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Regioselective C–C bond formation between ethylene and α-naphthylcarbaldimines catalyzed by $Ru_3(Co)_{12}$: NMR spectroscopic investigations on the proceeding of the reaction

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Abstract

The reaction of ethylene with imines derived from α-naphthylcarbaldehyde catalyzed by $Ru_3(CO)_{12}$ leads to the selective and quantitative formation of products in which one molecule of ethylene has been inserted into the C–H bond in ortho position with respect to the exocyclic imine substituent. The stoichiometric reaction of the same ligands with $Ru_3(CO)_{12}$ leads to dinuclear ruthenium carbonyl complexes showing the same regioselectivity of C–H activation but the hydrogen atom is shifted in an intramolecular hydrogen transfer reaction towards the former imine carbon atom. If the catalytic alkylation of α-naphthylcarbaldimines is monitored by NMR the occurrence of the dinuclear product of the stoichiometric reaction is observed before the reaction again quantitatively yields the imines bearing an ethyl group in 2-position of the naphthalene core. This proofs that there must be an equilibrium between the dinuclear ruthenium carbonyl complex which is also observed if α-naphthylcarbaldimines are treated with an equimolar amount of $Ru_3(CO)_{12}$ and another ruthenium compound where the ethylene might be inserted catalytically into a ruthenium carbon bond.

Keywords: Ruthenium; C–H activation; C–C bond formation; Alkylation; Olefin insertion

1. Introduction

During the last years the formation of C–C bonds by direct catalytic functionalization of C–H bonds has attracted growing interest [1,2]. Our approach to this field of chemistry came from the observation that aromatic imines may be reacted with $Fe_2(CO)_9$ to produce dinuclear iron carbonyl complexes in which a C–H activation reaction by means of an ortho metalation had occurred. The corresponding hydrogen atom is transferred to suitable acceptor sites in the ligand by intramolecular hydrogen transfer reactions [3–7]. It is possible to use this type of C–H activation in catalytic C–C bond formations with CO and/or olefins if $Ru_3(CO)_{12}$ is used as the catalyst precursor. Related reactions had already been published by Murai et al. starting from aromatic ketones [8–14]. If aromatic imines are used instead, Murai and co-workers describe the alkylation in ortho position which works very well for reactive olefins like $H_2C{=}C(H)Si(OEt)_3$ [15]. On the other hand, if the reaction is performed in the presence of both CO and an olefin an acyl group is built up in the ortho position [16]. In a similar way the reaction of imines derived from cinnamaldehyde leads to the formation of dihydro-pyrrole-2-one derivatives since the CO insertion reaction is followed by an intramolecular cyclization [17,18]. This reaction pathway is also very closely related to the

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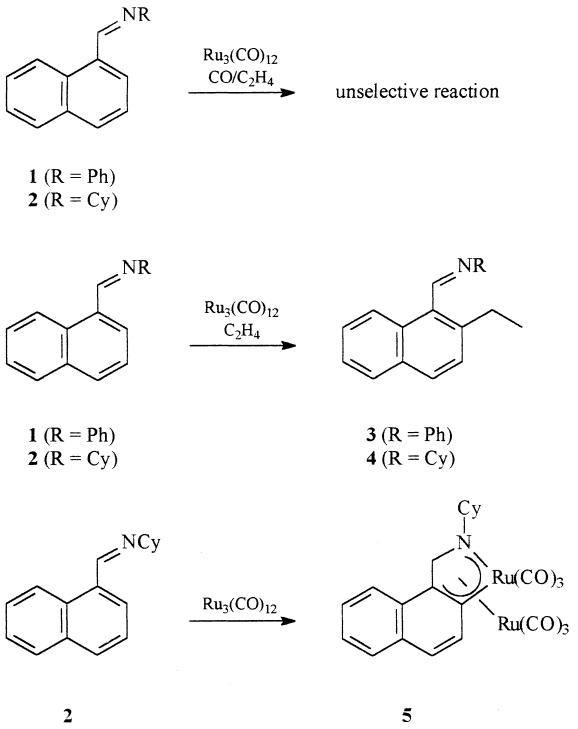
treatment of β-naphthylcarbaldehydes in the presence of catalytic amounts of $Ru_3(CO)_{12}$ with ethylene and CO producing dihydro-benzoisoindole-1-ones [19].

