

The cleavage of tetrahydrofuran by cyclopentadienylphenylnickel species

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Abstract

Tetrahydrofuran is cleaved at room temperature by low valent nickel species $\{(\text{NiCp})_2\}$ yielding cyclopentadienylnickel clusters: $(\text{NiCp})_3\text{CCH}_3$, $(\text{NiCp})_3\text{CCH}_2\text{Ph}$, $(\text{NiCp})_4\text{H}_2$ and $(\text{NiCp})_2(\mu\text{-C}_5\text{H}_6)$. Unstable $\{(\text{NiCp})_2\}$ species is formed in the reaction of nickelocene with phenyllithium in THF as solvent. The evidence for the cleavage of THF was obtained by studying the reactions using deuterated reagents and solvents. © 1997 Elsevier Science S.A.

Keywords: Nickel; Cyclopentadienylnickel clusters; Cleavage of tetrahydrofuran

1. Introduction

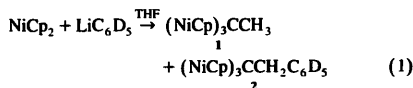
We have previously found that the tris(η^5 -cyclopentadienyl)(μ_3 -ethylidene)trinickel cluster $(\text{NiCp})_3\text{-CCH}_3$ **1** is formed in the reactions of bis(cyclopentadienyl)nickel with lithium and magnesium aryls [1]. However, at that time we had not been able to explain how this cluster is formed. We have recently studied reactions of nickelocene with phenyllithium in the presence of terminal olefins $\text{CH}_2=\text{CHR}$. Beside the main products, i.e. tris(η^5 -cyclopentadienyl)(μ_3 -alkylidene)trinickel clusters $(\text{NiCp})_3\text{CCH}_2\text{R}$, the cluster **1** has also been present in the products of these reactions [2]. Cluster **1** is not formed in reactions of nickelocene with such organolithium compounds as LiCH_2Ph [3], $\text{LiCH}_2\text{C}(\text{CH}_3)_3$ and $\text{LiCH}_2\text{Si}(\text{CH}_3)_3$ [4] as well as with vinyl lithium compounds $\text{LiC}(\text{CH}_3)=\text{C}(\text{CH}_3)_2$ [5], $\text{LiC}(\text{Ph})=\text{C}(\text{CH}_3)_2$ [5,6]. The above observations indicate that the cluster **1** is formed if phenyllithium is one of the substrates. The purpose of this paper is to explain the course of reactions leading to the formation of the cluster **1**.

2. Results

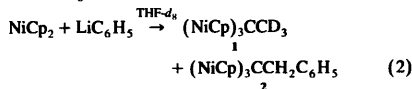
The reaction of nickelocene with phenyllithium was studied in the temperature range from -60°C to room

temperature. The reaction products were hydrolysed with water, then the organic layer was dried and chromatographed on neutral alumina with hexane/toluene mixtures as eluents. Up to date, analyses of ^1H NMR, ^{13}C NMR and mass spectra showed the presence of four various cyclopentadienylnickel clusters, viz. $(\text{NiCp})_3\text{-CCH}_3$ **1**, $(\text{NiCp})_3\text{CCH}_2\text{Ph}$ **2**, $(\text{NiCp})_4\text{H}_2$ **3** [7] and $(\text{NiCp})_2(\mu\text{-C}_5\text{H}_6)$ **4** [6].

Reaction of nickelocene with deuterated phenyllithium was performed to find out if the ethylidene group in cluster **1** was derived from cleavage of the phenyl ring. It was shown that cluster **1** did not possess any deuterium while the phenyl group in cluster **2** contained deuterium atoms:



Then the reaction of nickelocene with phenyllithium in THF- d_6 was examined:



In the products of reaction (2), deuterium was found in the ethylidene group of cluster **1** and in the C- CD_2 group of cluster **2**. The above results proved that the phenyl group was not cleaved and it did not take part in

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the formation of cluster **1**. As a result of an insertion reaction, the phenyl group was added to the C–CH₂ group and formed cluster **2**. Cluster **1** was formed by the cleavage of the THF ring because both the ethylidene group C–CD₃ in cluster **1** and the C–CD₂C₆H₅ group in cluster **2** possessed deuterium. The presence of deuterium atoms was clearly demonstrated by the mass spectra in which the parent ions of clusters with and without deuterium atoms were compared. The presence of three deuterium atoms in cluster (NiCp)₃CCD₃ was further confirmed by a high-resolution mass spectrum.

