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APPLICATION OF AMPP-Pd CATALYSTS IN AN UNUSUAL ASYMMETRIC ALLYLIC COUPLING REACTION OF 1-TRIMETHYLSILYL VINYL MAGNESIUM BROMIDE.

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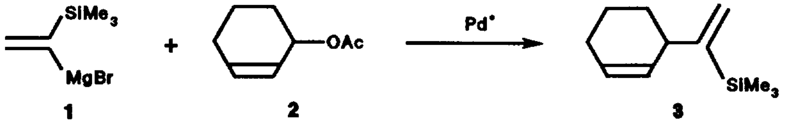
Abstract : Unusual palladium catalyzed allylation of a silylated Grignard reagent by cyclohexenyl acetate gives in high yields a versatile synthon, 3-(1-trimethylsilyl vinyl) cyclohexene; use of chiral AMPP ligands results in e.e. up to 33 %.

Catalytic allylation reactions of Grignard compounds are of great importance in organic synthetic strategies[1]. Indeed, nickel or palladium catalyze reactions of allylic substrates such as ethers, alcohols and phosphates[2]; furthermore, asymmetric induction can be achieved by using chiral ligands[3]. We report here an unusual reaction between 1-trimethylsilyl vinyl magnesium bromide 1 and 3-cyclohexenyl acetate 2 catalyzed by palladium complexes, giving 3-(1-trimethylsilyl vinyl) cyclohexene 3 in high yields (Equation 1).



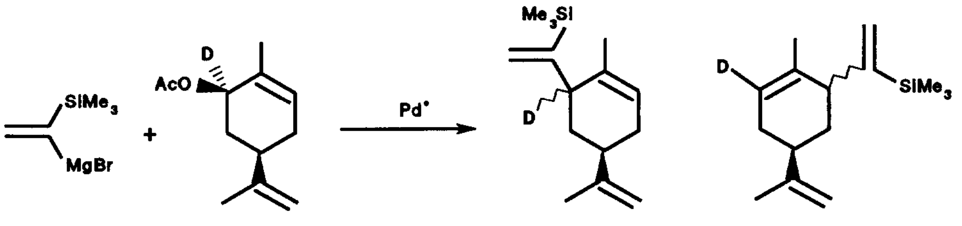
Equation 1

To our knowledge, this is the first example of a palladium catalyzed coupling of an organomagnesium compound with an allylic acetate. Generally, Grignard reagents undergo nucleophilic attack at the carbonyl carbon of the ester group[4]. Indeed, the reaction under our conditions, with alkyl- and vinylmagnesium bromide proceeds smoothly to afford solely the reduction products. Moreover, the catalyzed reaction between 1 and geranyl or myrtenyl acetate gave, besides reduction products, unexpectedly 5-trimethylsilyl-5-hexene-2-one[5]. This compound may formally result from an attack of 1 on the acetyl group of the allylic substrates to afford the corresponding methyl 1-(trimethylsilyl)vinyl ketone. Subsequent Michaël addition of a second equivalent of 1 and Brook-type rearrangement followed by hydrolysis may lead to the byproduct isolated[6]. In the case of allyl acetate, the coupling product 2-trimethylsilyl-1,4-pentadiene could be isolated in 50% yield.

Palladium catalyzed cross-coupling of 3-cyclohexenyl magnesium bromide with 1-bromo-1-trimethylsilyl ethene and allylic coupling of 1 with 3-cyclohexenyl bromide failed to yield 3.

3 may prove a versatile synthon, for example as an intermediate in the preparation of methylene lactones[7]. This pathway represents an alternative to the codimerisation of vinyltrimethylsilane with 1,3-cyclohexadiene, previously studied[8].

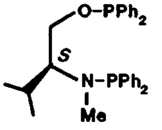
Since the reaction is mostly catalytic (Table II, entries 1 and 2), we could show in a deuterium labelling study with *d*-carveyl acetate **4** that it proceeds *via* a π-allyl complex (Equation 2). This was further confirmed by the resulting 1 : 1 mixture of products **5a** and **5b**, as determined by ^{2}D NMR spectroscopy[9].



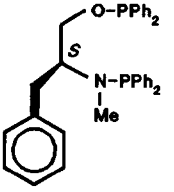
Equation 2

The reactivity of **1** may be compared to that of a soft stabilized carbanion[10] or to phenylzinc chloride[11]. The stereochemistry of the attack (*syn* or *anti* to the palladium[4]) on the π-allyl complex remains to be determined with the above allylic compounds.

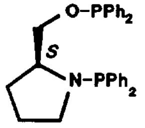
Enantioselectivity is obtained when chiral AMPP ligands[12] are used. $PdCl_2$(AMPP) complexes (Table I), reduced in situ by 2 equivalents of **1**, were employed as precursors of the Pd^0 catalytic species.



