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REGIO- AND STEREO-CHEMISTRY IN ALLYLATION OF ARYL GRIGNARD REAGENTS CATALYZED BY PHOSPHINE-NICKEL AND -PALLADIUM COMPLEXES *

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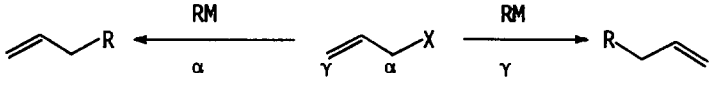
Summary

Nickel and palladium complexes with the 1,1'-bis(diphenylphosphino)ferrocene ligand effectively catalyze regioselective cross-coupling of allylic ethers such as 1- or 3-methyl-2-propenyl silyl ethers with aryl-Grignard reagents, where the nickel catalyst leads to carbon–carbon bond formation at the more substituted position while carbon–carbon bond formation occurs at the less substituted position in the case of the palladium catalyst. Allylation of *cis*- and *trans*-5-methyl-2-cyclohexenyl silyl ethers was found to proceed with inversion of configuration with both the nickel and palladium catalysts. The stoichiometric reaction of a (1-methyl-π-allyl)palladium complex with the phenyl-Grignard reagent in the presence of phosphine ligands was also studied. A mechanism involving formation of the π-allyl(aryl)ML_2 intermediate is proposed.

Introduction

There has been great interest and activity in the control of regiochemistry in allylic systems [1], and a considerable effort has been made to direct organometallic reagents selectively to either the α or γ position of allylic substrates [2] (Scheme 1).

SCHEME 1



In this paper we describe a new type of regioselective and high-yielding allylation reaction of Grignard reagents catalyzed by nickel- or palladium-phosphine complexes, where the regiochemistry of the product is entirely dependent on the nature of the catalyst, and either of the isomeric products can be obtained selectively by the choice of an appropriate catalyst from either of the starting allylic substrates (Scheme 2).

* A preliminary account of this work appeared in J. Chem. Soc., Chem. Commun., (1981) 313.

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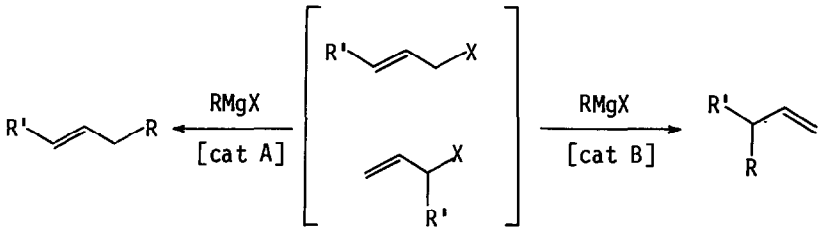
SCHEME 2

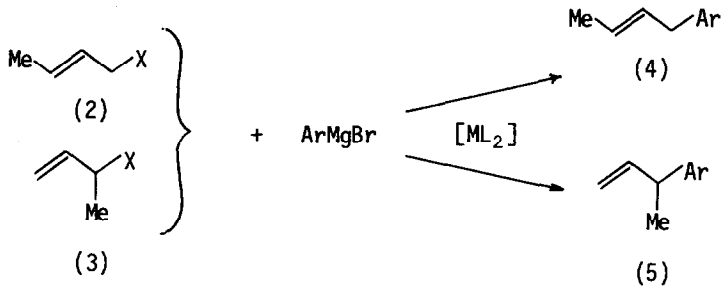


The nickel-catalyzed reaction of allyl alcohols or sulfides with Grignard reagents has been studied in detail from both a synthetic and a mechanistic viewpoint [3,4], but there have been no reports on the allylation with palladium catalysts. Here we also describe both the stoichiometric reaction of a π-allylpalladium complex with a Grignard reagent and the stereochemistry of the palladium-catalyzed allylation, which will provide significant information concerning the mechanism of the allylation.

Results and discussion

Regioselectivity

Some phosphine-nickel and -palladium complexes were tested for catalytic activity and regioselectivity in the reaction of phenylmagnesium bromide (**1a**) with



(1)

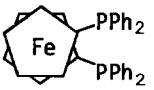
a: X = $OSiEt_3$
b: X = $OSiMe_3$
c: X = OPh
d: X = OTHP
e: X = Cl
f: X = OH

a: Ar = Ph
b: Ar = p-MeC_6H_4
c: Ar = o-MeC_6H_4

a: Ar = Ph
b: Ar = p-MeC_6H_4
c: Ar = o-MeC_6H_4

L_2 = $Ph_2P(CH_2)_nPPh_2$
n = 2 (dppe)
n = 3 (dppp)

L_2 = 2 PPh_3

L_2 = 

(dppf)

(*E*)-1-triethylsiloxy-2-butene (**2a**) and 3-triethylsiloxy-1-butene (**3a**) (eq. 1). The reaction conditions and results are summarized in Table 1.

The reaction of **2a** in the presence of $NiCl_2$(dppf) [5] catalyst, where dppf stands for 1,1′-bis(diphenylphosphino)ferrocene [6], gave 3-phenyl-1-butene (**5a**) selectively over its isomer 1-phenyl-2-butene (**4a**). The reaction of **3a** catalyzed by $NiCl_2$(dppf) also gave **5a** as the main product. Thus, $NiCl_2$(dppf) is a unique catalyst in that it can give rise to regioselective carbon–carbon bond formation at the more substituted position, starting with either regioisomeric allylic ether **2a** or **3a**. Use of other nickel complexes, $NiCl_2(PPh_3)_2$ and $NiCl_2$(dppp) (dppp = 1,3-bis(diphenylphosphino)-propane), resulted in the formation of both regioisomers **4a** and **5a** in comparable amounts. Felkin and Swierczewski [7] and Okamura and Takei [4] have reported similar results, in that the $NiCl_2(PPh_3)_2$ or $NiCl_2$(dppp) catalyst lacks regioselectivity in the reaction of PhMgBr with α- and γ-methylallyl alcohols or sulfides.