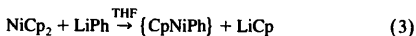
3. Discussion

The cleavage of the THF ring may be induced by phenyllithium, organonickel species {CpNiPh} or (NiCp)_n, or simultaneously by both organolithium and -nickel species.

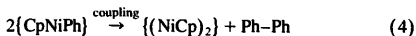
Bates et al. have found that butyllithium cleaves THF to form butane, ethylene and lithium enolate of acetaldehyde at 35 °C [8]. To verify if phenyllithium cleaves THF under the reaction conditions we performed reaction of phenyllithium with THF at room temperature and at 35 °C. We have found that at room temperature (about 25 °C) cleavage of THF by phenyllithium is negligible (in the ¹H NMR spectrum ethylene was not observed; traces of acetaldehyde were detected after hydrolysis of the reaction product). Warming of the reaction mixture up to 35 °C for 2 h caused the formation of traces of ethylene (observed in the ¹H NMR spectrum). We conclude from this observations that phenyllithium in the temperature range from –60 °C to room temperature does not cleave the THF ring to a considerable extent. Therefore the cleavage of THF and the formation of cluster **1** is due to the reaction of {NiCp} (low valent nickel) with THF.

Eisch and Im have shown that allyl phenyl ether and benzyl phenyl ether undergo allylic carbon–oxygen bond scission with bis(1,5-cyclooctadiene)nickel(0) [9]. The reaction proceeds via oxidative addition of zero valent nickel complexes to organic oxygen-containing substrates (in this case ethers). Eisch et al. have demonstrated that geminal bonds between carbon on the one hand and halogen, sulphur, sulphur and nitrogen, sulphur and lithium and carbon in strained rings on the other hand, can be efficiently cleaved by nickel(0) complexes in a stoichiometric or catalytic manner [10]. Banerji and coworkers [11] have described a method for the dealkoxylation of alkyl aryl ethers with low valent titanium [Ti(0)] reagent. They suppose that deallylation/debenzylation reaction proceeds via oxidative addition of Ti(0) to the substrate (R–O–R') followed by the cleavage of the Ti–O bond to form the alkoxide/phenoxide anion.

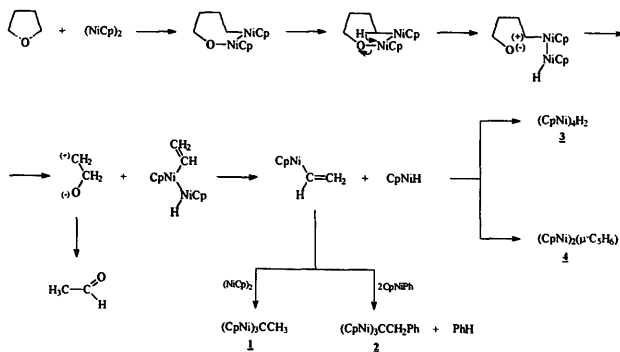
In our case nickelocene reacts with phenyllithium to form unstable species {CpNiPh}:



{CpNiPh} reacts further to form several products. The most important pathway is the coupling reaction yielding biphenyl and low valent {NiCp} species [1]:



Tetrahydrofuran undergoes carbon–oxygen bond scission with low valent nickel species (NiCp)₂ forming organonickel and organic products. We assume that the cyclopentadienylvinylnickel complex (CpNiCH=CH₂), which has been shown previously [12] to yield the ethylidene nickel cluster **1**, is an intermediate product, which in the presence of {CpNiPh} gives also cluster **2**. Unstable {CpNiH} probably also oligomerises to produce (NiCp)₃H₂ **3** [7]; it also hydrogenates a cyclopent-



Scheme 1.

tadienyl ring to cyclopentadiene, forming $(\text{NiCp})_2(\mu\text{-C}_5\text{H}_6)_4$ [6]. For the reaction in THF- d_5 we are not able to determine if the cluster 3 contains deuterium atoms. The proposed reaction course is shown in Scheme 1.

