Rhodium catalysed cross-coupling of alkenes by C–H activation: addition of alkenic C–H bonds of 2-vinylpyridines to alkenes

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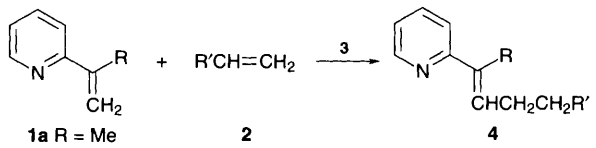
2-Vinylpyridines react with alkenes in the presence of rhodium(I) as catalyst to give alkylated products.

The formation of C–C bonds by activation of π-unsaturated C–H bonds is of particular value. Transition metal complexes have been reported to activate the C–H bonds.[1] Vinylic C–H activation of the olefins has been especially investigated.[2] Alkylation at the vinylic position of alkenes *via* C–H bond activation by Rh^I has not been reported. Recently, Trost *et al.*[3] and Muria *et al.*[4] independently reported that addition of C–H bonds in trisubstituted α,β-enones to alkenes was successfully achieved by use of $(Ph_3P)_3RuH_2(CO)$ as a catalyst. During the course of our studies of alkylation using rhodium complex catalysts,[5] we have found that 2-vinylpyridines reacted with olefins at the β-position in the presence of the rhodium(I) complex, $(Ph_3P)_3RhCl$, as a catalyst to give the highly chemoselective cross coupled β-alkylated products.

Treatment of 2-isopropenylpyridine **1a** and 2-α-styrylpyridine **1b** with 5 equiv. of alkene **2** in toluene with 10% $(Ph_3P)_3RhCl$ **3** at 100–130 °C gave excellent isolated yields of the linear alkylated products **4**, respectively (Scheme 1). Other alkylated and self-dimerized products of **1** could not be detected in the reaction mixture. When an excess amount of **2** was used compared to **1a** [**2**:**1a** = 5, **2**; R′=$Me(CH_2)_3$], the reaction time to completion was 19 h (Table 1, run 1). But when the ratio was 10, the reaction took 4 h (run 2). The results of the alkylation are listed in Table 1. The alkylated products of **1a** were a mixture of *trans*- and *cis*-isomers in a 9:1 ratio. 2-α-Styrylpyridine **1b** reacted with hex-1-ene at low temperature to exclusively give the *cis*-isomer in an 8% yield (run 8). As the reaction temperature increased, the ratio of *trans*-isomer increased as shown in run 9. 3,3-Dimethylbut-1-ene also gave the bisalkylated product in a minor amount together with the monoalkylated product (run 12).

6-Methyl-2-vinylpyridine **5** reacted with pent-1-ene (5 fold excess) at 120 °C in toluene with 10% **3** to give the alkylated product **6** and two self-dimerized products of **5** in a 35:65 ratio in a quantitative yield after chromatographic isolation (Scheme 2). The alkylated product, 6-methyl-2-(hept-1-enyl)pyridine **6** was a mixture of *cis*- and *trans*-isomers in a 90:10 ratio.† At 90–100 °C, the reaction of **5** with non-1-ene exclusively gave the *cis*-isomer (*J* 11.86 Hz), 6-methyl-2-(undec-1-enyl)pyridine in 15% yield; the *trans*-isomer could not be detected in the reaction mixture by ^1H NMR and GC–mass spectroscopy. But, at 160 °C, **5** reacted with non-1-ene to give the *trans*-isomer as the major product in 25% yield (*trans*:*cis* = 98:2).



1a R = Me
b R = Ph

2 **4**

Scheme 1

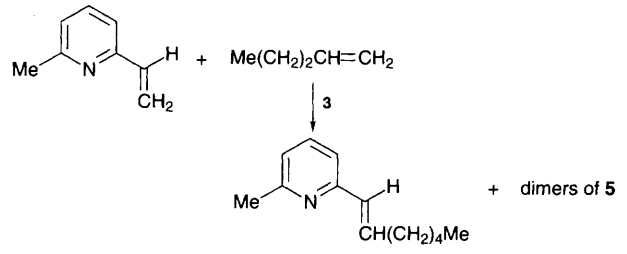
To understand the effect of the pyridine ring in cyclometallation, 1,1-diphenylethylene **7** which does not contain a nitrogen atom was treated with hex-1-ene [R = $Me(CH_2)_3$] under the same conditions (Scheme 3). No reaction occurred; the starting material was quantitatively recovered. This fact shows that the pyridine ring plays an important role in cyclometallation for C–H bond activation.