Palladium complexes exhibited opposite regioselectivity to $NiCl_2$(dppf), that is, formation of the carbon–carbon bond took place preferably at the less substituted terminal position to produce **4a** selectively from either **2a** or **3a** [8]. Of the palladium complexes, $PdCl_2$(dppf) [9] is by far the best catalyst, having both a high catalytic activity and a high regioselectivity. Similar high regioselectivity was observed in the reaction with $PdCl_2$(dppp) or $Pd(PPh_3)_4$, but they catalyzed the reaction only sluggishly. The low catalytic activity of $Pd(PPh_3)_4$, which has been conventionally used as a typical palladium catalyst, may be the reason why there have been no examples of the palladium-catalyzed allylation of Grignard reagents. $PdCl_2$(dppe)

TABLE 1

REACTION OF ALLYL SILYL ETHERS **2** AND **3** WITH ARYL GRIGNARD REAGENTS **1** IN THE PRESENCE OF NICKEL AND PALLADIUM COMPLEXES [a]

ArMgBr	Allyl ether	Catalyst	Reaction time (h)	Total yield [b] (%)	Product ratio [c] **4**(*E*/*Z*)/ **5**
1a	**2a**	$NiCl_2$(dppf)	4	100 (85)	12(11/1)/88
		$NiCl_2$(dppp)	40	44	59(59/0)/41
		$NiCl_2(PPh_3)_2$	4	100	67(66/1)/33
		$PdCl_2$(dppf)	4	100 (75)	96(92/4)/ 4
		$PdCl_2$(dppe)	40	3	———
		$PdCl_2$(dppp)	40	68	93(80/13)/ 7
		$Pd(PPh_3)_4$	20	52	90(85/5)/10
1a	**3a**	$NiCl_2$(dppf)	4	91	19(10/9)/81
		$NiCl_2$(dppp)	40	81	58(53/5)/42
		$NiCl_2(PPh_3)_2$	4	93	55(39/16)/45
		$PdCl_2$(dppf)	4	83	91(75/16)/ 9
		$PdCl_2$(dppp)	40	60	88(80/8)/12
1b	**2b**	$NiCl_2$(dppf)	26	(97)	16(15/1)/84
		$PdCl_2$(dppf)	26	(85)	92(86/6)/ 8
1c	**2b**	$NiCl_2$(dppf)	25	(53)	17(16/1)/83
		$PdCl_2$(dppf)	25	(69)	84(79/5)/16

[a] To a mixture of allyl ether (2 mmol) and catalyst (0.04 mmol) was added the Grignard solution (4 mmol) in ether. The mixture was stirred at room temperature for a given period, hydrolyzed, and then analyzed by GLC. [b] Determined by GLC using an internal standard. Isolated yields are given in parentheses. [c] Isomeric purity was determined by ^{1}H NMR and GLC analysis.

TABLE 2

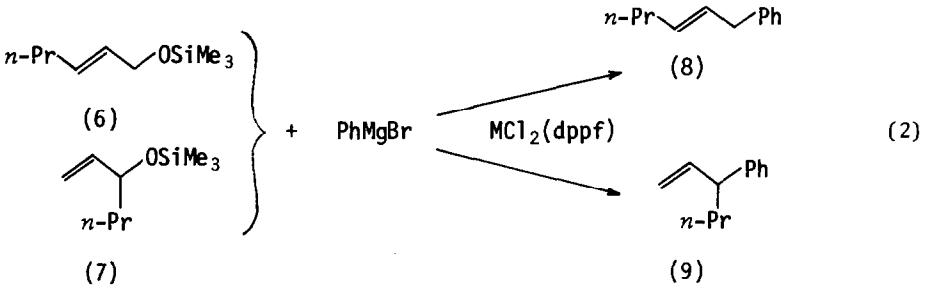
REACTION OF ALLYL SILYL ETHERS **6** AND **7** WITH PHENYLMAGNESIUM BROMIDE (**1a**) IN THE PRESENCE OF NICKEL- OR PALLADIUM-dppf CATALYSTS [a]

Allyl ether	Catalyst	Reaction time (h)	Total yield [b] (%)	Product ratio [c] **8**(*E*/*Z*)/ **9**
6	$NiCl_2$(dppf)	20	92	17(16/1)/83
	$PdCl_2$(dppf)	20	91	93(87/6)/ 7
7	$NiCl_2$(dppf)	18	88	19(10/9)/81
	$PdCl_2$(dppf)	18	91	87(67/20)/13

[a] The reaction was carried out in a similar manner to that in Table 1. [b] Isolated yields. [c] Isomeric purity was determined by ^1H NMR and GLC analysis.

(dppe = 1,2-bis(diphenylphosphino)ethane) was almost inactive, as is usual for the Grignard cross-coupling reaction [9]. The high catalytic activity of $PdCl_2$(dppf) compared with other palladium complexes may be due to the unique steric and electronic nature of the dppf ligand [9]. Table 1 also contains the results obtained for the reaction of *p*- and *o*-tolylmagnesium bromide (**1b,c**). The Grignard reagents reacted with the allyl silyl ether **2b** selectively, similar to the phenyl Grignard reagent, to give either of the regioisomers, depending on the catalyst, $NiCl_2$(dppf) or $PdCl_2$(dppf), used.

A pair of allyl silyl ethers, (*E*)-1-trimethylsiloxy-2-hexene (**6**) and 3-trimethylsiloxy-1-hexene (**7**), were also used successfully for regioselective phenylation (eq. 2) (Table 2). Thus, the nickel catalyst with the dppf ligand preferred formation of the



(2)

terminal alkene **9** starting with either of the allyl ethers **6** or **7**, while the palladium catalyst gave the non-terminal alkene **8** selectively.

The reaction of other 2-butenyl derivatives (**2c–2f**) was also examined in the presence of $NiCl_2$(dppf) or $PdCl_2$(dppf) as catalyst. The reaction conditions and results are summarized in Table 3. Phenyl ether (**2c**), tetrahydropyranyl ether (**2d**), and chloride (**2e**) were all converted selectively into the phenylated product **4a** or **5a** in over 80% yield. The ratios of **4a/5a** obtained in the $NiCl_2$(dppf)-catalyzed reaction of **2c**, **2d**, and **2e** were 14/86, 19/81, and 25/75, respectively, and those obtained in the $PdCl_2$(dppf)-catalyzed reaction were 90/10, 89/11, and 82/18, respectively. The lower regioselectivity observed with the chloride **2e** is ascribed to a competing non-catalyzed reaction, which gives both **4a** and **5a** in a 2/1 ratio. Alcohol **2f** was also phenylated regioselectively by the $NiCl_2$(dppf) (**4a/5a** = 20/80) or $PdCl_2$(dppf) catalyst (**4a/5a** = 91/9) [10], though the conversion was low.

