disfavored over oligomers **4** (Scheme 2).

Product (*S*)-**1** is oxidized easily by either silver triflate or nitrosonium tetrafluoroborate, affording corresponding nonracemic ferrocenium salt (*S*)-**9** in a high yield.

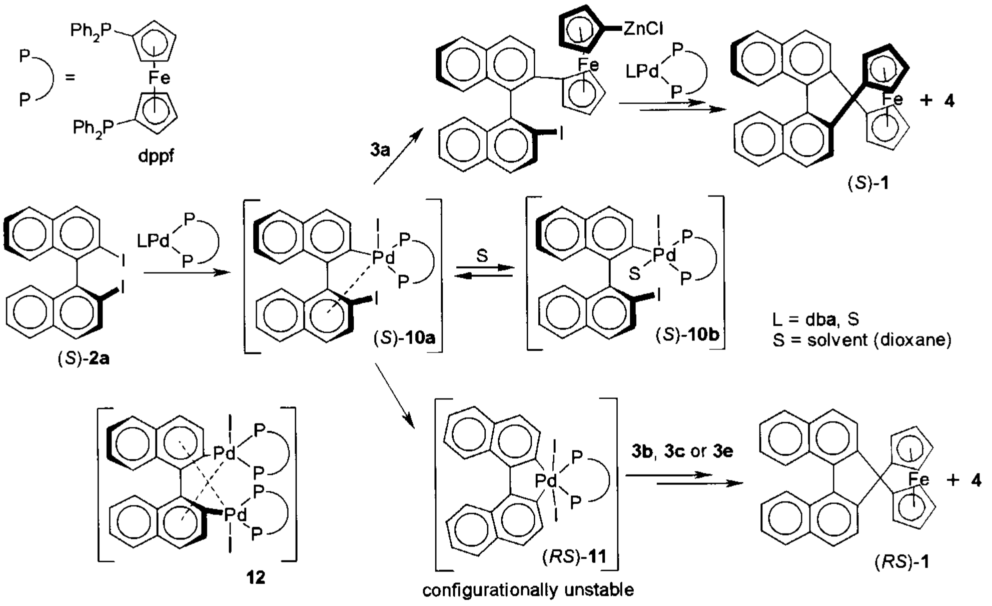
*2.3. Proposed mechanism for cross-coupling reaction from **2a** and palladium intermediates*

There have to be different pathways considering that the stereochemical results of Negishi versus Suzuki and Stille coupling yielding **1** are so different. If we consider methylation to **6c** (stereoconservative in Grignard coupling [5] and with complete racemization in Stille coupling by us), there is an apparent connection between the reactivity of the organometallic counterpart (Mg > Zn > Sn ~ B) and the stereochemical result. Thus, the following mechanism can be proposed (Scheme 3). The first step is common-an oxidative addition of **2a** to the palladium complex (insertion of palladium to C–I bond of **2a** in position 2) giving palladium(II) complex **10**, analogous to usual intermediates in cross-coupling reaction from aryl halides [26]. If the 1,1′-dimetalloferrocene is sufficiently reactive (dizinc **3a**), transmetallation can take a place and the first C–C bond is formed. A C–C bond in position 2′ is formed analogously. In such a mechanism there is no reason for racemization, and product **1** is obtained enantiopure-with complete conservation of stereogenic information from substrate.

If the organometallics are less reactive (e.g. B **3b** and **3c**, and Sn **3e**), transmetallation is slower than insertion of palladium in **10** to C–I bond in the position 2′ to form a palladacyclic complex **11** containing palladium(IV). It is known that 1,1′-binapthalene derivatives having positions 2 and 2′ bridged with one-atom linker have a low racemization barrier (between 45 and 65 kJ mol^{-1} [27]) because there are not nonbonding interactions in positions 2 and 2′ (ring flipping of fused unsaturated five-membered ring requires only low acti-



Scheme 2.



Scheme 3.

vation energy) and also nonbonding interactions in positions 8 and 8′ are decreased (the outer benzene rings of naphthalene units are dragged away). Thus, the binaphthyl moiety is easily racemized in this step. The palladacyclic complex **11** is not necessary an intermediate, this can be also considered as an activated complex, through which either reversible migration of palladium from position 2 to 2′ accompanied by racemization can occur or the reactivity of binaphthyl–palladium species towards transmetalation can be increased. Then, after transmetallation and formation of C–C bonds in the both 2 and 2′ positions, racemic products **1** and **6c** are formed.

