[5] A salt-free solution of **8** [obtained from $(C_6H_5)_3PCH_3Br$ (3 g, 8.40 mmol) and an excess of NaH (80% suspension in white oil)] was treated with 1.5 g (2.06 mmol) of **2** and the mixtured boiled under reflux for 14 h. After subsequent treatment with silica gel (10 g) the solvent was removed by evaporation. The solid residue was extracted with 100 mL of ether and the extract, after filtration, was concentrated by evaporation and chromatographed on silica gel (0.05–0.2, 40 × 2.5 cm, hexane). A small amount of **2** was first eluted with toluene, and then the red colored **7** was eluted with toluene/ether (1:1). Yield 40% referred to **2**, m.p. 163°C, red crystals. Spectroscopic data of **7**: IR (ν(CO) [cm^{-1}], KBr): 1946 (s), 1902 (s), 1857 (sh), 1836 (vs), 1817 (s); FD-MS (toluene) *m/z* 1001 (M^+); ^{1}H-NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ = 7.91–7.49 (m, 15H, Ph_3). 5.21 (s, 5H, C_5H_5), 4.91 (s, 5H, C_5H_5), 4.60 (s, 5H, C_5H_5), 2.31 (d, 1H, ^2J = 3.52 Hz); correct total analysis; m.p. 163°C.

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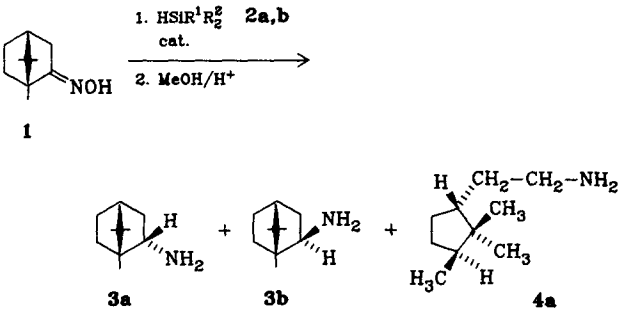
Cleavage of a C–C Bond in the Catalytic Hydrosilylation of Camphor Oxime**

By *Henri Brunner** and *Richard Becker*

Rhodium-catalyzed hydrosilylation of ketoximes and subsequent hydrolysis leads to formation of primary amines, e.g. in the case of acetophenone oxime to the enantiomers of 1-phenylethylamine.[1a] Thirteen other alkylaryl- and alkylbenzyl ketoximes gave exclusively the corresponding amines[1b] in the amine fraction. All the more surprising was the finding that, in the hydrosilylation of (−)-(1*R*,4*R*)-camphor oxime **1**, not only the expected bornylamines **3a** and **3b** were formed, but also, and as main product, optically pure (+)-(1*R*,3*S*)-1-(2-aminoethyl)-2,2,3-trimethylcyclopentane **4a**.



2a, R^1 = H, R^2 = Ph; **2b**, R^1 = Me, R^2 = Cl

The reaction of 1 mole equivalent of **1** with 3.3 mole equivalents of diphenylsilane **2a** in toluene is catalyzed by 1 mol-% [$RhCl(PPh_3)_3$] (Table 1).[2] Gas chromatographic analysis[3] of the distilled product revealed a mixture of three amines, which were identified by GC/MS. Besides the expected mass peaks of the trifluoroacetamide derivatives of *endo*- and *exo*-bornylamine, **3a** and **3b**, respectively, the main product, two mass units higher, indicated cleavage of a C–C bond in the camphor skeleton. That this cleavage was a hydrogenolytic cleavage between the bridgehead carbon atom and the oxime carbon atom, with formation of **4a**, followed from the ^{1}H-NMR spectrum (two methyl singlets, one methyl doublet[4]) and the ^{13}C-NMR spectrum.[5]

In the reaction of **1** to give **4a**, the (*R*)-configuration at C4 of the educt (C3 of the product) is preserved. That the configuration at C1 of **4a** is also retained was established as follows: α-campholenonitrile **5**[6] was hydrogenated with H_2/Raney nickel. The two diastereomers **4a** (1*R*,3*S*) and **4b** (1*R*,3*R*) were formed in the ratio 36:64; the base lines of their trifluoroacetamide derivatives are separated on gas chromatographic analysis.[3] Co-injections with the trifluoroacetamide derivative of **4a** obtained on hydrosilylation show that only one of the two diastereomers is formed. The retention behavior on a Chirasil-L-Val® column (shorter retention time for *R*-compounsds[7]) lends support for assignment of the (*S*)-configuration at C3 in **4a**, which is also consistent with the concept that cleavage of the C–C bond and addition of hydrogen to the two C atoms takes place at one metal center.