4. Experimental section

All reactions were carried out under an atmosphere of dry argon using Schlenk tube techniques. Solvents were dried by conventional methods. Bromobenzene was obtained from POCh Gliwice, bromobenzene- d_5 (99.5 at.% D) from Aldrich Chemical Co., tetrahydrofuran- d_5 (> 99.50 at.% D) from Dr. Glaser AG Basel. ^1H and ^{13}C NMR spectra were recorded on a Varian VXR-300 instrument at room temperature. Mass spectra were recorded on an AMD-604 mass spectrometer. GC/MS analyses were performed on a Hewlett Packard 5971 Series mass selective detector with a HP 35 column (30 m \times 0.25 mm).

4.1. Reaction of nickelocene with phenyllithium in THF

4.1.1. Preparation of phenyllithium in THF

A solution of 3.20 cm^3 (4.77 g, 30.4 mmol) of bromobenzene in 5 cm^3 of THF was added drop by drop during 2 h to a suspension of 0.50 g (72.0 mmol) of finely cut lithium in 50 cm^3 of THF at room temperature. The mixture was left with stirring overnight at room temperature. Samples of the resulting deep brown solution were titrated with HCl to determine the concentration (0.38 N). This solution was used on the same day for the next reaction.

4.1.2. Reaction of nickelocene with phenyllithium

The isolated yields based on the starting amount of nickelocene were mean values of two runs. Considerable amounts of the organometallic products were lost during chromatographic separation due to the band tailing. A typical experimental procedure is as follows. A solution of NiCp_2 (0.73 g, 3.87 mmol) in 60 cm^3 of THF was cooled to -60°C , then a solution of phenyllithium in THF (10.5 cm^3 , 4.00 mmol) was added drop by drop during 1.5 h (the temperature was maintained from -60 to -50°C). The mixture was stirred at this temperature for the next hour, then it was allowed to warm up slowly to room temperature (2 h). Stirring was continued overnight. The resulting brown solution was concentrated to 10 cm^3 , then 40 cm^3 of toluene was added; the products were hydrolysed with 40 cm^3 of deoxygenated water. The organic layer was separated and dried, the solvents were evaporated, the residue was redissolved in toluene and separated by column chromatography on Al_2O_3 (35 \times 2 cm, deactivated with 5% of water) using hexane/toluene mixtures as eluents. Organic products eluted before the first organometallic

band were collected and subjected to GC/MS analyses; the following compounds (selected) were identified: biphenyl, *o*-terphenyl (spectra in agreement with DATABASE\NBS75K.L), ethyl-biphenyl: *m/e* (rel. int.) 182 (M^+ , 40%), 167 (100%), 152 (23%), 139 (6.8%), 128 (6.8%), 115 (14%), 89 (8.5%), 77 (14%), 63 (15%), 51 (20%), 39 (18%), 27 (15%) (this compound could also be identified as 1,1-diphenylethane). The first coloured band was identified as NiCp_2 (hexane/toluene 14/1), then a blue band was eluted, $(\text{NiCp})_2(\mu\text{-C}_5\text{H}_6)$ (yield 1–2%): EIMS (70 eV), *m/e* (rel. int.) 312 (M^+ , 15%), 246 (68%), 188 (100%), 123 (34%), 66 (13%), 58 (9%). A brown-red band was then collected (hexane/toluene 3/1) which was shown to consist of a mixture of $(\text{NiCp})_3\text{CCH}_3$ and $(\text{NiCp})_3\text{CCH}_2\text{C}_6\text{H}_5$ (ca. 95.5 and 80.20) (yield 4–5%). $(\text{NiCp})_3\text{CCH}_3$: ^1H NMR (C_6D_6) δ [ppm] 5.15 (s, 15H, Cp), 3.71 (s, 3H, CH_3); ^{13}C NMR (C_6D_6) δ [ppm] 289.16 (C methylidyne), 87.98 (Cp), 46.02 (CH_3); EIMS (70 eV) *m/e* (rel. int.) (^{58}Ni) 396 (M^+ , 74%), 330 (54%), 304 (92%), 246 (24%), 188 (17%), 123 (8%). $(\text{NiCp})_3\text{CCH}_2\text{C}_6\text{H}_5$: ^1H NMR (C_6D_6) δ [ppm] (signals of aromatic protons obscured by the solvent) 5.07 (s, 15H, Cp), 4.93 (s, 2H, CH_2); EIMS (70 eV) *m/e* M^+ 472 (^{58}Ni). The next brown fraction was also collected (hexane/toluene 1/1): $(\text{NiCp})_2\text{H}_2$ (yield 6–7%): ^1H NMR (C_6D_6) δ [ppm] 5.35 (s, Cp), -20.3 (s, H); EIMS (70 eV) *m/e* (rel. int.) 496 (31%), 494 (40%), 492 (34%), 428 (30%), 426 (32%), 424 (25%), 306 (24%), 246 (23%), 188 (100%), 123 (77%), 66 (54%), 58 (25%).