We gained additional information about palladium intermediates from the reaction of diiodide **2a** with Pd(dba)$_2$ and dppf (1:1:1) in dioxane. When the reaction was run at room temperature, we isolated a complex with proposed structure **10**. It exhibits two broad signals in ^{31}P-NMR spectrum (C_1-symmetry) at 28.3 and 24.9 ppm in CDCl$_3$ (possibly **10a**) or 34.6 and 28.7 in dioxane/CDCl$_3$ mixture (possibly **10b**). The observed values are comparable to those of other Pd(dppf)Ar(I) complexes (8–30 ppm [28]). Also the signals in ^{1}H-NMR spectrum were broad, probably due to fluxional behavior of this complex. η^x-Coordination ($x = 2$ or more) of palladium to the neighboring naphthalene unit (as shown in **10a**) was observed in some palladium [29] and ruthenium [30] binaphthyl complexes. Additional stabilization of coordinationally unsaturated palladium(II) intermediates of cross-coupling reactions by solvent (as in **10b**) was reported in recent mechanism revising study [26a].

When the reaction mentioned above was performed in boiling dioxane, it resulted in another palladium complex, quite unstable under inert conditions, most probably **11**. It exhibits C_2-symmetry—a single signal in ^{31}P-NMR spectrum (27.1 ppm). Another alternative C_2 - symmetric structure that should be considered as a possible intermediate is **12**. The formation of complex **12** instead of **11** is less probable especially in the course of a catalytic reaction, if the high ratio of C–I bonds (in **2a**) to palladium precursor 20:1 in the reaction mixture is taken into account. An additional factor in favor of structure **11** over **12** is the expected higher difference of its activity towards transmetallation compared to **10**. At the same time, complex **11** should be less configurationally stable than **12** (its structure gives a more acceptable explanation for the observed complete racemization of the binaphthyl moiety). All known examples of lowered configurational stability of 2,2′-substituted 1,1′-binaphthyl derivatives are limited to those that have a bonding interaction between the positions 2 and 2′ [4]. In any case, organopalladium(IV) complexes are accepted as possible intermediates in some palladium-catalyzed processes [31], for instance in Heck couplings [32]. Some arylpalladium(IV) complexes stabilized with dinitrogen ligand were isolated [33]. The first Pd–arylphosphapalladacycle containing palladium(IV) was characterized recently [31b], but NMR data were not given. Further characterization of complexes **10** and **11** is under way and will be reported later.

3. Experimental

All cross-coupling experiments were performed in dried deoxygenated solvents under argon atmosphere using Schlenk technique, protected from the light. Pd(dba)$_2$ [34], Pd(dppf)Cl$_2$ [35], palladacycle **8** [36], (*RS*)- and (*S*)-2,2′-diamino-1,1′-binaphthyl [23], (*RS*)-**2a** and (*S*)-**2a** [23]; (*RS*)-**2b** [20], 1,1′-dibromoferrocene [37], **3a** from ferrocene/BuLi/TMEDA [3c] and 1,1′-dibromoferrocene/BuLi [8h], **3b** [11a], **3d** [38], **3e** [39], **3f** [40], and **3g** [41] were prepared according to the literature procedures. LiCl, NaI, KF, K$_3$PO$_4$, and ZnCl$_2$ were dried prior to use.

Melting points were measured on a Kofler block and are uncorrected. IR spectra were recorded on a Specord M 80 spectrophotometer, UV–vis spectra on a Hewlett Packard 8452A instrument. NMR spectra were measured on a Varian Gemini 300 instrument: ^{1}H-NMR (300 MHz) and ^{13}C-NMR (75.5 MHz) in CDCl$_3$ with tetramethylsilane as an internal standard, ^{31}P-NMR (121.5 MHz) with conc. H$_3$PO$_4$ as an external standard. Flash column chromatography was performed on 30–60 μm silica gel and thin-layer chromatography (TLC) on Silufol UV 254 foils. HPLC separation was done on a Chiracel OJ (Diacel) column with 1% propane-2-ol in methanol as an eluent, with UV detection at 254 nm. Specific optical rotation was measured on a Perkin–Elmer 241 polarimeter at 22 °C. Elemental analysis was determined on an Erba Science 1106 instrument, atomic absorbance spectroscopy (AAS) on a Perkin–Elmer 1100 instrument.

*3.1. 1,1′-bis(1,3,2-Dioxaborolane-2-yl)ferrocene (**3c**)*

A mixture of ferrocene-1,1′-diboronic acid (**3b**, 2.75 g, 10 mmol) and ethane-1,2-diol (1.25 ml, 22 mmol) in benzene (30 mol) was heated to reflux with azeotropic removal of water for 20 h. The solvent was evaporated and the residue crystallized from toluene/hexanes mixture. Product **3b** was obtained as an orange crystalline solid (3.08 g, 95%), m.p. 160–163 °C. Anal. Calc.: C, 51.80; H, 4.93; Found: C, 51.52; H, 4.90%. ^{1}H-NMR (CDCl$_3$), δ: 4.42 (br s, 4H, Cp-α), 4.40 (br s, 4H, Cp-β), 4.36 (s, 8H, OCH$_2$) ppm.