Thus, the regioselectivity in the present catalytic allylation is independent of the

TABLE 3

REACTION OF 2-BUTENYL DERIVATIVES **2c–2f** WITH PHENYLMAGNESIUM BROMIDE (**1a**) IN THE PRESENCE OF NICKEL- AND PALLADIUM-dppf CATALYSTS [a]

2-Butenyl derivative	Catalyst	Reaction time (h)	Total yield [b] (%)	Product ratio [c] **4a**(*E*/*Z*)/**5a**
2c: X = OPh [d]	$NiCl_2$(dppf)	4	95	14(13/1)/86
	$PdCl_2$(dppf)	4	89	90(86/4)/10
2d: X = OTHP	$NiCl_2$(dppf)	4	83	19(17/2)/81
	$PdCl_2$(dppf)	20	80	89(81/8)/11
2e: X = Cl	$NiCl_2$(dppf)	4	87	25(21/4)/75
	$PdCl_2$(dppf)	20	82	82(74/8)/18
	none	4	18	68(67/1)/32
2f: X = OH	$NiCl_2$(dppf)	4	46	20(18/2)/80
	$PdCl_2$(dppf)	4	23	91(91/0)/ 9

[a] The reaction was carried out in a similar manner to that in Table 1. [b] Determined by GLC using an internal standard. [c] Isomeric purity was determined by ^{1}H NMR and GLC analysis. [d] The regiosomer mixture was **2c**/(*Z*)-1-phenoxy-2-butene/**3c** = 79/16/5.

nature of the leaving group. The nearly identical product distribution from all of the starting allylic compounds with each catalyst suggests the formation of a common intermediate, most likely π-allyl(aryl)ML_2 (M = Ni [7] or Pd [11]) species (see below). The nature of both the metal and the phosphine ligand must influence the regiochemistry of carbon–carbon bond formation in the process of reductive elimination from the intermediate, although the precise effect of the metal and ligand remains to be clarified.

Stereochemistry

The stereochemistry of the present allylation was studied using cyclic silyl ethers,

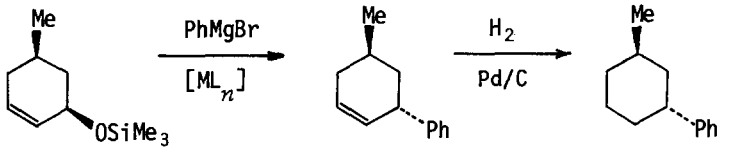
TABLE 4

REACTION OF 5-METHYL-2-CYCLOHEXENYL SILYL ETHER (**10**) WITH PHENYLMAGNESIUM BROMIDE (**1a**) IN THE PRESENCE OF NICKEL- AND PALLADIUM-dppf CATALYSTS [a]

Allyl ether **10** [b] *cis*/*trans*	Catalyst	Total yield [c] of **11** (%)	Isomeric ratio [d] *cis*/*trans*
92/8	$NiCl_2$(dppf)	80	8/92
	$PdCl_2$(dppf)	84	12/88
71/29	$NiCl_2$(dppf)	79	32/68
	$PdCl_2$(dppf)	82	27/73
2/98	$NiCl_2$(dppf)	81	95/5
	$PdCl_2$(dppf)	82	78/22

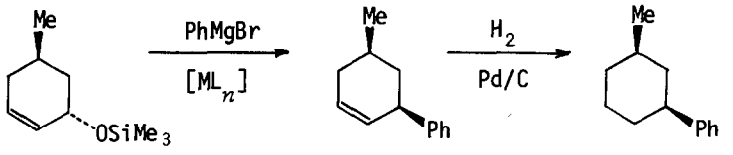
[a] To a mixture of allyl ether (3 mmol) and catalyst (0.03 mmol) was added the Grignard solution (6 mmol) in ether. The mixture was stirred at room temperature for 48 h, and then hydrolyzed. [b] Isomeric purity was determined by ^{1}H NMR and GLC analysis. [c] Isolated yields. [d] 3-Phenyl-5-methylcyclohexene (**11**) was converted into 1-phenyl-3-methylcyclohexane (**12**), and the isomeric purity of **12** was determined by ^{1}H NMR and GLC analysis.

cis- and *trans*-5-methyl-2-cyclohexenyl silyl ether (**10**) (eqs. 3 and 4). The *cis*/*trans* ratio of the coupling product, phenyl-5-methyl-1-cyclohexene (**11**), was determined by ^{1}H NMR and GLC analysis of 1-phenyl-3-methylcyclohexane (**12**), which was derived quantitatively from **11** by hydrogenation. Table 4 shows that the *cis*-ether **10** gave *trans*-3-phenyl-5-methylcyclohexene (**11**), while the *trans*-ether **10** gave *cis*-**11**



(3)

cis-(10) *trans*-(11) *trans*-(12)

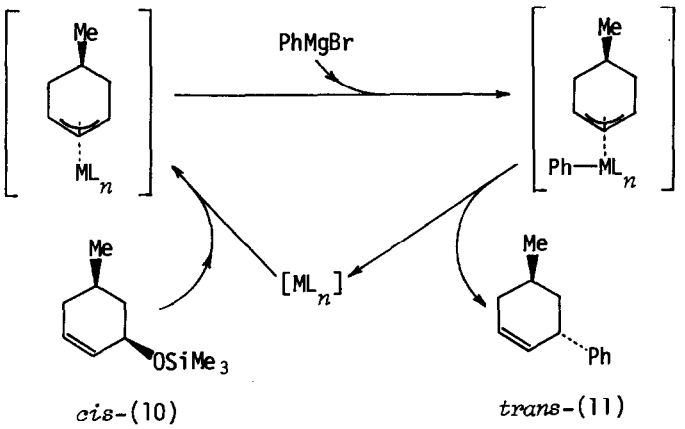


(4)

trans-(10) *cis*-(11) *cis*-(12)

with both the $NiCl_2$(dppf) and $PdCl_2$(dppf) catalysts, though a slight decrease of specificity was observed in the reaction of *trans*-**10** catalyzed by $PdCl_2$(dppf). Thus, the catalytic phenylation is stereospecific and takes place on the side of the ring opposite to that of the replaced siloxy group (inversion). The inversion of stereochemistry can be rationalized by the mechanism involving the π-allyl(phenyl)metal intermediate (Scheme 3). The formation of π-allylpalladium complexes from pal

SCHEME 3



cis-(10) *trans*-(11)

ladium(0) species and allylic substrates has been shown to proceed with inversion of configuration [12], and it has been established that the reaction of Grignard reagents with π-allylpalladium proceeds with retention (attack from the same side as the palladium) [13]. This stereochemistry (inversion followed by retention) is in good

TABLE 5

REACTION OF DI-μ-CHLOROBIS(1-METHYL-π-ALLYL)DIPALLADIUM (13) WITH PHENYLMAGNESIUM BROMIDE (1a) [a]