Since the key-step in those catalytic reactions seems to be the C–H activation by an ortho metalation step we considered imines derived from α-naphthylcarbaldehydes to be the even better substrates compared to their β-isomers, because there exists only one C–H function in ortho position with respect to the exocyclic imine substituent. We also wanted to look for the products of stoichiometric reactions of these imines with $Ru_3(CO)_{12}$ to get some insight into the substrate catalyst interactions during the catalytic reactions.

2. Results and discussion

Scheme 1 shows the reactions we performed. The α-naphthylcarbaldimines **1** and **2** were reacted with 12 bar CO and 8 bar ethylene in the presence of a catalytic amount of $Ru_3(CO)_{12}$ (4 mol%). If the starting compound is **2** we observed from ^{1}H-NMR measurements of the crude reaction product as well as from GC–MS and GC–IR analyses that this reaction is completely unselective and that we obtained about 15–20 different product species most of which we were not able to identify. Nevertheless, the major component of the product mixture seemed to be one compound in which just one molecule of ethylene had been incorporated into the substrate.



Scheme 1.

The analogous reaction starting from **1** produces **3** with 80% yield again besides several side-products which we were not able to identify.

So we carried out the reaction under the same conditions but only in the presence of 8 bar ethylene. The result was the selective and quantitative formation of **3** and **4**. From the substitution position of the ethyl group we can conclude that obviously during the catalytic reaction there is also taking place a transition metal induced C–H activation in ortho position with respect to the imine substituent in **1** and **2**. In contrast to the corresponding β-naphthylcarbaldimines the carbon ruthenium bond that is built up by the ortho metalation reaction may not be selectively attacked by CO. On the other side, in the reactions starting from the β-naphthylcarbaldimines we were not able to obtain any product in which just the ethylene was inserted into the corresponding aromatic C–H bond [19]. It is also remarkable that in the only reference which describes the alkylation of an aromatic imine by the reaction with olefins catalyzed by $Ru_3(CO)_{12}$ the reaction proceeded as well fast as selective with very reactive olefins like $H_2C{=}C(H)Si(OEt)_3$ whereas ethylene showed a considerably lower reactivity [15]. So using α-naphthylcarbaldimines provides us not only with a very regioselective alkylation reaction even for non-activated olefins but also with a very effective synthesis, since as we will see later this reaction also works with just 1 bar of ethylene.

For us it was also of great importance to examine the reactions of **1** and **2** with stoichiometric amounts of $Ru_3(CO)_{12}$. First of all we wanted to check the regioselectivity of the ruthenium induced C–H activation reaction. We were interested in the question whether the products are comparable with those from the reactions of the same ligands with $Fe_2(CO)_9$ [6], since we would very much like to develop iron complexes acting as the catalyst precursors in C–C coupling reactions. In addition, the reaction of aro-

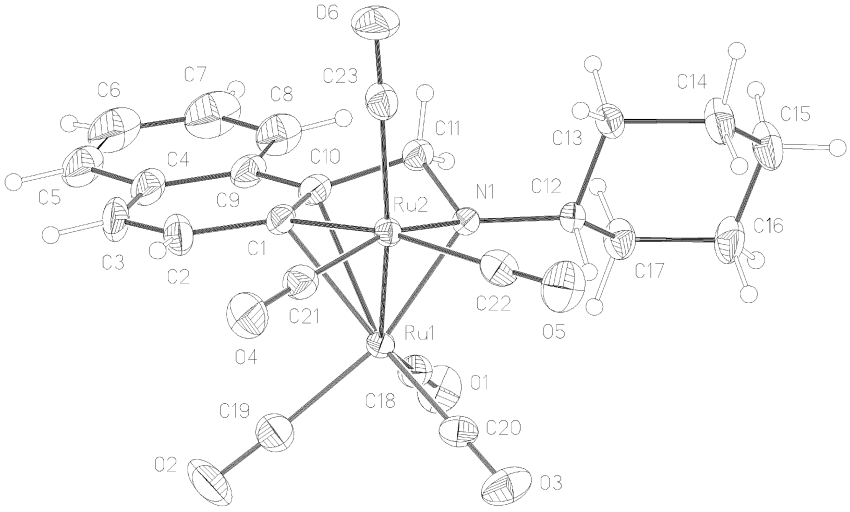


Fig. 1. Molecular structure of **5**.

matic imines with $Ru_3(CO)_{12}$ was reported to produce mononuclear complexes of the general formula $Ru(CO)_2(imine)_2$ or trinuclear complexes with three side-on coordinated imine ligands [20,21]. In contrast, imines derived from cinnamaldehyde react with $Ru_3(CO)_{12}$ in a first step to give a dinuclear ruthenium carbonyl complex which is also produced by a C–H activation hydrogen transfer reaction sequence which then in subsequent reaction steps produces trinuclear and tetranuclear ruthenium cluster compounds [22].