Table 1. Hydrosilylation of 2.7 g of (D)-camphor oxime **1** with the silanes **2a**, **b** in 5 mL of toluene.

No.	Catalyst		Rh:**1** or Pt:**1**	**1**:**2a/b**	*t* [h]	*T* [°C]	Total yield [%] (**3a**+**3b**+**4a**)	Relative yield [%] **3b**	**3a**	**4a**
1	$[RhCl(PPh_3)_3]$	**2a**	1:200	1:3.3	408	−10→20	29	14	2	84
2	$[RhCl(PPh_3)_3]$	**2a**	1:100	1:3.3	90	−10→20	38	15	4	81
3	$[RhCl(PPh_3)_3]$	**2a**	1:100	1:3.3	24	−10→50	24	25	3	72
4	$[RhCl(PPh_3)_3]$	**2a**	1:100	1:3.3	46	+ 5	29	27	2	71
5	$[RhCl(PPh_3)_3]$	**2a**	1:100	1:3.3	192	0	12	27	2	71
6	$[RhCl(PPh_3)_3]$ [a]	**2a**	1:100	1:3.3	24	−10→20	18	33	2	65
7	$[RhCl(PPh_3)_3]$ [b]	**2a**	1:100	1:3.3	23	−10→20	18	28	2	70
8	$K[PtCl_3C_2H_4]$	**2b**	1:100	1:6	48	0→b.p.	20	18	16	66
9	$K[PtCl_3C_2H_4]$	**2b**	1:200	1:6	70	0→b.p.	24	9	9	82
10	$PtO_2 \cdot H_2O$	**2b**	1:100	1:6	70	0→b.p.	16	13	5	82

[a] Addition of 0.5 mL (4 mmol) of $BF_3 \cdot OEt_2$ to **1** and catalyst, stirred for 5 min at 20°C, then addition of silane at −10°C. [b] Addition of 0.5 mL (4 mmol) of $BF_3 \cdot OEt_2$ to the mixture **1**/**2a** at −10°C, then addition of catalyst.

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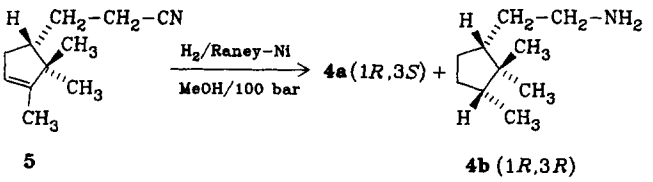

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Hydrosilylation of **1** with diphenylsilane, **2a**, furnishes **4a** in 80–85% relative yield (total yield 30–40%; Table 1, entries 1 and 2). Increasing or lowering the reaction temperature reduces the selectivity with respect to **4a** in the same way as addition of $BF_3 \cdot OEt_2$, which should catalyze the Beckmann rearrangement (Entries 3–7). **4a** is also obtained with dichloromethylsilane, **2b**, on homogeneous catalysis with Zeise salt and on heterogeneous catalysis with $PtO_2 \cdot H_2O$ (Entries 8–10).

Hence, the enantiomerically pure primary amine (+)-**4a** which, hitherto, has only been described in the form of a **4a/4b** diastereomeric mixture[8] can be synthesized in one step by catalytic hydrosilylation of (D)-camphor oxime.

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[2] Work-up with methanol/20% aqueous hydrochloric acid, addition of KOH in excess, extraction with ether, and purification by distillation (55°C/0.1 torr).

[3] A solution of the amine (100 mg) in 2 mL of tetrahydrofuran (THF) was treated with 0.2 mL of trifluoroacetic anhydride. After 10 min, the mixture was neutralized with 3 mL of a saturated $NaHCO_3$ solution. The amines were extracted with ether (1.5 mL). The ether phase was dried with Na_2CO_3. GC: silicon phase Chirasil-L-Val®; glass capillary 25m, 110°C; injector 230°C. Error ± 1%.

[4] **4a**·HCl (enriched by recrystallization from ethyl acetate to 97%): ^{1}H-NMR (250 MHz, $CDCl_3$, TMS): $\delta = 0.53$ (s, 3H), 0.83 (d, 3H), 0.89 (s, 3H), 1.09–1.23 (m, 2H), 1.47–1.56 (m, 3H), 1.71–1.95 (m, 3H), 2.86–3.09 (m, 2H).