Ligand	PhMgBr (equiv/Pd)	Additive	Reaction time (h)	Yield [b] (%)	
				4a(E/Z)	5a
none	4	–	4	7.5(7.5/0)	0
dppf	4	–	4	30(28/2)	5
2 PPh_3	4	–	4	18(18/0)	5
dppe	4	–	4	16(16/0)	1
dppf	20	–	4	32(32/0)	3
none	10	14	1.5	7(7/0)	1
dppf	10	14	1.5	50(50/0)	5
2 PPh_3	10	14	1.5	31(30/1)	10
dppe	10	14	1.5	21(21/0)	2

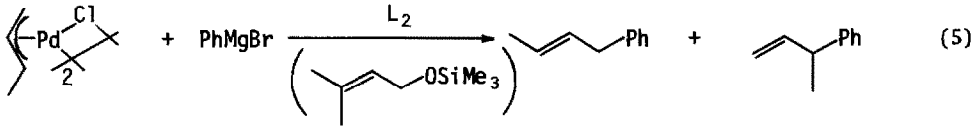
[a] To a mixture of π-allylpalladium 13 (1.0 mmol), a ligand (2.0 mmol), and/or additive 14 (4.0 mmol) in ether was added the Grignard solution in ether. The mixture was stirred at room temperature for a given period, hydrolyzed, and then analyzed by GLC. [b] Determined by GLC using an internal standard.

agreement with the net inversion of the catalytic allylation. The reaction with nickel catalysts is considered to proceed in a similar way to that with the palladium catalysts.

Recently, inversion of configuration has been reported in the nickel-catalyzed reaction of Grignard reagents with allylic alcohols [3b,c] and in the palladium-catalyzed reaction of organozirconium, -zinc, and -aluminium reagents with allylic acetates [14,15].

Stoichiometric reaction

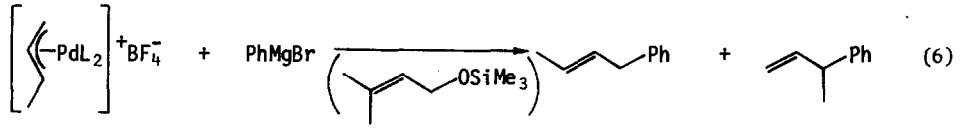
To confirm the mechanism in which the π-allylpalladium species is proposed as the key intermediate, the stoichiometric reaction of di-μ-chlorobis(1-methyl-π-allyl)dipalladium(II) (13) with phenylmagnesium bromide (1a) was examined in the absence and presence of phosphine ligands and an allyl silyl ether, 3-methyl-1-trimethylsiloxy-2-butene (14) (eq. 5). The reaction conditions and results are sum-



(13) (1a) (14) (4a) (5a) (5)

marized in Table 5. In the absence of 14, the yields of the coupling products, 4a and 5a, were generally low, though the dppf ligand was found to be more effective than dppe or PPh_3. Use of a large excess of the phenyl Grignard reagent did not improve the yields. Higher yields were obtained by running the reaction in the presence of the allyl silyl ether. Here again, dppf was the best ligand, giving 4a and 5a in 50 and 5% yields, respectively.

The stoichiometric reaction of cationic π-allylpalladium complex 15 containing phosphine ligand dppf or dppe was also examined (eq. 6) (Table 6). Similar to the reaction of 13 (eq. 5), only low yields of allylated products 4a and 5a were obtained in the absence of 14, while the reaction in the presence of 14, especially with the

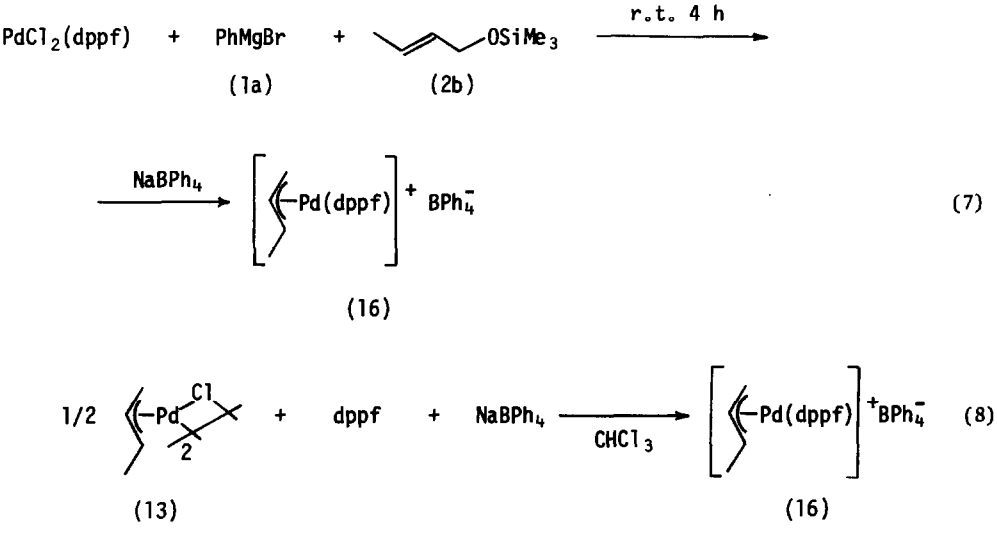


(15a) : L_2 = dppf
(15b) : L_2 = dppe

(14) (4a) (5a)

dppf complex (**15a**), gave a higher yield. It should be noted that the results obtained for the stoichiometric reactions are consistent with those for catalytic reactions. Thus, in both reactions dppf was the most effective ligand and the phenyl group attacked the less hindered π-allyl carbon regioselectively. The allylic silyl ether is considered to accelerate the reductive elimination of the allylated products from the π-allyl(phenyl)palladium intermediate.

A cationic π-allylpalladium complex with dppf ligand (**16**) was isolated from the reaction of $PdCl_2$(dppf) with phenylmagnesium bromide (**1a**) and an excess of



(16)

(13) (16)

TABLE 6

REACTION OF CATIONIC π-ALLYLPALLADIUM COMPLEXES **15** WITH PHENYLMAGNESIUM BROMIDE (**1a**) [a]

π-Allylpalladium **15**	PhMgBr (equiv./Pd)	Additive	Yield [b] (%)	
			4a(*E*/*Z*)	**5a**
15a: L_2 = dppf	4	–	13(13/0)	1
15b: L_2 = dppe	4	–	8(8/0)	0
15a: L_2 = dppf	10	**14**	73(73/0)	3
15b: L_2 = dppe	10	**14**	42(42/0)	0