Scheme 1 also shows the reaction of **2** with an equimolar amount of $Ru_3(CO)_{12}$ producing **5**. We were able to obtain single crystals of **5** suitable for X-ray structural analysis. The molecular structure of **5** is depicted in Fig. 1, the most important bond lengths and angles are summarized in Table 1.

It is obvious that the reaction of **2** with $Ru_3(CO)_{12}$ follows the same pathway as it was described for the treatment of the same ligands with $Fe_2(CO)_9$ [6] and as the reaction of $Ru_3(CO)_{12}$ with imine ligands of the cinnamaldehyde type [22]. The reaction proceeds via a C–H activation 1,3 hydrogen transfer reaction sequence. The ligand is metalated in ortho position with respect to the imine substituent and the corresponding hydrogen atom has been transferred towards the former imine carbon atom thus producing a methylene group instead. The ligand may now formally be described as a six electron donating enyl-amido ligand which coordinates a $Ru_2(CO)_6$ moiety. The bond lengths and angles are very similar to the ones that have been observed for the iron analogues [6]. Especially the coordination of the aromatic carbon–carbon bond C1–C10 towards the apical ruthenium atom is very unsymmetrical, although, it may formally be described as the side-on coordination of an aromatic C–C bond to the apical ruthenium atom.

So in the stoichiometrical reaction of **2** with $Ru_3(CO)_{12}$ we observe a dinuclear complex that shows the C–H activation reaction to occur with the same regioselectivity as it is the case for the catalytic

Table 1
Selected bond lengths (pm) and angles (°) of **5**

Ru1–Ru2	265.81 (**3**)	Ru1–N1	211.3 (**2**)	Ru1–C1	232.6 (**2**)
Ru1–C10	241.4 (**3**)	Ru2–N1	212.1 (**2**)	Ru2–C1	208.9 (**3**)
C1–C10	142.4 (**4**)	C10–C11	151.4 (**3**)	C11–N1	148.0 (**3**)
Ru2–C1–C10	114.6 (**2**)	C1–C10–C11	114.7 (**2**)	C10–C11–N1	102.7 (**2**)
C11–N1–Ru2	110.8 (**1**)	N1–Ru2–C1	76.23 (**9**)		