From the above results a possible mechanism for this reaction can be postulated (Scheme 4). The first step must be the formation of the rhodium(III) hydride **9** *via* the vinylic C–H bond cleavage of 2-vinylpyridine by Rh^I. The stable vinyl metal complexes resulting from the vinylic C–H bond activation of

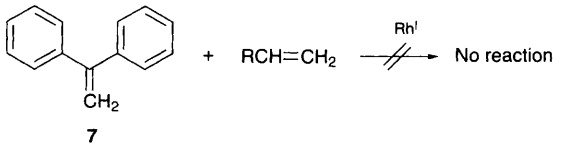
Table 1 Chemoselective catalysed addition of 2-vinylpyridines to alkenes[a]

Run	R	R′	Reaction temp/°C	Reaction time /h	Yield[b] (%)	*trans*:*cis*
1	Me	$Me(CH_2)_3$	110	19	96	93:7
2		$Me(CH_2)_3$[c]	110	4	100[d]	60:40
3		$Me(CH_2)_5$	115	20	99	90:10
4		$Me(CH_2)_6$	115	20	99	92:8
5		Me_3Si	110	19	64[e]	90:10
6		$PhOCH_2$	110	20	65	90:10
7	Ph	$Me(CH_2)_2$	90	18	77	73:27
8		$Me(CH_2)_3$	60–67	18	8	0:100
9		$Me(CH_2)_3$	130	24	99	70:30
10		$Me(CH_2)_5$	100	24	86	76:24
11		$Me(CH_2)_7$	110	18	78	75:25
12		Me_3C	100	16	92[f]	64:36
13		*p*-MePh	120–130	42	31	76:24
14		$(EtO)_3Si$	110	18	73	50:50

[a] Substrate:$(Ph_3P)_3RhCl$:alkene = 1:0.1:5. [b] Isolated yield based on substrate. [c] 10 equiv. of the alkene was used. [d] GC-yield. [e] Yield including the bisalkylated product (44%). [f] Yield including the bisalkylated product (13%).



Scheme 2



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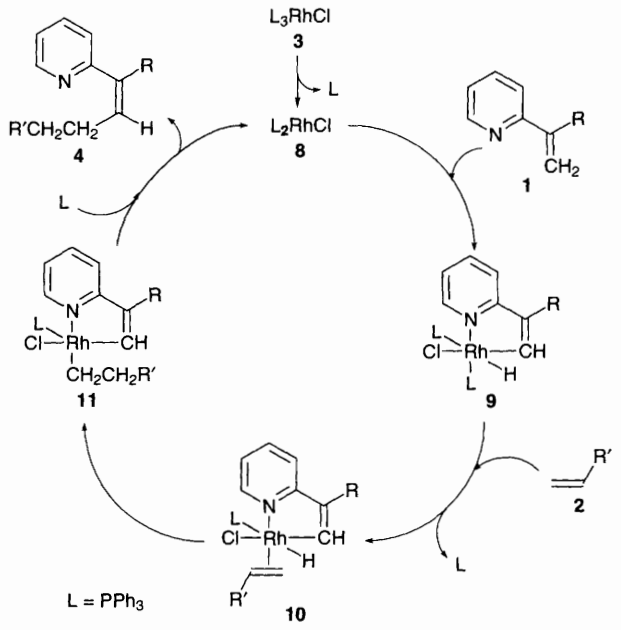
Scheme 3

2-vinylpyridine by the transition metal complex have been previously reported.[6] Hydride insertion into the coordinated alkene in the complex **10** gave the alkyl metal complex **11** as an intermediate in an anti-Markownikoff fashion. The stable primary metal alkyl complex **11**, an anti-Markownikoff intermediate, underwent reductive elimination to give the *cis*-isomer **4** by the external ligand.[7] The *cis*-isomer forms first and then isomerizes to the *trans* isomer.



Scheme 4 Proposed alkylation mechanism of the vinyl moiety in 2-vinylpyridine

This work was supported by Agency for Defense Development, Korea Advanced Institute of Science and Technology and CBM.

Footnote

† The structure was confirmed by comparison of the authentic *trans*-isomer of 6-methyl-2-(1-heptenyl)pyridine prepared from 6-methyl-2-pyridylcarboxaldehyde with hexyl(triphenyl)phosphonium bromide/sodium hydride.

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Received, 20th November 1995; Com. 5/07555F