*3.2. (S)-1,1′-(1,1′-Binaphthyl-2,2′-diyl)ferrocene (**1**)*

3.2.1. Negishi coupling (Table 1, entry 2)

A solution of 1,1′-bis(chlorozincio)ferrocene (**3a**, 4.5 mmol, prepared as in Ref. [3c]) in THF (20ml) was added to a suspension of (*S*)-2,2′-diiodo-1,1′-binaphthyl ((*S*)-**2a**, 0.984 g, 1.94 mmol) and Pd(dppf)Cl$_2$ (0.146 g, 0.2 mmol) in THF (10 ml). The resulting dark red–brown reaction mixture was stirred for 72 h at room temperature (r.t.), then poured into 10% aqueous HCl (100 ml), and extracted twice with dichloromethane (2 × 100 ml). The combined extracts were washed with water and dried over anhydrous magnesium sulfate. After removal of the solvent under vacuum, the residue was purified by flash chromatography on silica gel, eluted first with isohexane up to elution of ferrocene. Following elution with isohexane:dichloromethane mixture 9:1 (v/v) gave (*S*)-**1** together with a small amount of **5a** (orange, the second colored band). Crystallization from hexane gave pure (*S*)-**1** (0.297 g, 35% yield, > 95% e.e.) as an orange crystalline solid.

The value of specific rotation corrected with respect to the contents of **1** in its mixture with **5a** after chromatography before crystallization (found from ^{1}H-NMR spectrum) compared with that of crystallized pure **1** showed that e.e. of **1** was not affected by the crystallization.

3.2.2. Suzuki coupling (Table 1, entry 7)

A suspension of (*S*)-**2a** (0.253 g, 0.5 mmol), 1,1′-bis(1,3,2-dioxaborolane-2-yl)ferrocene (**3c**, 0.325 g, 1 mmol), Pd(dba)$_2$ (0.029 g, 0.05 mmol), K$_3$PO$_4$ (1.06 g, 5 mmol) in THF (5 ml) was heated to reflux for 24 h. Reaction mixture cooled to r.t. was diluted with dichloromethane (25 ml), extracted with 10% aqueous NaHCO$_3$, washed with water and brine, and dried over anhydrous magnesium sulfate. After removal of the solvent under vacuum, the residue was chromatographed on flash silica gel. Elution with isohexane:dichloromethane 19:1 allowed isolation of unreacted (*S*)-**2a** (0.251 g, 50%). Following elution with isohexane:dichloromethane 9:1 gave, after evaporation, racemic **1** (orange, the first colored band; 0.026 g, 12% yield, < 1% e.e.).

3.2.3. Stille coupling (Table 1, entry 10)

A solution of 1,1′-bis(trimethylstannyl)ferrocene (**3e**, 1.022 g, 2 mmol) in THF (10 ml) was added via syringe to the suspension of (*S*)-**2**a (0.506 g, 1 mmol), Pd(dba)$_2$ (0.058 g, 0.1 mmol), PPh$_3$ (0.104 g, 0.4 mmol) and LiCl (0.133 g, 3 mmol) in THF (5 ml) and the reaction mixture was heated to reflux for 48 h. Subsequently, it was cooled to r.t., diluted with dichloromethane (50 ml), washed with 10% aqueous HCl, twice with water, then with brine, and finally dried over magnesium sulfate. After removal of the solvent under vacuum, the residue was chromatographed on flash silica gel. Elution with isohexane allowed isolation of racemic 2,2′-dimethyl-1,1′-binaphthyl (**6c**, 0.129 g, 46%, 0% e.e.), 2-iodo-2′-methyl-1,1′-binaphthyl (**7c**, 0.24 g, 6%), unreacted (*S*)-**2a** (0.024 g, 5%). Following elution with isohexane:dichloromethane 9:1 gave after evaporation racemic **1** (orange, the first colored band; 0.048 g, 11% yield, 0% e.e.).