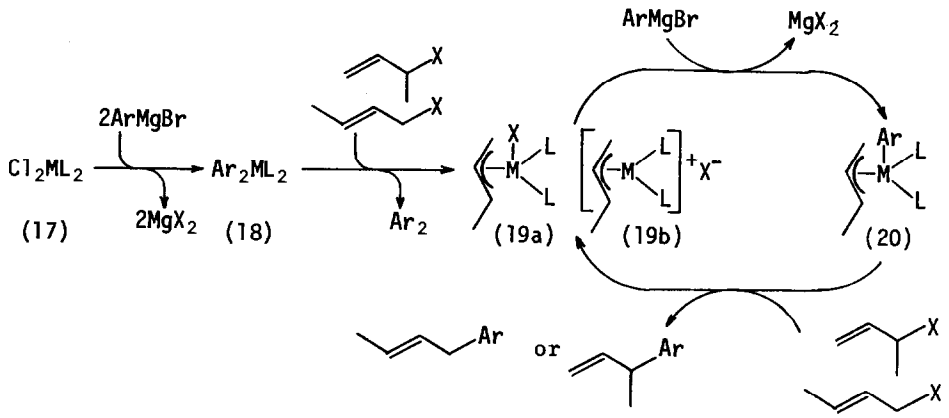
[a] To a mixture of π-allylpalladium complex **15** (2 mmol) and/or additive **14** (4 mmol) in ether was added the Grignard solution in ether. The mixture was stirred at room temperature for 0.5 h, hydrolyzed, and then analyzed by GLC. [b] Determined by GLC using an internal standard.

1-trimethylsiloxy-2-butene (**2b**) (eq. 7). This π-allylpalladium complex (**16**) was identified with the authentic sample prepared independently from π-allylpalladium **13** and dppf (eq. 8).

Mechanism

The catalytic allylation is concluded to proceed via the catalytic cycle shown in Scheme 4, which is analogous to that proposed for nickel-catalyzed cross-coupling of

SCHEME 4



Grignard reagents with aryl and alkenyl halides. Thus, the complex MCl_2L_2 (**17**) reacts with two equivalents of an aryl-Grignard reagent to form the diarylmetal species **18**, which is subsequently converted to π-allyl complex **19** by reaction with an allylic substrate. At present, it is not clear whether the π-allyl complex is neutral with a M–X bond (**19a**) or cationic, with the anion X^- outside the coordination sphere (**19b**). The Grignard reagent attacks the palladium or nickel atom in **19** to form the key intermediate, (π-allyl)ArML_2 (**20**), from which the allylation product is released by the aid of the approaching allylic substrate to regenerate **19**.

This mechanism is consistent with all the significant features observed above: (1) the catalytic allylation proceeded with inversion of configuration; (2) the ratio of the regioisomeric products in the catalytic allylation was independent of the isomeric structure and the leaving group of the starting allylic substrates; and (3) the stoichiometric reaction of the preformed relevant π-allylpalladium complex showed similar regioselectivity and ligand efficiency to those in the palladium-catalyzed allylation.

Experimental

Materials

Phosphine-nickel and -palladium complexes were prepared as described previously [5,9]. (*E*)-1-Chloro-2-butene (**2e**) and (*E*)-1-hydroxy-2-butene (**2f**) were available commercially and used without further purification. (*E*)-2-Butenyl tetrahydropyranyl ether (**2d**) was prepared by the reaction of (*E*)-1-hydroxy-2-butene (**2f**) with dihydropyran in the presence of a catalytic amount of hydrochloric acid (81% yield,

87–89°C/21 mmHg) [16]. A mixture of (*E*)-1-phenoxy-2-butene (**2c**), (*Z*)-1-phenoxy-2-butene, and 3-phenoxy-1-butene (**3c**) (79/16/5) was prepared by the known method [17]. Phenyl-, *p*-tolyl-, and *o*-tolylmagnesium bromides were prepared in a standard way. Di-μ-chlorobis(1-methyl-π-allyl)dipalladium(II) (**13**) was prepared by the reaction of 1-trimethylsilyl-2-butene with lithium chloropalladate [18], and identified by spectral comparison with established spectral data [19].

Preparation of allylic silyl ethers. General procedure

To a solution of an allylic alcohol (20 mmol) in 3.3 ml of pyridine was added a trialkylchlorosilane (20 mmol) dropwise at 0°C with stirring. After stirring for 3 h at room temperature, ice-water was added. The organic layer and pentane extracts from the aqueous layer were combined, successively washed four times with 5% $CuSO_4$ solution, twice with water, and dried over Na_2SO_4. The solvent was removed in vacuo, and the allylic silyl ether was isolated by distillation. Spectral and elemental analyses of allylic silyl ethers are given below.

*(E)-1-Triethylsiloxy-2-butene (**2a**).* 70% yield; b.p. 81–83°C/20 torr; ^{1}H NMR (CCl_4) 0.40–0.73 (m, 6 H), 0.80–1.10 (m, 9 H), 1.62–1.76 (m, 3 H), 3.96–4.10 (m, 2 H), 5.45–5.60 (m, 2 H) ppm. Found: C, 64.23; H, 12.06. $C_{10}H_{22}OSi$ calcd.: C, 64.44; H, 11.81%.

*(E)-1-Trimethylsiloxy-2-butene (**2b**).* 56% yield; b.p. 80°C/125 torr; ^{1}H NMR (CCl_4) − 0.02 (s, 9 H), 1.54–1.25 (m, 3H), 3.87–3.98 (m, 2 H), 5.35–5.55 (m, 2 H) ppm; IR (liquid film) 2963, 1254, 1050, 966 cm^{-1}. Found: C, 58.05; H, 11.31. $C_7H_{16}OSi$ calcd.: C, 58.27; H, 11.18%.

*3-Triethylsiloxy-1-butene (**3a**).* 68% yield; b.p. 66–68°C/20 torr; ^{1}H NMR (CCl_4) 0.38–0.65 (m, 6 H), 0.8–1.1 (m, 9 H), 1.19 (d, *J* 6 Hz, 3 H), 4.24 (quint, *J* 6 Hz, 1 H), 4.85–5.15 (m, 2 H), 5.76 (ddd, *J* 6, 8, and 17 Hz, 1 H) ppm. Found: C, 64,44; H, 11.92. $C_{10}H_{22}OSi$ calcd.: C, 64.44; H, 11.81%.

*(E)-1-Trimethylsiloxy-2-hexene (**6**).* 79% yield; b.p. 69–71°C/21 torr; ^{1}H NMR (CCl_4) 0.02 (s, 9 H), 0.84 (t, *J* 7 Hz, 3 H), 1.34 (sext, *J* 7 Hz, 2 H), 1.80–2.04 (m, 2 H), 3.90–3.99 (m, 2 H), 5.36 (t, *J* 2 and 14 Hz, 1 H), 5.45 (dd, *J* 7 and 14 Hz, 1 H) ppm; IR (liquid film) 2950, 1250, 1103, 1060, 970, 875, 840 cm^{-1}. Found: C, 62.90; H. 11.66. $C_9H_{20}OSi$ calcd.: C, 62.73; H, 11.70%.

