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CROSS-COUPLING OF TERTIARY ALKYL GRIGNARD REAGENTS WITH β-BROMOSTYRENE CATALYZED BY DICHLORO[1,1'-BIS(DIPHENYLPHOSPHINO)FERROCENE]NICKEL(II)

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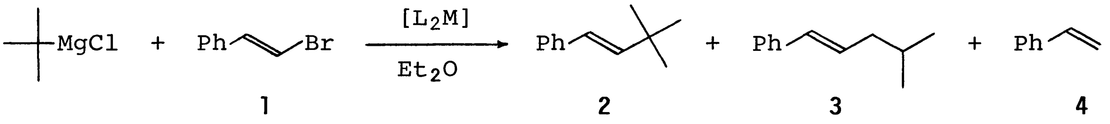
Dichloro[1,1'-bis(diphenylphosphino)ferrocene]nickel(II) was found to be an effective catalyst for the cross-coupling of *tert*-butylmagnesium chloride with β-bromostyrene to give β-*tert*-butylstyrene selectively.

Nickel or palladium complexes catalyze the reaction of organometallics (R-m) such as Grignard reagents with olefinic or aromatic halides (R'-X) to yield cross-coupling products (R-R'), the facility of the coupling reaction depending upon the structure of R in the organometallics.[1] While the reaction with aryl, alkenyl, benzyl, and methyl derivatives is generally successful, alkyl counterparts containing β-hydrogen(s) have often suffered side-reactions arising from β-hydride elimination of the alkyl-transition metal species generated in the catalytic cycle,[2] and no example of the coupling of tertiary alkyl groups has been reported in the nickel- or palladium-catalyzed reaction. We have recently shown that the β-hydride elimination could be controlled by using a catalyst with an appropriate phosphine ligand.[3] Here we report that a nickel complex of 1,1'-bis(diphenylphosphino)ferrocene (dppf) is an effective catalyst for the cross-coupling of tertiary alkyl Grignard reagents with β-bromostyrene.

The reaction of *tert*-butylmagnesium chloride with (*E*)-β-bromostyrene (1) was carried out in the presence of a variety of phosphine-nickel and -palladium complexes. Reaction conditions and the results obtained are summarized in Table 1.



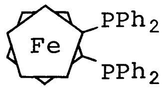
L_2 =  (dppf), $Ph_2P[CH_2]_nPPh_2$: n = 2 (dppe), n = 3 (dppp), n = 4 (dppb)

Table 1 shows that the nickel complex $NiCl_2(dppf)$[4] is the most selective catalyst giving rise to (*E*)-β-*tert*-butylstyrene (2) exclusively. Other nickel complexes, $NiCl_2(PPh_3)_2$, $NiCl_2$(dppp), and $NiCl_2$(dppb), also catalyzed the coupling reaction, but it was accompanied by *tert*-butyl group isomerization to give (*E*)-β-isobutylstyrene (3) as a by-product. The use of palladium complexes as catalysts led to the formation of reduced product, styrene (4), along with the coupling

Table 1. Cross-Coupling of *tert*-Butylmagnesium Chloride with β-Bromostyrene (**1**)[a)]

Catalyst	Reaction Conditions		Yield (%)[b)]			
	Temp (°C)	Time (hr)	**2**	**3**	**4**	recovered **1**
$NiCl_2$(dppf)	0	24	67	0	0	8
$NiCl_2$(dppf)	35	11	61	0	0	0
$NiCl_2(PPh_3)_2$	0	24	66	3	0	0
$NiCl_2(PPh_3)_2$	35	4	34	46	0	0
$NiCl_2$(dppp)	0	24	46	13	0	0
$NiCl_2$(dppb)	0	24	49	8	0	0
$PdCl_2$(dppf)	0	24	60	16	9	0
$PdCl_2(PPh_3)_2$	20	24	18	5	1	63
$PdCl_2$(dppe)	0	24	9	3	10	50
$PdCl_2$(dppp)	20	20	60	21	6	0
$PdCl_2$(dppb)	0	24	6	49	12	0

a) The Grignard reagent (3.0 mmol) in ether was added at -78°C under argon to a mixture of **1** (2.0 mmol) and a catalyst (0.02 mmol). The mixture was stirred at a given temperature, and then hydrolyzed with dilute hydrochloric acid. b) Yields were determined by GLC using an internal standard. The coupling products **2** and **3** have *E* configuration (>99%). When the palladium catalysts were used, 1,4-diphenylbutadiene was formed in about 15% yield.

products **2** and **3**. Interestingly, $PdCl_2$(dppb) afforded isomerized coupling product **3** mainly rather than **2**.

The dppf-nickel complex was also found to catalyze the reaction of 1-methylcyclohexylmagnesium chloride with **1** to give the tertiary alkylated coupling product in 40% yield. Other catalysts shown in Table 1 were all less effective, the yield being at most 25%.

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References and Notes

1) For a pertinent review concerning transition metal catalyzed coupling reactions, see K. Tamao and M. Kumada, in "Organometallic Reactions and Syntheses", E. I. Becker and M. Tsutsui, Eds., Plenum, New York, in press.

2) a) For example, see K. Tamao, Y. Kiso, K. Sumitani, and M. Kumada, J. Am. Chem. Soc., 94, 9268 (1972); b) J. K. Kochi, "Organometallic Mechanisms and Catalysis", Academic Press, New York, 1978.

3) T. Hayashi, M. Konishi, and M. Kumada, Tetrahedron Lett., 1871 (1979); *idem*, J. Organomet. Chem., 186, C1 (1980).

4) $NiCl_2$(dppf) was prepared as follows: To a suspension of 1,1'-bis(diphenylphosphino)ferrocene (dppf) (1.0 mmol) in 40 ml of hot 2-propanol was added $NiCl_2$-$6H_2O$ (1.0 mmol) dissolved in 30 ml of 2:1 2-propanol:methanol. A dark green precipitate was formed immediately, and after refluxing for 2 h, the dark green product was collected and dried *in vacuo* (80-90% yield); λ_{max} (CH_2Cl_2): 860 nm (log ε 2.5). Anal. Calcd for $C_{34}H_{28}P_2Cl_2FeNi$; C, 59.70; H, 4.13. Found: C, 59.74; H, 3.99%.

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