3.2.4. Free radical arylation (Table 1, entry 13)

A solution of NaNO$_2$ (0.37 g, 5.37 mmol) in water (2.5 ml) was slowly added to the solution of (*S*)-2,2′-diamino-1,1′-binaphthyl (0.51 g, 1.79 mmol, 91% e.e.) in 50% aqueous H$_2$SO$_4$ (10 ml) at − 10 °C and the resulting mixture was stirred for 45 min bellow − 5 °C. Then, saturated aqueous solution of urea (0.107 g, 1.79 mmol) was added. This mixture was stirred for additional 30 min bellow − 5 °C and added at once to the ice-cooled dark blue solution of ferrocene (**3h**, 0.667 g, 3.58 mmol) in 50% aqueous H$_2$SO$_4$ (prepared as follows: a mixture of ferrocene in conc. H$_2$SO$_4$ (1.5 ml) was left standing overnight at r.t. and then poured into water (1.5 ml). The reaction mixture turned green–brown, and formation of dinitrogen was observed (foaming). The reaction mixture was stirred for 2 h at 0 °C, then allowed to warm to r.t. and stirred overnight. Afterwards, the solution of K$_2$S$_2$O$_5$ (0.89 g, 4 mmol) in water (10 ml) was added. The resulting mixture was stirred for 30 min, and extracted with dichloromethane (2 × 50 ml). The combined organic extracts were washed with 10% aqueous NaHCO$_3$ solution, water, dried over magnesium sulfate. After evaporation of the solvent, the residue was chromatographed on flash silica gel, eluted first with isohexane: dichloromethane mixture 19:1 (v/v), after elution of **1** (second colored band) with dichloromethane. Unreacted ferrocene (**3h**, 0.092 g, 14%), (*S*)-**1** (0.016 g, 2%, 24% e.e.), and mixture of oligomers **4** (0.420 g) were obtained one after the other.

1: ^{1}H- and ^{13}C-NMR spectra were in good agreement with Ref. [3c], elemental analysis was satisfactory. TLC: $R_F = 0.47$ (isohexane:dichloromethane 9:1). HPLC separation (retention times, flow 0.70 ml min^{-1}): 13.9 min. (−)-(*S*)-**1**, 18.7 (+)-(*R*)-1 (peaks were partially tailing). Polarimetry, (*S*)-**1**: $[\alpha]_D = -1165 \pm 30°$ cm^2 g^{-1} dm^{-1} ($c = 0.15$, CHCl$_3$).

*3.3. (S)-1,1′-(1,1′-Binaphthyl-2,2′-diyl)ferrocenium tetrafluoroborate (**9**)*

A solution of (*S*)-**1** (0.078 g, 0.18 mmol) in dichloromethane (2 ml) was added to the solution of NOBF$_4$ (0.021 g, 0.18 mmol) in dichloromethane (3 ml). The reaction mixture turned brown immediately; the reaction was accompanied with gas evolution. The reaction mixture was stirred for 1.5 h at r.t., filtered, and the solvent was evaporated. The residue was washed with methanol, ether, and dried in vacuum. Ferrocenium salt (*S*)-**9** was obtained as a dark brown powder (0.083 mg, 88% yield). M.p. 267–268 °C with decomposition. Anal. Calc.: Fe, 10.68; Found: Fe, 10.22%. UV–vis (CHCl$_3$), λ (log ε): 248 (1.85), 293 shoulder, 332 shoulder nm (log m^2 mol^{-1}). IR (CHCl$_3$), ν: 1635, 1610, 1520, 1480, 1390, 1080 br, 880, 845, 765 cm^{-1}. Polarimetry (*S*)-**9**: $[\alpha]_D = -865 \pm 50°$ deg cm^2 g^{-1} dm^{-1} ($c = 0.1$, CHCl$_3$).

3.4. Palladium complexes

*3.4.1. Compound **10a** (assumed as)*

A solution of **2a** (12.6 mg, 0.025 mmol) in dioxane (0.5 ml) was added to a solution of Pd(dba)$_2$ (14.4 mg, 0.025 mmol) and dppf (13.8 mg, 0.025 mmol) in dioxane (0.5 ml) and the resulting solution was stirred for 5 h at r.t. The solution was concentrated under vacuum and hexane was allowed to diffuse into it. Mother liquor was removed, the residue was washed with hexane and dried under vacuum. ^{1}H-NMR (CDCl$_3$): broad multiplets in Ar and Fc regions. ^{31}P-NMR (CDCl$_3$), δ: 28.3, 24.9 ppm (broad singlets).

*3.4.2. Compound **10b** (assumed as)*

A solution of **2a** (12.6 mg, 0.025 mmol) in dioxane (0.3 ml) was added to a solution of Pd(dba)$_2$ (14.4 mg, 0.025 mmol) and dppf (13.8 mg, 0.025 mmol) in dioxane (0.2 ml) in a NMR tube and left for 5 h at r.t. Then CDCl$_3$ was added (0.5 ml). ^{31}P-NMR (dioxane/CDCl$_3$, 1:1), δ: 34.6, 28.7 ppm (broad singlets).