3-Trimethylsiloxy-1-hexene (7). 67% yield; b.p. 51°C/20 torr; ^{1}H NMR (CCl_4) 0.07 (s, 9 H), 0.76–0.97 (m, 3 H), 1.26–1.50 (m, 4 H), 3.89–4.13 (m, 1 H), 4.85–5.20 (m, 2 H), 5.55–5.94 (m, 1 H) ppm. Found: C, 62.90; H, 11.66. $C_9H_{20}OSi$ calcd.: C, 62.73; H, 11.70%.

*3-Methyl-1-trimethylsiloxy-2-butene (**14**).* 60% yield; b.p. 45–47°C/17 torr; ^{1}H NMR (CCl_4) 0.05 (s, 9 H), 1.63 (bs, 3 H), 1.72 (bs, 3 H), 4.05 (d, *J* 7 Hz, 2 H), 5.14–5.35 (m, 1 H) ppm. Found: C, 60.67; H; 11.46. $C_8H_{18}OSi$ calcd.: C, 60.69; H, 11.46%.

*cis-3-Trimethylsiloxy-5-methylcyclohexene (**10**)*

Following the reported procedure [20], reduction of 5-methyl-2-cyclohexenone [21] with lithium aluminium hydride gave an 88% yield of *cis*-5-methyl-2-cyclohexenol, b.p. 87°C/23 torr (lit. [20] b.p. ca. 95°C/22 torr), which was contaminated with 8% *trans* isomer (GLC). The *cis* product (6.19 g, 55.2 mmol) was silylated with trimethylchlorosilane (10.6 ml, 83 mmol) in the presence of pyridine (9.0 ml) in THF (18 ml) to afford an 89% yield of *cis*-3-trimethylsiloxy-5-methylcyclohexene (**10**),

which was purified by preparative GLC (Silicone DC550 30% on Celite); b.p. 85°C/23 torr; ^{1}H NMR (CCl_4) − 0.05 (s, 9 H), 0.85 (d, *J* 6 Hz, 3 H), 1.33–1.95 (m, 5 H), 3.96–4.24 (m, 1 H), 5.32–5.60 (m, 2 H) ppm; IR (liquid film) 2950, 1250, 1074, 894, 840 cm^{-1}. Found: C, 65,37; H, 11.20. $C_{10}H_{20}OSi$ calcd.: C, 65.15; H, 10.94%.

trans-3-Trimethylsiloxy-5-methylcyclohexene (10)

Following the reported procedure [20], reduction of 5-methyl-2-cyclohexenone with aluminium isopropoxide gave a 77% yield of a mixture of *cis*- and *trans*-5-methyl-2-cyclohexenols (79/21). In a similar manner, it was silylated and purified by preparative GLC (Silicone DC550 30% on Celite). *trans*-3-Trimethylsiloxy-5-methylcyclohexene (**10**): ^{1}H NMR (CCl_4) 0.10 (s, 9 H), 0.95 (d, *J* 7 Hz, 3 H), 1.20–2.21 (m, 5 H), 4.00–4.14 (m, 1 H), 5.44–5.75 (m, 2 H) ppm.

The isomeric purity of 3-trimethylsiloxy-5-methylcyclohexene (**10**) was analyzed by GLC and is summarized in Table 4.

Coupling reaction

The reaction conditions and data obtained are listed in Table 1. Detailed procedures for the coupling of (*E*)-1-triethylsiloxy-2-butene (**2a**) with phenylmagnesium bromide (**1a**) in the presence of $NiCl_2$(dppf) are described below. All other reactions were carried out in essentially the same way.

Reaction of (E)-1-triethylsiloxy-2-butene (2a) with phenylmagnesium bromide (1a)

In a 25-ml two-necked flask equipped with a stirring bar, a serum cap and a three-way stopcock, 13.7 mg (0.04 mmol) of $NiCl_2$(dppf) [5] was placed. The reaction vessel was then filled with argon after evacuation and cooling at −78°C. To it were added 373 mg (2.0 mmol) of (*E*)-1-triethylsiloxy-2-butene (**2a**) and 3.3 ml (4.0 mmol) of phenylmagnesium bromide (**1a**) (1.2 *M*) in ether. The resulting mixture was stirred at room temperature for 4 h, and hydrolyzed with 5 ml of 10% hydrochloric acid at 0°C. An appropriate internal standard (normal alkane) was added to the organic layer. GLC analysis of the organic layer indicated the formation of 0.22 mmol (11%) of (*E*)-1-phenyl-2-butene (**4a**), 0.02 mmol (1%) of (*Z*)-1-phenyl-2-butene (**4a**), and 1.76 mmol (88%) of 3-phenyl-1-butene (**5a**). The organic layer and ether extracts from the aqueous layer were combined, washed with saturated $NaHCO_3$ solution and then water, and dried over anhydrous Na_2SO_4. After evaporation of solvent, bulb-to-bulb distillation (95–110°C bath temp./20 Torr) of the residue gave 224 mg (85%) of a mixture of coupling products, which was separated by preparative GLC (Silicone DC550 30% on Celite). Coupling products were identified by spectral comparison with established spectral data. The spectral data of the coupling products are listed below.

(E)-1-Phenyl-2-butene (4a) [22]. ^{1}H NMR (CCl_4) 1.69 (d, *J* 4 Hz, 3 H), 3.30 (d, *J* 5 Hz, 2 H), 5.30–5.79 (m, 2 H), 7.10–7.35 (m, 5 H) ppm.

3-Phenyl-1-butene (5a) [23]. ^{1}H NMR ($CDCl_3$) 1.35 (d, *J* 7 Hz, 3 H), 3.45 (quint. *J* 7 Hz, 1 H), 4.91–5.15 (m, 2 H), 6.00 (ddd, *J* 6, 9, and 17 Hz, 1 H), 1 H), 7.22 (bs, 5 H) ppm.

(E)-1-Phenyl-2-hexene (8). ^{1}H NMR (CCl_4) 0.92 (t, *J* 7 Hz, 3 H), 1.20–2.60 (m, 2 H), 2.00 (q, *J* 6 Hz, 2 H), 5.27–5.72 (m, 2 H), 7.17 (bs, 5 H) ppm; IR (liquid film) 2955, 1491, 1449, 968, 738, 696 cm^{-1}; high resolution MS *m/e* 160.1253 ($C_{12}H_{16}$ calcd.: 160.1252).

