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Preliminary communication

Novel synthesis of alkylidynetrinickel clusters

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Abstract

Nickelocene reacts with phenyllithium in the presence of terminal olefins to form tris(η^5-cyclopentadienyl)(μ_3-alkylidyne)trinickel clusters $(NiCp)_3CR$. It is a new, simple method for the synthesis of (μ_3-alkylidyne)trinickel clusters with various R groups.

Keywords: Nickel; Lithium; Cluster; Cyclopentadienyl

Alkylidynetrinickel clusters can be prepared by the reaction of nickelocene with LiR or RMgX if R does not possess a β-hydrogen atom, Eq. (1) [1,2].

$$NiCp_2 + LiCH_2R' \longrightarrow (NiCp)_3CR' \qquad (1)$$

$$R' = C_6H_5;\ C(CH_3)_3;\ Si(CH_3)_3$$

A trinickel cluster is also formed by the reaction of nickelocene with methyllithium, Eq. (2) [3]. The reaction proceeds with the formation of C–C bonds.

$$NiCp_2 + LiCH_3 \longrightarrow (NiCp)_3CCH_3 \qquad (2)$$

If R possesses β-hydrogen, then a β-H elimination reaction occurs causing the formation of saturated and unsaturated hydrocarbons and nickel clusters of the type $(NiCp)_n$, Eqs. (3, 4). Alkylidynetrinickel clusters are not formed in these reactions [4].

$$NiCp_2 + LiCH_2CH_2R \longrightarrow \{CpNiCH_2CH_2R\} \qquad (3)$$

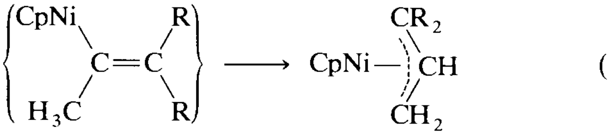
$$\{CpNiCH_2CH_2R\} \longrightarrow CH_3CH_2R + CH_2{=}CHR + (NiCp)_n \qquad (4)$$

We have worked out another method of synthesis of alkylidynetrinickel clusters: the reaction of nickelocene with vinyllithium or vinylmagnesium compounds, Eq. (5) [3].

$$NiCp_2 + LiCH{=}CR_2 \longrightarrow (NiCp)_3CCHR_2 \qquad (5)$$

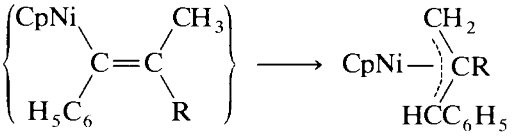
R = H or alkyl group

Despite the substantial increase in the possibilities of synthesis of various trinickel clusters, this method has some limitations because the vinyl group must possess an α-hydrogen atom. If this atom is replaced by an alkyl or aryl group trinickel clusters are not formed [5]. If the α-hydrogen is replaced by a methyl group, β-H elimination occurs and π-allylcyclopentadienylnickel complex is formed, Eq. (6) [6].



(6)

If a phenyl group replaces the α-hydrogen then π-allyl complex is formed by γ-H elimination, Eq. (7) [6].



(7)

In this work we have found that nickelocene reacts with phenyllithium in the presence of 1-hexene to form tris(η^5-cyclopentadienyl)(μ_3-n-hexylidyne)trinickel cluster **1**, Eq. (8).

$$NiCp_2 + LiC_6H_5 + CH_2{=}CH(CH_2)_3CH_3 \longrightarrow (NiCp)_3C(CH_2)_4CH_3 \qquad (8)$$

1

The cluster $(NiCp)_3CCH_3$ is also formed in the reaction (8); its yield depends on the conditions of the reaction and on the method of isolation of the prod-

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ucts. A phenyl group is not present in the organic chain of the cluster **1** and the π-bond olefin–nickel is replaced by the σ-bond Ni–C. This type of phenyl group elimination and simultaneous formation of the σ Ni–C bond is, to our knowledge, so far unknown in the organic chemistry of nickel or other transition metals.