*3.4.3. Compound **11** (assumed as)*

A solution of **2a** (12.6 mg, 0.025 mmol) in dioxane (0.3 ml) was added to a solution of Pd(dba)$_2$ (14.4 mg, 0.025 mmol) and dppf (13.8 mg, 0.025 mmol) in dioxane (0.2 ml) and the resulting solution was heated 5 h to reflux. Then it was transferred to a NMR tube and CDCl$_3$ was added (0.5 ml) to it. ^{31}P-NMR (dioxane:CDCl$_3$, 1:1), δ: 27.1 ppm (broad singlet).

Acknowledgements

This work was partially supported by the Slovak National Grant Agency, grant no. 1/4167/97 and 1/7013/20, and by the Comenius University, Grant for Young Scientists, no. UK/1528/97, /3904/98, /3724/99, /79/2000, /80/2000. The authors are thankful to Dr Š. Vyskočil (Charles University, Prague, Czech Republic) for performing the HPLC analysis.

References

[1] Reviews: (a) R.L. Halterman, Chem. Rev. 92 (1992) 965;
(b) A. Togni, R.L. Halterman, Metallocenes, Wiley-VCH, Weinheim, 1998;
(c) L. Haughton, J.M.J. Williams, J. Chem. Soc., Perkin Trans. 1 (2000) 3335;
(d) G.W. Coates, Chem. Rev. 100 (2000) 1223;
(e) L. Resconi, L. Cavallo, A. Fait, F. Piemontesi, Chem. Rev. 100 (2000) 1253.
Recent examples: (f) R.L. Halterman, C. Zhu, Z. Chen, M.S. Dunlap, M.A. Khan, K.M. Nicholas, Organometallics 19 (2000) 3824;
(g) M.S. Hansen, S.L. Buchwald, Org. Lett. 2 (2000) 713;
(h) G.V. Bondar, R. Aldea, C.J. Levy, J.B. Jaquith, S. Collins, Organometallics 19 (2000) 947;
(i) Z.K. Sweeney, J.L. Salsman, R.A. Andersen, R.G. Bergman, Angew. Chem., Int. Ed. Engl. 39 (2000) 2339.

[2] (a) A. Sudhakar, T.J. Katz, J. Am. Chem. Soc. 108 (1986) 179;
(b) T.R. Kelly, P. Meghani, J. Org. Chem. 55 (1990) 3684;
(c) K.-L. Gibis, G. Helmchen, G. Huttner, L. Zsolnai, J. Organomet. Chem. 445 (1993) 181;
(d) A.J. Locke, C.J. Richards, D.E. Hibbs, M.B. Hursthouse, Tetrahedron Asymm. 8 (1997) 3383;
(e) A.J. Locke, C.J. Richards, Organometallics 18 (1999) 3750.

[3] (a) T.J. Katz, J. Pesti, J. Am. Chem. Soc. 103 (1982) 346;
(b) M.E. Huttenloch, J. Diebold, U. Rief, H.-H. Brintzinger, A.M. Gilbert, T.J. Katz, Organometallics 11 (1992) 3600;
(c) B.M. Foxman, M. Rosenblum, V. Sokolov, N. Khrushchova, Organometallics 12 (1993) 4805;
(d) P.J. Shapiro, K.M. Kane, A. Vij, D. Stelck, G.J. Matare, R.L. Hubbard, B. Caron, Organometallics 18 (1999) 3468.

[4] (a) M. Putala, Enantiomer 4 (1999) 243;
(b) M. Putala, Chem. Listy 95 (2001) in press.

[5] (a) O. Takahashi, M. Kameda, K. Maruoka, J. Am. Chem. Soc. 121 (1999) 6519;
(b) D. Xiao, Z. Zhang, X. Zhang, Org. Lett. 1 (1999) 1679;
(c) M. Gingras, F. Dubois, Tetrahedron Lett. 40 (1999) 1309.

[6] (a) Methoxycarbonylation: T. Ohta, M. Ito, K. Inagaki, H. Takaya, Tetrahedron Lett. 34 (1993) 1615;
(b) Phosphanylation: D.W. Cai, J.F. Payack, D.L. Hughes, T.R. Verhoeven, P.J. Reider, J. Org. Chem. 59 (1994) 7180;
(c) Arsanylation: A. Kojima, C.D.J. Boden, M. Shibasaki, Tetrahedron Lett. 38 (1997) 3459;
(d) Cyanation: P. Kasák, M. Putala, Collect. Czech. Chem. Commun. 65 (2000) 729;
(e) Cyanation: L. Kurz, G. Lee, D. Morgans, M.J. Waldyke, T. Ward, Tetrahedron Lett. 31 (1990) 6321.

[7] M.-T. Lee, B.M. Foxman, M. Rosenblum, Organometallics 4 (1985) 539.