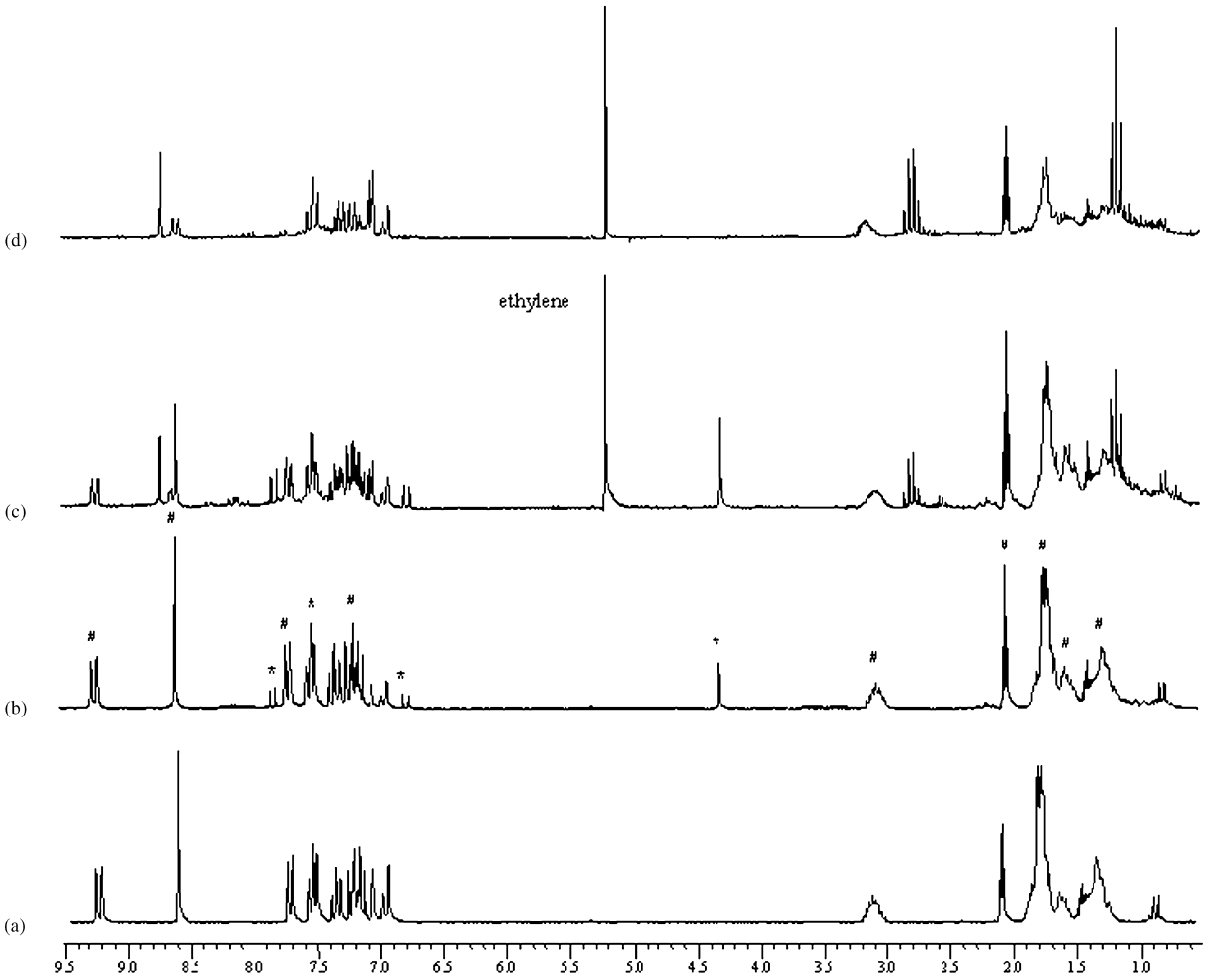


Fig. 2. NMR spectroscopic investigation of the reaction of **2** with $Ru_3(CO)_{12}$: (a) spectrum of **2** before heating; (b) spectrum of the mixture of **2** and 30 mol% $Ru_3(CO)_{12}$ after 1 h of heating to 110°C, the signals of **2** (#) and **5** (*) are observed; (c) spectrum of the same mixture after being under an atmosphere of ethylene for 1 h, the signals representing **2**, **4** and **5** are observed and (d) spectrum of the same mixture after a reaction time of 15 h, only the signals of **4** are observed.

reaction leading to **3**. But since we are able to isolate **5** it is obviously not part of the catalytic cycle producing **3**.

In order to get a deeper insight into the proceeding of the catalytic alkylation reaction producing **3** or **4**, respectively, we decided to investigate the reaction via NMR-spectroscopy. The results are depicted in Fig. 2. The spectrum at the bottom (a) has been recorded immediately after **2** and $Ru_3(CO)_{12}$ had been mixed together and shows the hydrogen NMR spectrum of pure **2**. The next spectrum (b) indicates the situation after heating of the reaction mixture to 110°C under an argon atmosphere for 1 h. It is easy to see that besides a certain amount of **2** which up to then has not reacted the only compound that may be identified by NMR is **5** with the typical singlet representing the methylene group which has been formed during the reaction at $\delta = 4.61$.

At this point the atmosphere inside the NMR tube was changed from argon to ethylene. The third spectrum (c) from the bottom shows the situation after another hour of heating to 110°C. Apart from ethylene

being dissolved in toluene, the starting compound **2** and the obviously thermodynamically most stable stoichiometric reaction product **5** may be identified. In addition, it can be seen that the typical triplet/quartet structure of the ethyl group in **4** arises. After 15 h the upper NMR spectrum (d) demonstrates that the reaction quantitatively yielded **4** as the only product, although, the pressure of ethylene in this experiment was just slightly above 1 bar.

So even if **5** is not part of the catalytic reaction circle there must be an equilibrium of **5** with another ruthenium carbonyl compound which then may react with ethylene to form the product **4**.

3. Experimental

3.1. General

All procedures were carried out under an argon atmosphere in anhydrous, freshly distilled solvents. Compounds **1** and **2** are prepared by condensation of α-naphthylcarbaldehyde with the corresponding amine in ethanol and after filtration both **1** and **2** are recrystallized from ethanol. Infrared spectra were recorded on a Perkin Elmer FT-IR System 2000 using 0.2 mm KBr cuvettes. NMR spectra were recorded on a Bruker AC 200 spectrometer (^{1}H, 200 MHz;^{13}C, 50.32 MHz; $CDCl_3$ as internal standard). Mass spectra were recorded on a Finnigan MAT SSQ 710 instrument. High resolution mass spectra were recorded on a Finnigan MAT 95 XL using ESI techniques and methanol as the solvent. Elemental analysis was carried out at the Institute of Organic and Macromolecular Chemistry of the Friedrich-Schiller-University, Jena.