3-Phenyl-1-hexene (9) [24]. ^{1}H NMR (CCl_4) 0.91 (t, *J* 7 Hz, 3 H), 1.11–1.52 (m, 2 H), 1.22 (q, *J* 7 Hz, 2 H), 3.26 (q, *J* 7 Hz, 1 H), 4.92–5.27 (m, 2 H), 6.02 (ddd, *J* 7, 9, and 18 Hz, 1 H), 7.28 (m, 5 H) ppm; high resolution MS *m/e* 160.1250 ($C_{12}H_{16}$ calcd.: 160.1252).

3-(4-Methylphenyl)-1-butene (5b). ^{1}H NMR (CCl_4) 1.31 (d, *J* 7 Hz, 3 H), 2.32 (s, 3 H), 3.37 (quint, *J* 7 Hz, 1 H), 4.86–5.10 (m, 2 H), 5.95 (ddd, *J* 7, 10, and 18 Hz, 1 H), 7.04 (bs, 4 H) ppm; high resolution MS *m/e* 146.1093 ($C_{11}H_{14}$ calcd.: 146.1096).

(E)-1-(4-Methylphenyl)-2-butene (4b). ^{1}H NMR (CCl_4) 1.60–1.75 (m, 3 H), 2.28 (s, 3 H), 3.22 (broad d, *J* 6 Hz, 2 H), 5.35–5.60 (m, 2 H), 6.97 (bs, 4 H) ppm; IR (liquid film) 2915, 1514, 969, 805 cm^{-1}; high resolution MS *m/e* 146.1098 ($C_{11}H_{14}$ calcd.: 146.1096).

3-(2-Methylphenyl)-1-butene (5c). ^{1}H NMR (CCl_4) 1.38 (d, *J* 7 Hz, 3 H), 2.42 (s, 3 H), 3.70 (m, 1 H), 5.01–5.30 (m, 2 H), 6.21 (ddd, *J* 6, 11, and 18 Hz, 1 H), 7.25–7.97 (m, 4 H) ppm; high resolution MS *m/e* 146.1099 ($C_{11}H_{14}$ calcd.: 146.1096).

(E)-1-(2-Methylphenyl)-2-butene (4c). ^{1}H NMR (CCl_4) 1.67 (broad d, *J* 5 Hz, 3 H), 2.35 (s, 3 H), 3.25 (broad d, *J* 5 Hz, 2 H), 5.35–5.55 (m, 2 H), 6.95–7.20 (m, 4 H) ppm; high resolution MS *m/e* 146.1097 ($C_{11}H_{14}$ calcd.: 146.1096).

Cross-coupling of 3-trimethylsiloxy-5-methylcyclohexene (10)

In a similar manner, reaction of *cis*- and *trans*-3-trimethylsiloxy-5-methylcyclohexenes (**10**) (3.0 mmol), respectively, with phenylmagnesium bromide (**1a**) (6.0 mmol) was carried out in the presence of the nickel- or palladium-dppf catalyst (0.03 mmol), and the coupling product was isolated by short column chromatography (silica gel/hexane). 3-Phenyl-5-methylcyclohexene (**11**): Found: C, 90.82; H, 9.53. $C_{13}H_{16}$ calcd.: C, 90.64; H, 9.36%.

trans-3-Phenyl-5-methylcyclohexene (11). ^{1}H NMR (CCl_4) 0.95 (d, *J* 6 Hz, 3 H), 1.50–1.90 (m, 4 H), 1.95–2.34 (m, 1 H), 3.32–3.56 (m, 1 H), 5.58–5.97 (m, 2 H), 7.15 (bs, 5 H) ppm.

cis-3-Phenyl-5-methylcyclohexene (11). ^{1}H NMR (CCl_4) 0.95 (d, *J* 6 Hz, 3 H), 1.50–2.28 (m, 5 H), 3.21–3.51 (m, 1 H), 5.55–5.89 (m, 2 H), 7.15 (bs, 5 H) ppm.

Hydrogenation of cis- and trans-3-phenyl-5-methylcyclohexenes (11)

A solution of 381 mg (2.2 mmol) of 3-phenyl-5-methylcyclohexene (**11**) and 14 mg (0.03 mmol) of chlorotris(triphenylphosphine)rhodium(I) in 3 ml of benzene was placed in a stainless steel micro-autoclave, and magnetically stirred with hydrogen at 50 atm for 24 h. Short column chromatography (silica gel/hexane) of the reaction mixture afforded 366 mg (98%) of 3-phenyl-5-methylcyclohexane (**12**). *cis*- and *trans*-1-Phenyl-3-methylcyclohexanes (**12**) were identified by ^{1}H NMR spectral comparison with established spectral data [25]. The isomeric ratio of 1-phenyl-3-methylcyclohexane was determined by GLC analysis (Silicone DC QF-1 20% on Chromosorb W AW).

Preparation of [Pd(1-Me-π-C_3H_4)(dppf)]$^+BF_4^-$ (15a)

The π-allylpalladium complex **15a** was prepared according to the reported procedure [26]. A mixture of di-μ-chlorobis(1-methyl-π-allyl)dipalladium(II) (**13**) (114.2 mg, 0.290 mmol), 1,1′-bis(diphenylphosphino)ferrocene (327.9 mg, 0.592 mmol), and sodium tetrafluoroborate (194.8 mg, 1.77 mmol) in 3 ml of chloroform was stirred for 24 h at room temperature. After white precipitates had been filtered

off, the filtrate was washed with water and dried over Na_2SO_4. Evaporation of solvent afforded 456 mg (98%) of a brown powder: ^1H NMR ($CDCl_3$) 1.12 (dt, J 6(t) and 12(d) Hz, 3 H), 3.13–3.65 (bs, 2 H), 4.30–4.80 (m, 8 H), 5.48–5.95 (m, 1 H), 7.45–7.91 (m, 20 H) ppm; IR (KBr) 1435, 1050, 1035, 750, 698 cm^{-1}. Found: C, 56,72; H, 4.23. $C_{38}H_{35}BF_4P_2FePd$ calcd.: C, 56,86; H, 4.39%.

