Journal of Organometallic Chemistry, 430 (1992) C15–C18
Elsevier Sequoia S.A., Lausanne
JOM 22692PC

Preliminary communication

Stereochemical aspects of the synthesis and reactivity of (diphosphine)(carbonyl)(cyclopentadienyl)-ruthenium complexes

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(Received January 23, 1992)

Abstract

The formation of the carbonyl complexes (S_{Ru},R_C)-[Ru(η^5-C_5H_5)(CO)(prophos)]PF_6 (**3a**) (prophos = $Ph_2PCH(CH_3)CH_2PPh_2$) and (R_{Ru},R_C)-[Ru(CO)(η^5-C_5H_5)(prophos)]PF_6 (**3b**) by reaction of the corresponding chloro compounds **1a** and **1b** with carbon monoxide in the presence of NH_4PF_6 is stereospecific, and takes place with retention of configuration at the ruthenium atom. The carbonyls **3a** and **3b** are also stereospecifically formed by reaction of the vinylidene complexes (S_{Ru},R_C)-[Ru(η^5-C_5H_5)(C=CHPh)(prophos)]PF_6 (**2a**) and (R_{Ru},R_C)-[Ru(C=CHPh)(η^5-C_5H_5)(prophos)]PF_6 (**2b**) with molecular oxygen. The reaction of **3a** with $LiAlH_4$ to give the methyl derivatives is stereospecific but that of **3b** shows extensive epimerization as well as a low chemoselectivity. A similar difference in stereoselectivity for the two diasteromers **3a** and **3b** is also observed in the reaction with $[N(C_2H_5)_4]OH$.

It has been reported that the ruthenium vinylidene complexes [Ru(η^5-C_5H_5)(C=CHR)$(PPh_3)_2$]$^+$ react with oxygen to give the carbonyl derivative [Ru(η^5-C_5H_5)(CO)$(PPh_3)_2$]$^+$ with concurrent formation of the corresponding aldehydes RCHO [1,2]. The same behaviour has been observed for the indenyl analogue [Ru(η^5-C_9H_7)(C=CHPh)$(PPh_3)_2$]$^+$ [3]. The mechanistic implications of this interesting transformation are, however, completely unknown [2,4], in spite of its possible correlation with the catalytic oxidative cleavage of the olefinic double bond by molecular oxygen, i.e. with the catalytic oxygen-olefin metathesis [5–7]. We report herein on the stereochemical aspects of this reaction at the level of the

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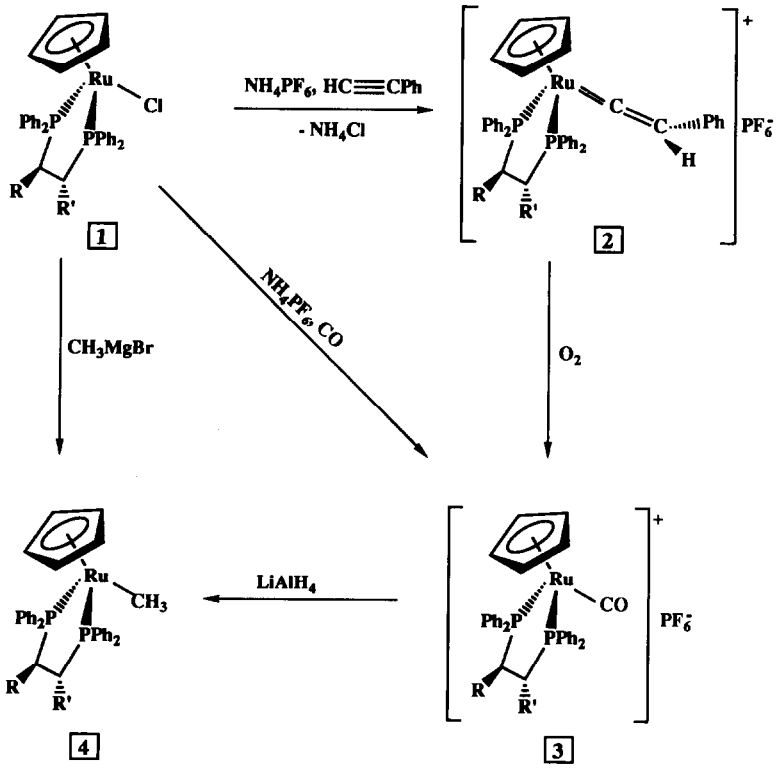

a : R = CH_3, R' = H; b : R = H, R' = CH_3

Scheme 1.

metal atom. We have also analysed the stereochemistry of the formation of the carbonyl derivatives from the parent chloro complex, as well as their reactions with strong nucleophiles such as $LiAlH_4$ and $[N(C_2H_5)_4]OH$. The reactions investigated, starting from (S_{Ru},R_C)-[RuCl(η^5-C_5H_5)(prophos)] (**1a**) are shown in Scheme 1. The same reactions were carried out on the other diastereoisomer, (R_{Ru},R_C)-[RuCl(η^5-C_5H_5)(prophos)] (**1b**) [8].