4.2. Reaction of nickelocene with phenyllithium- d_5 in THF

4.2.1. Preparation of phenyllithium- d_5 in THF

The same procedure as for phenyllithium was applied, using 0.17 g (24.5 mmol) of lithium in 15 cm^3 of THF and 1.0 cm^3 (1.54 g, 9.50 mmol) of bromobenzene- d_5 in 2 cm^3 of THF. A sample of this reagent was hydrolysed with H_2O : GC/MS analyses of the organic phase showed the presence of $\text{C}_6\text{D}_5\text{H}$ and THF.

4.2.2. Reaction of nickelocene with phenyllithium- d_5

The reaction was carried out as the previous ones, using a solution of NiCp_2 (0.88 g, 4.66 mmol) in 70 cm^3 of THF and a solution of phenyllithium- d_5 in THF (12.5 cm^3 , 5.00 mmol). After the usual work-up, the following compounds were identified: biphenyl- d_{10} ; terphenyl- d_{14} (three isomers); $(\text{NiCp})_2(\mu\text{-C}_5\text{H}_6)$ (yield 2%), mass spectrum as above; a mixture (ca. 1:1) of $(\text{NiCp})_3\text{CCH}_3$ (NMR and mass spectra as above) and $(\text{NiCp})_3\text{CCH}_2\text{C}_6\text{D}_5$ (yield 5%): ^1H NMR (C_6D_6) δ [ppm] 5.07 (s, 15H, Cp), 4.94 (s, 2H, CH_2); ^{13}C NMR (C_6D_6) δ [ppm] (partial spectrum) 88.07 (Cp), 62.91 (CH_2); EIMS (70 eV) *m/e* (rel. int.) (^{58}Ni) 477 (M^+ ,

51%), 411 (92%), 385 (32%), 304 (45%), 246 (36%), 188 (60%), 123 (42%), 66 (42%), 58 (14%); (NiCp)₂H₂ (yield 6%), NMR and mass spectra as above.

4.3. Reaction of nickelocene with phenyllithium in THF-d₈

4.3.1. Preparation of phenyllithium in THF-d₈

A similar procedure as for phenyllithium was applied, using 7.15 mg (1.03 mmol) of lithium in 1.2 cm³ of THF-d₈ and 50 μl (74.5 mg, 0.475 mmol) of bromobenzene at 0 °C.