[8] (a) Ref. 7;
(b) D.R. Talham, D.O. Cowan, Organometallics 6 (1987) 932;
(c) R. Arnold, S.A. Matchett, M. Rosenblum, Organometallics 7 (1988) 2261;
(d) B.M. Foxman, D.A. Gronbeck, M. Rosenblum, J. Organomet. Chem. 413 (1991) 287;
(e) Ref. 3b;
(f) Ref. 3c;
(g) J.G.P. Delis, P.W.N.M. van Leeuwen, K. Vrieze, N. Veldman, A.L. Spek, J. Fraanje, K. Goubitz, J. Organomet. Chem. 514 (1996) 125;
(h) I.R. Butler, L.J. Hobson, S.J. Coles, M.B. Hursthouse, K.M.A. Malik, J. Organomet. Chem. 540 (1997) 27;
(i) M. Iyoda, T. Kondo, T. Okabe, H. Matsuyama, S. Sasaki, Y. Kuwatani, Chem. Lett. (1997) 35;
(j) C.D. Hall, N. Sachsinger, S.C. Nyburg, J.W. Steed, J. Organomet. Chem. 561 (1998) 209;
(k) M. Iyoda, T. Okabe, M. Takada, Y. Kuwatani, J. Organomet. Chem. 569 (1998) 225;
(l) H.L. Pedersen, M. Johannsen, Chem. Commun. (1999) 2517;
(m) U. Siemeling, B. Neumann, H.-G. Stammler, O. Kuhnert, Polyhedron 18 (1999) 1815;
(n) R.D.A. Hudson, B.M. Foxman, M. Rosenblum, Organometallics 19 (2000) 469.

[9] A.V. Tsvetkov, G.V. Latyshev, N.L. Lukashev, I.P. Beletskaya, Tetrahedron Lett. 41 (2000) 3987.

[10] (a) D. Guillaneux, H.B. Kagan, J. Org. Chem. 60 (1995) 2502;
(b) C.-M. Liu, J.-J. Zhai, Y.-X. Ma, Y.-M. Liang, Synth. Commun. 28 (1998) 2731;
(c) C.-M. Liu, Q.-H. Xu, Y.-M. Liang, Y.-X. Ma, J. Chem. Res. S (1999) 636;
(d) S.J. Higgins, C.L. Jones, S.M. Francis, Synth. Met. 98 (1999) 211;
(e) C.-M. Liu, B.-H. Chen, W.-Y. Liu, X.-L. Wu, Y.-X. Ma, J. Organomet. Chem. 598 (2000) 348;
(f) R.S. Laufer, U. Veith, N.J. Taylor, V. Snieckus, Org. Lett. 2 (2000) 629.

[11] (a) R. Knapp, M. Rehahn, J. Organomet. Chem. 452 (1993) 235;
(b) Z.F. Plyta, D. Prim, J.P. Tranchier, F. Rosemunch, E. Rose, Tetrahedron Lett. 40 (1999) 6769.

[12] (a) C. Imrie, C. Loubser, P. Engelbrecht, C.W. McCleland, J. Chem. Soc. Perkin Trans. 1 (1999) 2513;
(b) Ref. 10f.

[13] (a) A.N. Nesmeyanov, V.A. Sazonova, V.N. Drozd, Chem. Ber. 93 (1960) 2717;
(b) M.D. Rausch, Inorg. Chem. 1 (1962) 414;
(c) A.N. Nesmeyanov, V.A. Sazonova, V.N. Drozd, Dokl. Akad. Nauk SSSR 154 (1964) 158;
(d) A.N. Nesmeyanov, V.A. Sazonova, V.N. Drozd, Dokl. Akad. Nauk SSSR 165 (1965) 575;
(e) E.W. Neuse, L. Bednarik, Transition Met. Chem. 87 (1979) 4;
(f) N.N. Meleshonkova, S.F. Min, S.K. Moiseyev, Zh. Obsch. Khim. 57 (1987) 2606;
(g) Ref. 8b.

[14] (a) A.N. Nesmeyanov, V.A. Sazonova, A.V. Gerasimenko, Dokl. Akad. Nauk SSSR 147 (1962) 634;
(b) K. Schlögl, M. Fried, Monatsh. Chem. 94 (1963) 537;
(c) C.I.R. Butler, J.-L. Roustan, Can. J. Chem. 68 (1990) 2212;
(d) I.R. Butler, N. Burke, L.J. Hobson, H. Findenegg, Polyhedron 11 (1992) 2435;
(e) I.R. Butler, Polyhedron 11 (1992) 3117;
(f) I.R. Butler, S.J. McDonald, M.B. Hursthouse, K.M.A. Malik, Polyhedron 14 (1995) 529.