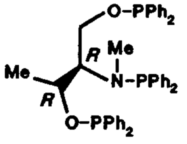
ValNOP



PhenylalaNOP



ProliNOP



ThreoNOOP

Table I: ^{31}P NMR Chemical Shifts of $PdCl_2$(AMPP) Complexes[a]

Ligand	Free ligand		Complex $PdCl_2$(AMPP)[b]		
	P-O	P-N	P-O	P-N	$^2J_{P-Pd-P}$
ValNOP	114.3	61.9	104.0	87.7	34.3
PhenylalaNOP	113.5	60.1	104.4	87.5	35.3
ProliNOP	112.8	45.1	107.9	72.0	27.2
ThreoNOOP[c]	114.0 111.6	64.7	106.0 111.7	89.8	34.7 -

a) Spectra were recorded on a Bruker AC100 spectrometer, solvent $CDCl_3$. Chemical shifts are reported in ppm (ref. H_3PO_4 85%), coupling constants in Hz.

b) Pd^{II} complexes were prepared by exchange reaction between $(CH_3CN)_2PdCl_2$ and AMPP ligands, molar ratio 1:1, in THF.

c) This potentially tridentate ligand behaves as a bidentate aminophosphine phosphinite ligand.

Typical allylation procedure : a suspension of $PdCl_2$(AMPP) (1.5 mmol; THF 15 ml) was treated first with 2 equivalents (3 ml) of a previously prepared solution of **1** (60 mmol; THF 60 ml). Then **2** (30 mmol) and the remaining solution of **1** were introduced successively. After stirring for 45 minutes at room temperature, the mixture was hydrolyzed with 10 ml of 10% HCl. **3** was isolated by extraction and chromatography (pentane), then distillation (b.p. 35°C / 0.5 mmHg)[13]. Measurement of e.e. by ^1H NMR spectroscopy allowed to evaluate the specific rotation of (-)-**3** to $[\alpha]_D^{20} = -80°$ (c=1, toluene), using Ag(fod)-Eu(hfbc)$_3$ for the resolution[14].

Table II: Allylic Coupling Reaction of 1-Trimethylsilyl Vinyl Magnesium Bromide with 3-Cyclohexenyl Acetate

Entry	Catalyst	Temp.(°C)	Yield(%)[a]	e.e.(%)
1[b]	-	r.t.	15	-
2	$Pd(PPh_3)_4$	r.t.	93	-
3	$PdCl_2(PPh_3)_2$	r.t.	79	-
4	$Ni(COD)_2/2PPh_3$	r.t.	20	-
5	$PdCl_2$(ValNOP)	r.t.	81	20
6[c]		10	82	23
7[c]		-10[d]	69	26
8	$PdCl_2$(PhAlaNOP)	r.t.	80	15
9[c]		10	83	18
10	$PdCl_2$(ProliNOP)	r.t.	80	26
11[c]		10	85	30
12[c]		-10[d]	53	33
13	$PdCl_2$(ThreoNOOP)	r.t.	70	7[e]

a) Total conversion of **2** except for entries 1 : 85%, and 7 : 80%.
b) Non catalytic reaction.
c) Reaction time 2h at 10°C, 4h at -10°C.
d) Below -10°C, the catalyst precipitated.
e) All AMPP ligands gave levorotatory products, except for Threophos.

This is the first example of a Pd^0 catalyzed reaction with asymmetric induction between a Grignard reagent and an allylic acetate. Although the catalytic pathway *via* a π-allyl complex was unambiguously proved, work is in progress to explain the atypic behaviour of this nucleophile on allylic substrates.

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(5) I.R. (cm^{-1}) 3020 (=CH$_2$), 1720 (C=O), 1250 (SiMe), 840 (Si-C); ^{1}H NMR (ppm) 0.25 (s, 9H), 2.31 (s,3H), 2.72 (m, 4H), 5.58 (d, 2H); ^{13}C NMR (ppm) -0.8, 31.5, 32.3, 45.1, 126.2, 153.1, 210.7

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(9) ^{2}D NMR (ppm) 3.28 (s, 1D), 6.00 (s, 1D).

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(13) I.R. (cm^{-1}) 3020 (=CH$_2$), 1250 (SiMe), 840 (Si-C); ^{1}H NMR (ppm) 0.35 (s, 9H), 1.62 (m, 6H), 2.92 (m, 1H), 5.78 (m, 4H); ^{13}C NMR (ppm) -0.9, 20.8, 25.1, 29.9, 41.0, 124.8, 127.4, 130.8, 156.0; ^{29}Si NMR (ppm) -4.06.

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