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Preliminary communication

Carbon–nitrogen bond cleavage of β-nitrostyrene promoted by acetatohydridocarbonylbis-(triphenylphosphine)ruthenium(II)

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Abstract

The reaction at room temperature of $[RuH(O_2CCH_3)(CO)(PPh_3)_2]$ (**1**) with β-nitrostyrene promotes the carbon–nitrogen bond cleavage and yields $[Ru(CO)(NO_2)(O_2CCH_3)(PPh_3)_2]$ (**2**), styrene, and traces of nitroethylbenzene. Infrared spectrometry data are consistent with a *N*-bonded nitro group in **2**.

During the course of the study of the catalytic hydrogenation of nitroolefins by various ruthenium hydrides complexes [1], we were interested to model such reactions. For this purpose the stoichiometric reactivity toward β-nitrostyrene of one of the active catalysts for these systems, $[RuH(O_2CCH_3)CO(PPh_3)_2]$ (**1**), was studied. Usually the products from the reaction of olefins (and especially activated olefins) with ruthenium monohydride complexes are the corresponding insertion products [2–4]. In this communication we report that the reaction of β-nitrostyrene occurs in a different way, and leads to carbon–nitrogen bond cleavage giving styrene and a Ru–NO_2 complex according to the equation shown.

$$[RuH(O_2CCH_3)CO(PPh_3)_2] + PhCH{=}CHNO_2 \rightarrow [RuNO_2(O_2CCH_3)CO(PPh_3)_2] + PhCH{=}CH_2$$

In a typical experiment $[RuH(O_2CCH_3)CO(PPh_3)_2]$ (0.36 g, 0.5 mmol) was dissolved in benzene (40 ml) with β-nitrostyrene (0.335 g, 2.2 mmol) and the solution was stirred for 24 h. Then the solution was concentrated to one third of its volume and left for one week at room temperature. Crystals slowly appeared and were collected giving 0.130 g of **2** as a pale yellow solid.

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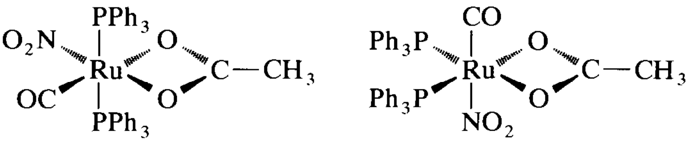

(2a) (2b)

Fig. 1. Proposed structures for **2**.

Mass spectrometry and chemical analysis [5*] are consistent with the formulation $[Ru(CO)(NO_2)(O_2CCH_3)(PPh_3)_2]$ for **2**. The absence of other organic fragments is confirmed by the ^{1}H and ^{13}C NMR spectra [5*] which give evidence of phenyl, acetato and carbon monoxide groups only. The ^{13}P NMR spectrum exhibits one resonance at 35.5 ppm showing that the two phosphine ligands are equivalent.

The infrared spectrum of **2** in a KBr pellet exhibits a ν(CO) stretching band at 1960 cm^{-1}, and there is no evidence of a Ru–H absorption. Compared to **1**, the CO absorption shifts to higher wave numbers by 35 cm^{-1}, which confirms that **2** is not the result of a simple insertion reaction of the alkene into the Ru–H bond (generally a small shift is observed in the case of insertion reactions [3]).

The ν_{as}(C=O) and ν_s(C=O) absorptions of the carboxylate group are only slightly affected, moving from 1530 in **1** to 1520 cm^{-1} in **2** and from 1460 in **1** to 1464 cm^{-1} in **2**. This shows that the carboxylate group remains chelate in **2**.

Comparison of the infrared spectra of **1** and **2** shows that two new strong bands are present in **2**, at 1390 and 1319 cm^{-1}. These absorptions are characteristic of *N*-bound nitro groups [6,7]. Crystals suitable for X-ray structure determination have not been obtained, but from the spectroscopic data two structures can be proposed (Fig. 1). One (**2a**), results from the substitution of the hydrido-ligand by the nitro-group in **1** and in the other (**2b**), the two phosphine ligands are *trans* to the aceto-group. The increase ν(CO) is more consistent with the structure **2b**, in which the CO is *trans* to the nitro-group.

To summarize, the reaction of β-nitrostyrene with acetatohydridocarbonylbis(triphenylphosphine)ruthenium leads to the first example of carbon–nitrogen bond cleavage in a nitroolefin promoted by an hydrido-transition metal complex.

Analysis by chromatography of the reaction solution of **1** with β-nitrostyrene shows the presence of styrene and traces of nitroethylbenzene.

This reaction closely resembles the reaction of alkenyl carboxylates with ruthenium hydride complexes, which results in the C–O bond cleavage [2,8]. The same type of mechanism [8] can be proposed, but in our case the vacant coordination site should be created by the change of the acetato-ligand from η^2 to η^1 coordination.

We have tried to extend this study to $[RuHCl(CO)(PPh_3)_3]$ but no clean reaction has been observed with β-nitrostyrene. ^{31}P NMR analysis reveals the formation of a complex mixture of unidentified complexes and triphenylphosphine oxide.

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* Reference number with asterisk indicates a note in the list of references.

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References and notes

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5 $[Ru(CO)(NO_2)(O_2CCH_3)(PPh_3)_2]$ (**2**), mass spectrometry m/z $M^+ = 759$. Chemical analysis. Found: C, 61.61; H, 4.48; N, 1.80; P, 7.57; Ru, 13.26. $C_{39}H_{33}NO_5P_2Ru$ calcd.: C, 61.74; H, 4.38; N, 1.85; P, 8.16; Ru, 13.32%. IR (KBr) 1960 cm^{-1} (ν(CO)); 1520, 1464 cm^{-1} ($\nu(CO_2)$); 1390, 1319 cm^{-1} ($\nu(NO_2)$). 200 MHz ^1H NMR (CD_2Cl_2) δ 7.68–7.32 (m, 30 H, Ph), 0.42 (s, 3H, Me). 62.9 MHz ^{13}C NMR (CD_2Cl_2) (except phenyl resonances) δ 203 (t, J(PC) = 15 Hz, CO), 185 (CO_2CH_3), 21.4 (q, J(CH) = 129 Hz, CO_2CH_3). 32.4 MHz ^{31}P NMR (CD_2Cl_2) δ 35.5.

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