[15] (a) A.N. Nesmeyanov, E.G. Perevalova, R.V. Golovnya, O.A. Nesmeyanova, Dokl. Akad. Nauk SSSR 97 (1954) 459;
(b) A.N. Nesmeyanov, E.G. Perevalova, R.V. Golovnya, Dokl. Akad. Nauk SSSR 99 (1954) 539;
(c) A.N. Nesmeyanov, E.G. Perevalova, R.V. Golovnya, L.S. Shilovtseva, Dokl. Akad. Nauk SSSR 102 (1955) 535;
(d) V. Weinmayr, J. Am. Chem. Soc. 77 (1955) 3012;
(e) G.D. Broadhead, P.L. Pauson, J. Chem. Soc. (1955) 367;

(f) A.N. Nesmeyanov, E.G. Perevalova, R.V. Golovnya, N.A. Simukova, O.V. Staravskii, Izv. Akad. Nauk SSSR (1957) 638;
(g) M. Rosenblum, J. Am. Chem. Soc. 81 (1959) 4530;
(h) W.F. Little, A.K. Clark, J. Org. Chem. 25 (1960) 1979;
(i) J.G. Mason, M. Rosenblum, J. Am. Chem. Soc. 82 (1960) 4206;
(j) E.G. Perevalova, N.A. Simukova, T.V. Nikitina, P.D. Reshetov, A.N. Nesmeyanov, Izv. Akad. Nauk SSSR (1961) 77;
(k) M. Rosenblum, W.G. Howells, A.K. Banerjee, C. Bennett, J. Am. Chem. Soc. 84 (1962) 2726;
(l) Ref. 14b;
(m) A.L.J. Beckwith, R.J. Leydon, Tetrahedron 20 (1964) 791;
(n) W.F. Little, B. Nielsen, R. Williams, Chem. Ind. (1964) 195;
(o) R.M.G. Roberts, J. Organomet. Chem. 388 (1990) 181;
(p) P.L. Pauson, T. Tanez, J. Chem. Soc. Perkin Trans. 1 (1990) 2437;
(q) A.L.J. Beckwith, R.A.: Jackson, R.W. Longmore, Aust. J. Chem. 45 (1992) 857;
(r) V. Gonzalo, C. Coudret, C. Patoux, J.P. Launay, C. R. Acad. Sci. Ser. II 2 (1999) 321;
(s) J. Hu, D.L. Mattern, J. Org. Chem. 65 (2000) 2277;
(t) G. Huang, B. Li, W. Li, L. Shi, Y. Ma, J. Chem. Res. (S) (2000) 491.

[16] (a) A.L.J. Beckwith, R.J. Leydon, Aust. J. Chem. 19 (1966) 1381;
(b) G.P. Sollott, W.R. Peterson, J. Org. Chem. 34 (1969) 1506.

[17] Q. Shelby, N. Kataoka, G. Mann, J. Hartwig, J. Am. Chem. Soc. 122 (2000) 10718.

[18] C. Imrie, D.C. Nonhebel, P.L. Pauson, J. Chem. Soc. Perkin Trans. 1 (1991) 2555.

[19] (a) P.L. Pauson, J. Am. Chem. Soc. 76 (1954) 2187;
(b) Ref. 15d;
(c) S. McVey, P.L. Pauson, J. Chem. Soc. (1965) 4312;
(d) M. Nilsson, R. Wahren, O. Wennerström, Tetrahedron Lett. (1970) 4583;
(e) Ref. 7;
(f) D.A. Gronbeck, S.A. Matchett, M. Rosenblum, Tetrahedron Lett. 30 (1989) 2881;
(g) Ref. 2b;
(h) B.M. Foxman, D.A. Gronbeck, N. Khruschova, M. Rosenblum, J. Org. Chem. 58 (1993) 4078;
(i) M. Rosenblum, H.M. Nugent, K.-S. Jang, M.M. Labes, W. Cahalane, P. Klemarczyk, W.H. Reiff, Macromolecules 28 (1995) 6330;
(j) K. Jang, Polymer Korea 23 (1999) 781;
(k) R.D.A. Hudson, B.M. Foxman, M. Rosenblum, Organometallics 18 (1999) 4098;
(l) Ref. 8n;
(m) M.P. Thornberry, C. Slebodnick, P.A. Deck, Organometallics 19 (2000) 5352.

[20] Y. Uozomi, A. Tanahashi, S.-Y. Lee, T. Hayashi, J. Org. Chem. 58 (1993) 1945.

[21] R. Pummerer, E. Prell, A. Rieche, Chem. Ber. 59 (1926) 2159.