3.2. X-ray crystallographic study

The structure determination of **5** was carried out on an Enraf Nonius Kappa CCD diffractometer, crystal detector distance 25 mm, 180 frames, using graphite monochromated Mo-Kα radiation. The crystal was mounted in a stream of cold nitrogen. Data were corrected for Lorentz and polarization effects but not for absorption. The structure was solved by direct methods and refined by full-matrix least squares techniques against F^2 using the programs SHELXS-86 and SHELXL-93 [23,24]. Computation of the structure was done with the program XPMA [25] and the molecular illustrations were drawn using the program XP [26]. The crystal and intensity data are given below.[1] Additional material on the structure analysis is available from the Cambridge Crystallographic Data Center by mentioning the deposition number CCDC-149595.

3.3. Catalytic reaction of **1** and **2** with ethylene

The reactions were carried out in a 75 ml stainless steel autoclave. 1 mmol of the corresponding imine (231 mg **1**, 237 mg **2**) were transferred into the autoclave together with 0.04 mol (25 mg) $Ru_3(CO)_{12}$ and 3 ml of toluene. Then the autoclave was carefully evaporated and pressurized with 8 bar ethylene. The autoclave was heated to 140°C for 15 h. After cooling down the reaction mixture to room temperature the pressure was released and the crude reaction mixture was transferred into a Schlenk tube and the solvent was evaporated. The resulting brown oil was used for the first NMR measurements showing that **3** and **4** were produced almost quantitatively.

3.4. Analytical data of **3**

MS (CI, H_2O) *m/z* (%): 259 (M^+, 100), 242 ($C_{18}H_{12}N^+$, 93), 230 ($C_{17}H_{12}N^+$, 78), 182 ($C_{13}H_{12}N^+$, 60), 167 ($C_{12}H_9N^+$, 97); IR (Nujol, 293 K) (cm^{-1}): 2023 s, 1975 m, 1945 s, 1689 m, 1627 s, 1591 s; ^{1}H-NMR ($CDCl_3$, 293 K) (ppm): 1.31 (t, $^3J_{HH}$ = 7.5 Hz, 3H, CH_3), 3.02 (q, $^3J_{HH}$ = 7.5 Hz, 2H, CH_2), 7.22–7.67 (m, 6H, $C_{ar}H$), 7.80–7.88 (m, 4H, $C_{ar}H$), 8.78 (d, $^3J_{HH}$ = 8.2 Hz, 1H, $C_{ar}H$), 9.15 (s, 1H, CH=N); ^{13}C-NMR ($CDCl_3$, 293 K) (ppm): 16.2 (CH_3), 27.0 (CH_2), 120.8 ($C_{ar}H$), 125.2 ($C_{ar}H$), 125.4 ($C_{ar}H$), 125.9 ($C_{ar}H$), 127.1 ($C_{ar}H$), 127.8 ($C_{ar}H$), 128.2 ($C_{ar}H$), 129.0 (C_{ar}), 130.8 ($C_{ar}H$), 131.6 (C_{ar}), 132.5 (C_{ar}), 143.5 (C_{ar}), 152.8 (C_{ar}), 160.2 (CH=N).

[1] Crystal and intensity data for **5**: 193 K; crystal color, yellow; crystal size, 0.3 × 0.2 × 0.2 mm; orthorhombic: a = 17.6978 (4), b = 8.4706 (2), c = 15.4851 (4) (Å); V(Å^3) = 2321.4 (**1**); Z = 4; F (0 0 0) = 1200; ρ_{calc} = 1.738 g cm^{-3}; spacegroup $Pna2_1$; abs. coeff. 1.319 mm^{-1}; θ limit, 3.33–27.47°; ϕ-scan and ω-scan; 11 569 refl. measured; 5049 independent refl.; 4950 obs. refl.; $F_o^2 > 2\sigma(F_o^2)$; 313 parameter; GOOF = 1.111; R_1 = 0.0212; wR_2 = 0.0498; final diff. map electron density (e Å^{-3}) 0.449.