To confirm that this type of reaction is general, we studied the reaction of nickelocene with phenyllithium in the presence of 1-decene. Tris(η^5-cyclopentadienyl)(μ_3-n-decylidyne)trinickel cluster **2** was formed in reaction (9).

$$\begin{aligned} &NiCp_2 + LiC_6H_5 + CH_2{=}CH(CH_2)_7CH_3 \\ &\longrightarrow \underset{\mathbf{2}}{(NiCp)_3C(CH_2)_8CH_3} \qquad (9) \end{aligned}$$

Small amounts of cluster $(NiCp)_3CCH_3$ were also found in the products of the reaction (9).

This new method of the synthesis of trinickel clusters is more convenient than the previous ones; the substrates are easily accessible, a wide variety of trinickel clusters can be prepared by varying the olefin.

1. Experimental

All reactions were carried out under an atmosphere of dry argon using Schlenk tube techniques. Solvents were dried by conventional methods. ^1H and ^{13}C NMR spectra were measured on a Varian VXR-300 instrument. Mass spectra were recorded on an AMD-604 mass spectrometer.

1.1. Reaction of nickelocene with phenyllithium in the presence of 1-decene

A solution of 0.65 g $NiCp_2$ (3.44 mmol) and 1.3 ml of 1-decene (6.89 mmol) in 50 ml THF was cooled to −60°C, then a solution of phenyllithium in THF (14 ml, 3.50 mmol) was added over 1 h, (temperature was maintained at $-60 \div -50$°C). The mixture was stirred at this temperature for the next hour, then it was allowed to warm up slowly to room temperature. Stirring was continued overnight. The solution was concentrated, then 40 ml of hexane was added: it was hydrolysed with 40 ml of deoxygenated water. The organic layer was dried, solvents were evaporated, the residue was redissolved in toluene and chromatographed on Al_2O_3 (deactivated with 5% water) using hexane : toluene (1 : 1); small amounts of $NiCp_2$ were eluted; then a brown-red band containing $(NiCp)_3C(CH_2)_8CH_3$ was collected.

^1H NMR (C_6D_6): δ[ppm] 5.20 (s, 15H, Cp), 3.74 (t, 2H, J = 7.7 Hz), 2.18 (m, 2H, J = 7.5 Hz), 1.70 (m, 2H, J = 7.7 Hz), 1.54–1.34 (unresolved multiplet, 10H), 0.91 (t, 3H, J = 7.4 Hz). ^{13}C NMR (C_6D_6): δ[ppm] 284.90; 87.90; 57.90; 36.05; 32.31; 30.47; 30.23; 30.21; 29.83; 23.08; 14.30. MS(70 eV): m/e = 510(M$^+$, 82%), 440(95%), 372(82%), 306(100%), 246(50%), 188(28%), 123(10%).

1.2. Reaction of nickelocene with phenyllithium in the presence of 1-hexene

The reaction was carried out as described in section 1.1. A mixture of two compounds was obtained.

1.2.1. $(NiCp)_3C(CH_2)_4CH_3$ (main product ca. 80%)

^1H NMR (C_6D_6): δ[ppm] 5.17 (s, 15H, Cp), 3.69 (t, 2H, J = 8.3 Hz), 2.13 (m, 2H, J = 8.78 Hz), 1.63 (m, 2H, J = 7.5 Hz), 1.48 (m, 2H, J = 7.4 Hz), 1.02 (3H, t, J = 7.2 Hz). ^{13}C NMR (C_6D_6): δ[ppm] 295.57; 87.88; 57.79; 35.64; 32.55; 23.13; 14.41.

1.2.2. $(NiCp)_3C\text{-}CH_3$ (side product ca. 20%)

^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] C methylidyne not observed, 88.01; 46.01. MS(70 eV) mixture: m/e = 454(M$^+$, 5%), 398(M$^+$, 73%), 330(76%), 306(100%), 266(58%), 246(32%), 188(26%), 123(14%).

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