[22] One from about fifty: Y. Wang, J. Sun, K. Ding, Tetrahedron 56 (2000) 4447.

[23] K.J. Brown, M.S. Berry, J.R. Murdoch, J. Org. Chem. 50 (1985) 4345.

[24] B. Schilling, D.E. Kaufmann, Eur. J. Org. Chem. (1998) 701.

[25] (a) A. Suzuki, J. Organomet. Chem. 576 (1999) 147;
(b) A.F. Littke, C. Dai, G.C. Fu, J. Am. Chem. Soc. 122 (2000) 4020;
(c) C. Griffiths, N.S. Leadbeater, Tetrahedron Lett. 41 (2000) 2487.

[26] (a) C. Amatore, A. Jutand, J. Organomet. Chem. 576 (1999) 254;
(b) A. Yamamato, Y. Kayaki, K. Nagayama, I. Shimizu, Synlett (2000) 925;
(c) C. Amatore, A. Jutand, Acc. Chem. Res. 33 (2000) 314 and references cited therein.

[27] (a) O. De Lucchi, Pure Appl. Chem. 68 (1996) 945;
(b) S. Gladiali, D. Fabbri, Chem. Ber. 130 (1997) 543.

[28] (a) J.M. Brown, J.J. Pérez-Torrente, N.W. Alcock, H.J. Clase, Organometallics 14 (1995) 207;
(b) C. Amatore, G. Brocker, A. Jutand, F. Khalil, J. Am. Chem. Soc. 119 (1997) 5176;
(c) M.S. Driver, J.F. Hartwig, J. Am. Chem. Soc. 119 (1997) 8232.

[29] (a) P. Kočovský, A.V. Malkov, Š. Vyskočil, G.C. Lloyd-Jones, Pure Appl. Chem. 71 (1999) 1425;
(b) P. Kočovský, Š. Vyskočil, I. Císařová, J. Sejbal, I. Tišlerová, M. Smrčina, G.C. Lloyd-Jones, S.C. Stephen, C.P. Butts, M. Murray, V. Langer, J. Am. Chem. Soc. 121 (1999) 7714.

[30] (a) T.J. Geldbach, D. Drago, P.S. Pregosin, Chem. Commun. (2000) 1629;
(b) C.J. den Reijer, M. Wörle, P.S. Pregosin, Organometallics 19 (2000) 309.

[31] (a) G. Dyker, A. Kellner, J. Organomet. Chem. 555 (1998) 141 and references cited therein;
(b) J.M. Brunel, M.-H. Hirlemann, A. Heumann, G. Buono, Chem. Commun. (2000) 1869.

[32] (a) M. Ohff, A. Ohff, M.E. van der Boom, D. Meilstein, J. Am. Chem. Soc. 119 (1997) 11687;
(b) B.L. Shaw, S.D. Perera, E.A. Staley, Chem. Commun. (1998) 1361;
(c) B.L. Shaw, S.D. Perera, Chem. Commun. (1998) 1863;
(d) B.L. Shaw, New J. Chem. 22 (1998) 77.

[33] (a) B.A. Markies, A.J. Canty, M.D. Janssen, A.L. Spek, J. Boersma, G. van Koten, Rec. Trav. Chim. Pay-Bas 110 (1991) 477;
(b) N.J. Hovestad, J.L. Hoare, J.T.B.H. Jastrzebski, A.J. Canty, W.J.J. Smeets, L. Spek, G. van Koten, Organometallics 18 (1999) 2970.

[34] T. Ukai, H. Kawazura, Y. Ishii, J.J. Bonet, J.A. Ihers, J. Organomet. Chem. 65 (1974) 253.

[35] T. Hayashi, M. Konishi, M. Kumada, Tetrahedron Lett. 21 (1979) 1871.

[36] W.A. Herrmann, C. Brossmer, K. Öfele, C.P. Reisinger, T. Priermeier, M. Beller, H. Fischer, Angew. Chem. Int. Ed. Engl. 34 (1995) 1844.

[37] A.N. Nesmeyanov, V.A. Sazonova, V.N. Drozd, Dokl. Akad. Nauk SSSR 126 (1959) 1004.

[38] M.E. Wright, Organometallics 9 (1990) 853.

[39] Z. Dawoodi, C. Eaborn, A. Pidcock, J. Organomet. Chem. 170 (1979) 95.

[40] H. Schottenberger, M. Buchmeiser, J. Polin, K.-E. Schwarzhans, Z. Naturforsch. Teil B 48 (1993) 1524.

[41] (a) M. Rausch, M. Vogel, H. Rosenberg, J. Org. Chem. 22 (1957) 900;
(b) R.W. Fish, M. Rosenblum, J. Org. Chem. 30 (1965) 1253.