4.3.2. Reaction of nickelocene with phenyllithium in THF-d₈

The reaction was carried out under similar conditions as the previous ones, from a solution of NiCp₂ (64.3 mg, 0.341 mmol) in 3 cm³ of THF-d₈ and the above described solution of phenyllithium in THF-d₈. After the hydrolysis, the distillate was analysed by GC/MS to show the presence of cyclopentadiene, benzene and THF-d₈. Due to the very small amounts of the substrates, only one brown band was separated by column chromatography (Al₂O₃ with 5% H₂O, 10 × 1 cm), hexane/toluene 1/1; the mass spectrum of the mixture showed the presence of the following compounds: (NiCp)₂CCD₃ (M⁺ (⁵⁸Ni), 399), (NiCp)₂CCD₂C₆H₅ (M⁺ (⁵⁸Ni), 474) and the fragment (NiCp)₄ (494) (biphenyl was also identified by GC/MS). The main product was then purified by column chromatography (Al₂O₃ with 5% H₂O, 10 × 1 cm), hexane/diethyl ether 25/1: (NiCp)₂CCD₃ EIMS (70 eV) *m/e* (rel. int.) (⁵⁸Ni) 399 (M⁺, 86%), 332 (45%), 304 (60%), 246 (27%), 188 (58%), 123 (48%), 65 (52%), 58 (24%). HRMS Found: 400.960524. ¹²C₁₇H₁₅D₃⁵⁸Ni⁶⁰Ni Calc.: 400.961164.

4.4. Cleavage of tetrahydrofuran by phenyllithium

A solution of phenyllithium in THF was prepared as usual at ambient temperature (25 °C). Stirring was continued overnight, then 0.4 cm³ of this solution was placed in an NMR tube together with 0.2 cm³ of benzene-d₆ and sealed. The NMR tube was stored at room temperature: a ¹H NMR spectrum recorded after 2 h did not show any cleavage products. Then the tube was kept for 2 h at 35 °C: in the ¹H NMR a singlet at 5.22 ppm appeared, which was assigned to ethylene. Signals corresponding to lithium enolate of acetaldehyde were not observed. 20 cm³ of the freshly prepared phenyllithium

solution in THF (stirred overnight at room temperature) was added drop by drop to excess of water at 0 °C. Acetaldehyde was detected by GC/MS in the distillate of the resulting aqueous solution.

4.5. Quenching of the reaction of nickelocene with phenyllithium

Reaction of NiCp₂ with phenyllithium in THF was performed as usual. When the reaction mixture warmed up to 0 °C it was added drop by drop to excess of water at 0 °C with vigorous stirring. The resulting slurry was evaporated: acetaldehyde and butanol were detected by GC/MS in this distillate. The brownish, greasy residue was extracted with methanol (acidified with a few drops of aq. HCl). The following compounds were identified in this methanolic solution by GC/MS: phenol, benzenebutanol, biphenyl, ethyl-biphenyl (or 1,1-diphenylethane), diethyl-biphenyl.

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References

- [1] A. Pietrzykowski and S. Pasykiewicz, *J. Organomet. Chem.*, **440** (1992) 401.
- [2] S. Pasykiewicz, W. Buchowicz and A. Pietrzykowski, *J. Organomet. Chem.*, **489** (1995) C48.
- [3] T.I. Voyevodskaya, I.M. Pribytkova and A.J. Ustynuk, *J. Organomet. Chem.*, **37** (1972) 187.
- [4] B.L. Booth and G.C. Casey, *J. Organomet. Chem.*, **178** (1979) 371.
- [5] S. Pasykiewicz, A. Pietrzykowski, W. Buchowicz and M. Poplawska, *J. Organomet. Chem.*, **463** (1993) 235.
- [6] S. Pasykiewicz, W. Buchowicz, J. Poplawska, A. Pietrzykowski and J. Zachara, *J. Organomet. Chem.*, **490** (1995) 189.
- [7] S. Pasykiewicz, W. Buchowicz, A. Pietrzykowski and T. Glowiak, in press.
- [8] R.B. Bates, L.M. Kroposki and D.E. Potter, *J. Organomet. Chem.*, **37** (1972) 560.
- [9] J.J. Eisch and K.R. Im, *J. Organomet. Chem.*, **139** (1977) C45.
- [10] J.J. Eisch, Y. Qian and M. Singh, *J. Organomet. Chem.*, **512** (1996) 207.
- [11] S.M. Kadam, S.K. Nayak and A. Banerji, *Tetrahedron Lett.*, **33** (1992) 5129.
- [12] H. Lehmkühl, C. Krüger, S. Pasykiewicz and J. Poplawska, *Organometallics*, **7** (1988) 2038.