Preparation of [Pd(1-Me-π-C_3H_4)(dppe)]$^+$ BF_4^- (15b)

In a similar manner, a solution of di-μ-chlorobis(1-methyl-π-allyl)dipalladium(II) (**13**) (286 mg, 0.726 mmol), 1,2-bis(diphenylphosphino)ethane (590 mg, 1.48 mmol), and sodium tetrafluoroborate (488 mg, 4.44 mmol) in 30 ml of chloroform was stirred at room temperature for 24 h. After white precipitates had been filtered off, the filtrate was washed with water and dried over Na_2SO_4. Evaporation of solvent afforded 920.3 mg (98%) of a yellow powder: ^1H NMR ($CDCl_3$) 1.69 (dt, J 7(d) and 9(t) Hz, 3 H), 2.67 (bs, 2 H), 2.76 (bs, 2 H), 3.64–4.13 (m, 2 H), 415–4.63 (m, 1 H), 5.79 (dt, J 10(d) and 12(t) Hz, 1 H), 7.40–7.80 (m, 20 H) ppm; IR (KBr) 1433, 1086, 705, 695, 528 cm^{-1}. Found: C, 54.61; H, 4.72. $C_{30}H_{31}BF_4P_2Pd$ calcd.: C, 55.72; H, 4.83%. The palladium complex **15b** was used for reaction with the phenyl Grignard reagent without further purification.

Stoichiometric reaction of di-μ-chlorobis(1-methyl-π-allyl)dipalladium(II) (13) with phenylmagnesium bromide (1a)

The reaction conditions and data obtained are listed in Table 3. Typical experimental procedures are given below.

(a) Reaction of di-μ-chlorobis(1-methyl-π-allyl)palladium(II) (13) with phenylmagnesium bromide (1a) in the presence of dppf. To a solution of **13** (39.2 mg, 0.0995 mmol) and 1,1'-bis(diphenylphosphino)ferrocene (110.9 mg, 0.20 mmol) in 2 ml of ether was added phenylmagnesium bromide (**1a**) (0.8 mmol, 1.0 ml of 0.80 M solution) in ether at room temperature. After the mixture had been stirred at room temperature for 4 h, 10% hydrochloric acid was added at 0°C. An appropriate internal standard (n-tetradecane) was added to the organic layer. GLC analysis of the organic layer indicated the formation of 0.056 mmol (28%) of (E)-1-phenyl-2-butene (**4a**), 4.0×10^{-3} mmol (2%) of (Z)-1-phenyl-2-butene (**4a**), and 1.0×10^{-2} mmol (5%) of 3-phenyl-1-butene (**5a**).

(b) Reaction of di-μ-chlorobis(1-methyl-π-allyl)palladium(II) (13) with phenylmagnesium bromide (1a) in the presence of dppf and 3-methyl-1-trimethylsiloxy-2-butene (14). To a solution of **13** (40.9 mg, 0.104 mmol) and 1,1'-bis(diphenylphosphino)-ferrocene (110.9 mg, 2.0 mmol) in 2 ml of ether were added 3-methyl-1-trimethylsiloxy-2-butene (**14**) (114.0 mg, 0.72 mmol) and phenylmagnesium bromide (**1a**) (2.0 mmol, 2.5 ml of 0.80 M ether solution) at room temperature. After the mixture had been stirred for 1.5 h, 10% hydrochloric acid was added at 0°C. An appropriate internal standard (n-tetradecane) was added to the organic layer. GLC analysis of the organic layer indicated the formation of 0.104 mmol (50%) of (E)-1-phenyl-2-butene (**4a**) and 0.01 mmol (5%) of 3-phenyl-1-butene (**5a**).

Stoichiometric reaction of cationic (1-methyl-π-allyl)palladium(II) complex (15) with phenylmagnesium bromide (1a).

The reaction conditions and data obtained are listed in Table 4.

(a) Reaction of 15 with phenylmagnesium bromide (1a). General procedure. To a

solution of **15** (0.20 mmol) in 2.5 ml of ether was added phenylmagnesium bromide (**1a**) in ether (0.8 mmol, 0.68 ml of 1.18 *M* ether solution) at room temperature. After the mixture had been stirred at room temperature for 30 min, 10% hydrochloric acid was added at 0°C. The organic layer was analyzed by GLC using an internal standard.

*(b) Reaction of **15** with phenylmagnesium bromide (**1a**) in the presence of 3-methyl-1-trimethylsiloxy-2-butene (**14**). General procedure.* To a solution of **15** (0.20 mmol) and 3-methyl-1-trimethylsiloxy-2-butene (**14**) (0.80 mmol) in 2.5 ml of ether was added phenylmagnesium bromide (**1a**) (2.0 mmol, 1.70 ml of 1.18 *M* ether solution) at room temperature. After the mixture had been stirred at room temperature for 30 min, 10% hydrochloric acid was added at 0°C. The organic layer was analyzed by GLC using an internal standard.

*Preparation of [Pd(1-Me-π-C_3H_4)(dppf)]$^+BPh_4^-$ (**16**)*

The π-allylpalladium complex **16** was prepared according to the reported procedure [26]. A mixture of **13** (235.0 mg, 0.597 mmol), 1,1′-bis(diphenylphosphino)ferrocene (661.5 mg, 1.193 mmol), and sodium tetraphenylborate (1.25 g, 3.65 mmol) in 24 ml of chloroform was stirred for 26 h at room temperature. After white precipitates had been filtered off, the filtrate was concentrated under reduced pressure. The brown powder obtained, on short activated alumina column chromatography (chloroform as eluent), gave 1.21 g (98%) of **16**: ^{1}H NMR ($CDCl_3$) 0.55–1.05 (m, 3 H), 2.50–2.87 (m, 1 H), 3.15–3.40 (m, 1 H), 4.50–5.70 (m, 9 H), 4.80–5.20 (m, 1 H), 6.20–7.67 (m, 40 H) ppm; IR (KBr) 3060, 1480, 1435, 1100, 748, 735, 700 cm^{-1}. Found: C, 72.22; H, 5.36. $C_{62}H_{55}BP_2FePd$ calcd.: C, 71.94; H, 5.36%.

*Isolation of **16** from the reaction of $PdCl_2$(dppf) with phenyl Grignard reagent in the presence of excess (E)-1-trimethylsiloxy-2-butene (**2b**)*

To a suspension of dichloro[1,1′-bis(diphenylphosphino)ferrocene]palladium(II) (61.3 mg, 0.0838 mmol) in 2.0 ml of ether were added phenylmagnesium bromide (**1a**) in ether (0.59 mmol, 0.5 ml of 1.18 *M* solution) and 323 mg (2.24 mmol) of 1-trimethylsiloxy-2-butene (**2b**) at room temperature. The mixture was stirred at room temperature for 4 h, and sodium tetraphenylborate (65.6 mg, 0.192 mmol) was added. After the mixture had been stirred for 1 h, water was added. The organic layer and dichloromethane extracts from the aqueous layer were combined and dried over $MgSO_4$. Evaporation of solvent followed by short activated alumina column chromatography (chloroform as eluent) of the residue gave 78.1 mg (90%) of **16**. It was identified with the sample prepared from di-μ-chlorobis(1-methyl-π-allyl)dipalladium(II) (**13**) (see above).

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