3.5. Analytical data of **4**

MS (CI, H_2O) *m/z* (%): 266 (M^+, 100), 236 ($C_{17}H_{18}N^+$, 10), 182 ($C_{13}H_{12}N^+$, 60); IR (Nujol, 293 K) (cm^{-1}): 2021 vs, 1970 m, 1939 vs, 1682 s, 1646 vs, 1615 s, 1596 s; ^{1}H-NMR ($CDCl_3$, 293 K) (ppm): 1.25 (t, $^3J_{HH}$ = 7.6 Hz, 3H, CH_3), 1.30–1.95 (m, 10H, CH_2), 2.89 (q, $^3J_{HH}$ = 7.6 Hz, 2H, CH_2), 3.31–3.45 (m, 1H, CH), 7.15–7.51 (m, 3H, $C_{ar}H$), 7.73–7.81 (m, 2H, $C_{ar}H$), 8.34 (d, $^3J_{HH}$ = 7.5 Hz, 1H, $C_{ar}H$), 8.95 (s, 1H, CH=N); ^{13}C-NMR ($CDCl_3$, 293 K) (ppm): 15.7 (CH_3), 24.6 (CH_2), 25.6 (CH_2), 26.5 (CH_2), 34.5 (CH_2), 71.1 (CH), 124.9 ($C_{ar}H$), 125.0 ($C_{ar}H$), 126.4 ($C_{ar}H$), 127.4 ($C_{ar}H$), 127.9 ($C_{ar}H$), 129.2 ($C_{ar}H$), 130.4 (C_{ar}), 131.4 (C_{ar}), 132.2 (C_{ar}), 141.1 (C_{ar}), 157.7 (CH=N).

3.6. Synthesis of **5**

0.5 mmol $Ru_3(CO)_{12}$ (320 mg) were stirred together with an equimolar amount of **2** (119 mg) in 20 ml *n*-heptane at 60°C for 2 h. During the reaction the color of the solution changes from pale orange to deep brown. After the solvent is nearly completely evaporated the reaction mixture is cooled down to −20°C. This procedure yielded **5** as yellow crystals besides orange colored crystals of $Ru_3(CO)_{12}$. Chromatographic workup of the reaction mixture under inert conditions leads to decomposition processes.

3.7. Analytical data of **5**

Elemental analysis (%) found (calculated): $C_{23}H_{19}NO_6Ru_2$ (M = 607.4), C 45.33 (45.48), H 3.23 (3.15), N 2.23 (2.31); MS (FAB in NBA) *m/z* (%): 607 (M^+, 6), 579 (M^+–CO, 10), 551 (M^+–2 CO, 36), 523 (M^+–3 CO, 28), 495 (M^+–4 CO, 32), 238 ($C_{17}H_{20}N^+$, 100); IR (Nujol, 293 K) (cm^{-1}): 2068, 2043, 2031, 1993, 1964; ^{1}H-NMR ($CDCl_3$, 293 K) (ppm): 1.02–1.86 (m, 10H, CH_2), 2.20–2.34 (m, 1H, CH), 4.61 (s, 2H, CH_2), 7.13 (d, $^3J_{HH}$ = 8.7 Hz, 1H, $C_{ar}H$), 7.47–7.73 (m, 3H, $C_{ar}H$), 7.80 (d, $^3J_{HH}$ = 8.7 Hz, $C_{ar}H$), 7.96–7.99 (m, 1H, $C_{ar}H$); ^{13}C-NMR ($CDCl_3$, 293 K) (ppm): 25.9 (CH_2), 26.1 (CH_2), 35.4 (CH_2), 64.4 (CH_2), 72.9 (CH), 105.2 (C_{ar}), 124.2 ($C_{ar}H$), 124.3 ($C_{ar}H$), 126.4 ($C_{ar}H$), 127.2 ($C_{ar}H$), 129.1 ($C_{ar}H$), 132.3 ($C_{ar}H$), 135.9 (C_{ar}), 140.4 (C_{ar}), 157.1 (C_{ar}), 198.0 (br, CO).

3.8. NMR spectroscopic investigations

0.05 mmol (12 mg) **2** together with 1/3 of the equimolar amount of $(Ru_3(CO)_{12}$ (11 mg) were dissolved in d^8-toluene and transferred into a Young NMR tube with 5 mm diameter. The first spectrum was recorded immediately. Then the mixture was heated to 110°C for 1 h. Afterwards argon was removed carefully so that the solvent did not boil and ethylene (1 bar) was added. The mixture was left at 110°C for 15 h. A NMR spectrum was recorded every 30 min during the first 3 h and then again at the end of the reaction time.

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