A mixture of the two diastereoisomers **1a** and **1b** (diastereomeric ratio ~ 55/45) reacts with carbon monoxide at atmospheric pressure and room temperature in the presence of a methanol solution of NH_4PF_6 as the halogen scavenger to give a mixture of the carbonyl derivatives (S_{Ru},R_C)-[Ru(η^5-C_5H_5)(CO)(prophos)]PF_6 (**3a**) and (R_{Ru},R_C)-[Ru(η^5-C_5H_5)(CO)(prophos)]PF_6 (**3b**) (diastereomeric ratio ~ 60/40). However, when **1a** (diastereomeric purity > 98%) was allowed to react under the same conditions, a mixture of **3a** and **3b** was obtained, again in about the same diastereomeric ratio. The absence of stereospecificity on the reaction appears to be due to the long life of the five-coordinate, 16-electron cationic intermediate [Ru(η^5-C_5H_5)prophos)]$^+$, which can epimerize at the metal atom before being trapped by carbon monoxide [9]. The reaction proceeds in a substan-

tially stereospecific fashion when carried out under 300 atm of carbon monoxide. Under these conditions **1a** (diastereomeric purity $\geq 98\%$) is converted into **3a** (diastereomeric purity 96%), whereas **1b** (diastereomeric purity $\geq 98\%$) affords **3b** (diastereomeric purity 95%) [10*]. The stereochemical outcome of these reactions (overall retention) is inferred from i) the earlier demonstration that substitution of the chlorine ligand by other 2-electron donors does not alter the geometry at the ruthenium atom [11,12], and ii) the empirical observation that in this type of compound the difference in chemical shift between the phosphorus atoms of each diastereoisomer is related to the absolute configuration at the metal [13].

Conditions for the stereospecific transformation of **1** into the vinylidene derivative **2** were found earlier [14]. In contrast to the previously reported reactions of vinylidene complexes with oxygen [1–3], the reactions of **1a** and **1b** are not very selective, about 20–30% of the starting material being transformed into other products which have been not yet identified. From the point of view of the stereochemistry, however, the reaction is stereospecific within the limits of the experimental error. Under 1 atm of oxygen in CH_2Cl_2, complex **1a** (diastereomeric purity 98%) is converted into **3a** (diastereomeric purity 97%) within 24 h, whereas **1b** (diastereomeric purity 94%) affords **3b** (diastereomeric purity 94%) more slowly, complete conversion taking four days.

The stereochemical outcomes of the reactions of species **3a** and **3b** with lithium aluminium hydride were also investigated. The $LiAlH_4$ reduction of the carbonyl species **3** proceeds with different chemo- and stereo-selectivities for the two diastereoisomers. Compound **3a** (diastereomeric purity 96%) reacts with a fourfold excess of $LiAlH_4$ in tetrahydrofurane solution at room temperature to give the methyl complex $[Ru(CH_3)(\eta^5\text{-}C_5H_5)(prophos)]$ (**4a**) (diastereomeric purity 98%) as the main product (Scheme 1). Complex **4a** was previously found to be formed stereospecifically from **1a** and methylmagnesium bromide (Scheme 1) [12,15]. The ^1H and ^{31}P NMR spectra of the crude product mixture after extraction into deuterobenzene indicate that, besides methyl derivative **4a** ($\sim 90\%$) and a small amount of unchanged **3a** ($\sim 5\%$), a third species ($\sim 5\%$) is present, which we tentatively formulate as the cyclopentadiene complex $[Ru(\eta^4\text{-}C_5H_6)(CO)(prophos)]$ (**5**) (see below). The reaction of **3b** (diastereomeric purity 95%) under the same conditions results in preferential formation of species **5** ($\sim 60\%$), derived from attack on the cyclopentadienyl ring [16*]. The methyl derivative **4b** (40%) which is also formed has a 83% diastereomeric purity. In contrast to the findings for $[Ru(\eta^5\text{-}C_5H_5)(CO)(PPh_3)_2]^+$ [17], the extent of the attack on the cyclopentadienyl ring increases when the reaction is performed at low temperature ($-50°C$), complex **5** being formed in an amount as high as 88%, and the stereospecificity of the formation of **4b** falling to 77%.

The outcome of the reaction of **3b** toward $LiAlH_4$ indicates that there is competition between the attacks on the carbonyl ligand and on the cyclopentadienyl ring, the latter attack giving a five-coordinate, stereochemically non-rigid species. The loss of stereospecificity observed in the formation of methyl derivative **4b** could be attributed to reversible formation of such a five-coordinate species, which would furnish an easy epimerization pathway. Though to our knowledge

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

there is no information for ruthenium-cyclopentadienyl systems to support this hypothesis, evidence has recently been found for a reversible carbanion attack onto the aromatic ring of [Cr(CO)$_3$(arene)] species [18].

Preliminary experiments show a similar difference in stereoselectivity for the reaction of **3a** and **3b** with [N(C$_2$H$_5$)$_4$]OH. These reactions yield two new species, which we formulate as hydroxycarbonyls (S_{Ru},R_C)-[Ru(COOH)(η^5-C$_5$H$_5$)(prophos)] (**7a**) and (R_{Ru},R_C)-[Ru(COOH)(η^5-C$_5$H$_5$)(prophos)] (**7b**) [19*]. The reaction is stereospecific for **3a**, whereas **3b** reacts with complete epimerization, the two diastereomeric species **7a** and **7b** being formed in a 1:1 ratio. In contrast to the behaviour of [Ru(COOH)(η^5-C$_5$H$_5$)(PPh$_3$)$_2$] [20], these compounds appear to be fairly stable and do not decompose to the corresponding hydrides [RuH(η^5-C$_5$H$_5$)(prophos)] when kept at 50°C in acetone solution for several hours; only partial epimerization was observed. A similar inertness toward β-hydrogen elimination has been observed for the related ethyl derivatives [Ru(C$_2$H$_5$)(η^5-C$_5$H$_5$)(prophos)] [12]. In this case, also, the epimerization during the reaction of diastereoisomer **3b** could involve a fast, reversible attack of the hydroxyl ion on the cyclopentadienyl ring, to give a stereochemically non-rigid, five-coordinate species.

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