[5] **4a**·HCl: ^{13}C-NMR (22.64 MHz, 20% solution in $CDCl_3$, TMS, broadband decoupled): $\delta = 13.7$ (q), 14.4 (q), 25.6 (q), 27.8 (t), 28.7 (t), 30.1 (t), 39.7 (t), 42.5 (s), 45.0 (d), 48.0 (d).

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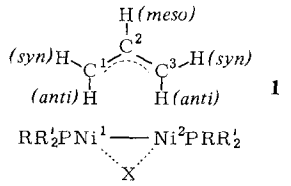
Dinuclear Nickel Complexes with Bridging Allyl Ligands**

By *Rudolf Hanko**

Dedicated to Professor Günther Wilke on the occasion of his 60th birthday

The great synthetic and catalytic potential of mononuclear η^3-allylnickel-X compounds **2** (X = halogen, allyl, H)[1] and the increasing importance of multinuclear transition metal complexes in homogeneous catalysis attracted interest in multinuclear Ni-complexes with bridging allyl ligands (type **1**). To my knowledge no such complexes have, as yet, been documented, although unsuccessful attempts at their synthesis have been reported.[2]



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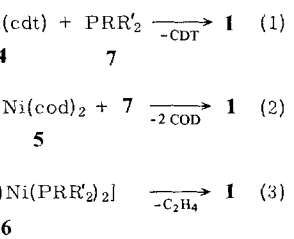
In the following communication a simple and versatile entry to this special class of compounds is described: Reaction of a 1:1 mixture of a triorganophosphane **7** and a nickel(0)-complex **4** or **5** with an η^3-allylnickel halide complex **2** [Reactions (1) and (2), respectively (Scheme 1)] or of the bis(phosphane)ethylenenickel complex **6** with the complex **3** [Reaction (3)] leads, via displacement of the olefin ligands to formation of a crystallizable dinuclear nickel compound of the type **1** in high yields. The liberated olefin can be removed under vacuum or by recrystallization. Reaction (1) affords the best yields (ca. 80%)[3] (Table 1). With exception of the PMe_3-adduct **1a**, these wine-red, dinuclear complexes **1** are stable under argon at room temperature.[4]



Scheme 1. CDT = all-*trans*-1,5,9-cyclododecatriene; COD = *cis,cis*-1,5-cyclooctadiene.

Table 1.

Product	X	PRR'_2	Educts	Reaction	Yield [%]
1a	Br	PMe_3	**2a**, **4**, **7a**	(1)	82 [a]
1b	Cl	$P(iPr)_3$	**2b**, **4**, **7b**	(1)	63
1b	Cl	$P(iPr)_3$	**2b**, **5**, **7b**	(2)	54
1c	Cl	$P(c\text{-}C_6H_{11})_3$	**2c**, **4**, **7c**	(1)	80
1c	Cl	$P(c\text{-}C_6H_{11})_3$	**3c**, **6c**	(3)	41 [a]
1d	Br	$P(c\text{-}C_6H_{11})_3$	**2d**, **4**, **7d**	(1)	82
1e	Br	$P(t\text{Bu})(i\text{Pr})_2$	**2e**, **4**, **7e**	(1)	81
1f	C_3H_5	$P(i\text{Pr})_3$	**2f**, **4**, **7f**	(1)	84

[a] Determined by NMR spectroscopy.

The nuclear resonance spectra[5] are reconcilable with dinuclear structures. In each case, only one signal is to be seen in the ^{31}P-NMR spectrum. In the ^{13}C-NMR spectra[6,7] the signals of the carbon atoms bound to phosphorus can be interpreted as X-parts of ABX spin systems (A,B = ^{31}P; X = ^{13}C), from which a phosphorus-phosphorus coupling constant of ca. 25 Hz can be calculated for **1b** and **1d**. According to the ^{13}C- and ^{1}H-NMR spectra the allyl groups are symmetrically bound. Particularly striking is the upfield shift of the signal ($\delta = 32$–38) of the *meso*-carbon atom of the halogen-bridged compounds compared to that of the mononuclear analogues (e.g. $\delta = 31.8$ for **1e** compared to $\delta = 107.2$[8] for **2e**). In the case of the bis(allyl) compound **1f**, the upfield shifts of the allyl carbon atoms are less pronounced compared to those of the mononuclear starting complex ($\delta = 87.1$ (*meso*), 27.6 (terminal) for **1f** compared to $\delta = 112.2$ (*meso*), 52.6 (terminal) for **2f**[9]).

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