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Short communication

Degradation of the ruthenium-based metathesis catalyst [$RuCl_2$(=CHPh)(H_2IPr)(PCy_3)] with primary alcohols

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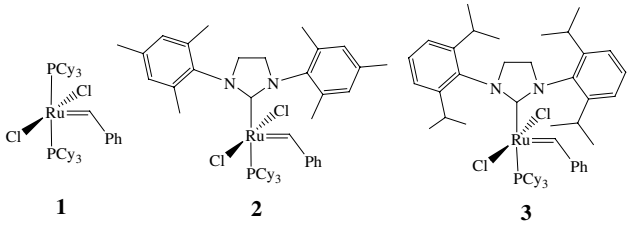
Abstract

A new ruthenium hydride species, showing high catalytic isomerization and hydrogenation properties, was isolated via a ligand exchange reaction. The same species was also present in the mixture of degradation products of the monophosphinic complex RuCl(CO)$(PCy)_3$(IPr)CH(Ph), **3**, after reaction with alcohols under basic conditions.

Keywords: Metathesis; Isopropylidene ligand; Hydride; Isomerization; Hydrogenation

The last decade has seen an increasing exploitation of olefin metathesis for synthetic purposes [1], mainly due to the discovery and development of well-defined and stable ruthenium carbene species such as the classical first- and second-generation Grubbs' catalysts **1** and **2** [2] and the more recently described catalyst **3** [3a,b] bearing a modified version of the imidazolylidene ligand (so-called Mol's catalyst [3c]). The ruthenium benzylidene species **3** was found to be very active showing a particularly high turnover number in self-metathesis reactions of terminal alkenes [3a] and also exhibiting the highest initial ADMET (Acyclic Diene Metathesis) rate of any phosphine ligated ruthenium complex [3c].



1 **2** **3**

Species **1** and **2** were recently found to be not only active metathesis catalysts, but also precursors to isomerization and hydrogenation catalysts when treated with alcohols in the presence of a base [4]. These findings are rather intriguing since isomerization products are sometimes found as by-products in metathesis reactions [5]. It is therefore of primary importance that a complete understanding of possible degradation pathways under different conditions is resolved, in order to minimize or exploit these side reactions for synthetic purposes [5d].

Given the high catalytic activity shown by the benzylidene species **3**, it was necessary to investigate first its degradation process under basic conditions in the presence of a primary alcohol. The aim was to possibly

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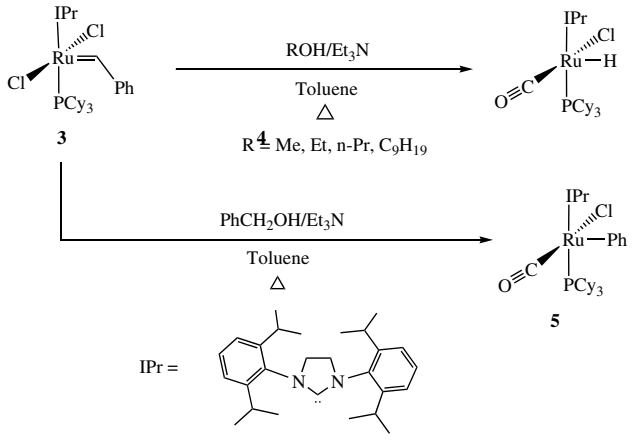


Scheme 1. Degradation of catalyst **3** in base/alcohol.

obtain new isomerization or hydrogenation species from catalyst **3** as a first step into selective tandem metathesis/isomerization or tandem metathesis/hydrogenation reactions.

In analogy with what was previously done for species **1** and **2** [4], catalyst **3** was reacted with primary aliphatic alcohols and benzylic alcohol (Scheme 1). As for catalyst **2**, these reactions with catalyst **3** did not give selectively one product.

Upon reaction of catalyst **3** with an aliphatic alcohol at 80 °C two major hydride products were formed. The major one showed a doublet at $\delta = -24.34$ ppm ($J_{P-H} = 21$ Hz) and was identified as the monophosphine species **4** (Scheme 2). The phosphorous signal for this species gave a doublet at $\delta = 47.04$ ppm ($J = 24$ Hz). It was not possible to obtain selectively this species through this route even at low temperatures. The ^{1}H NMR of the reaction mixture showed the presence of a second hydride giving a singlet at $\delta = -7.07$ ppm as a minor product (20–25%) and in the ^{31}P NMR a signal at $\delta = 46.61$ ppm (s). Two more unidentified species were present in the ^{31}P NMR spectra, giving two signals at $\delta = 51.03$ ppm and $\delta = 34.61$ ppm, respectively. This last species was also present in the mixture of degradation products of catalyst **3** when left to stand for 24 h under nitrogen in a CH_2Cl_2 solution.

When reacting the same species with benzyl alcohol the same four major species were evident in the ^{31}P NMR having $\delta = 51.02$ (s), 47.04 (d, $J = 24$ Hz), 46.61 (s) and 34.61 ppm (s). The ^{1}H NMR spectrum showed the formation of three hydride species. Along with the major product (complex **4**) displaying a doublet at $\delta = -24.32$ ppm ($J = 25$ Hz) (ca. 80%), a minor product with $\delta = -7.09$ ppm (s) (ca. 10%) and a new species giving a doublet at $\delta = -13.31$ ppm (d, $J = 33$ Hz) (ca. 5%) were detected in the mixture. To our surprise there was no signal in the phosphorous region at around 25 ppm where we would anticipate the signal for the phenyl species **5** [4].

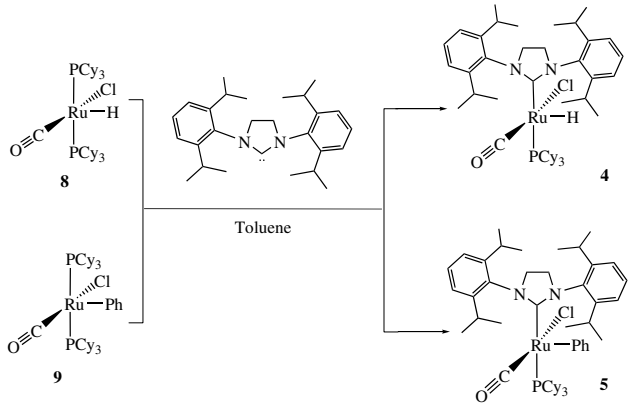
The formation of by-products could be due to the predicted increased lability of the *N*-heterocyclic carbene ligand H_2IPr relative to H_2IMes [6] though the same mixture of products was obtained at lower temperatures (r.t; 40 °C).

Since catalysts **4** and **5** were not obtained selectively they must be formed and isolated via an independent route. As for the mixed ligand species RuCl(CO)(P-Cy_3)(H_2IMes)(X) (where X = H, **6** or Ph, **7**) [4], ligand exchange reactions between complexes **8** and **9** and the free carbene **10** were attempted (Scheme 2).

The free carbene **10** was obtained in situ by reacting the corresponding hydrochloride salt with a toluene suspension of potassium *tert*-pentoxide. The solution containing the free carbene **10** was then filtered by cannula into a toluene solution of catalyst **8** or **9**. The two reactions were followed by ^{31}P NMR spectroscopy.

The reaction of complex **8** proceeded to 95% conversion. It was possible to isolate complex **4** from the mixture via careful multiple precipitations [7].

In the case of the phenyl complex **9**, the ligand exchange stopped at 70% conversion even upon addition of subsequent batches of free carbene solution of the substrate. Attempts to isolate the monophosphine species **5** from **9** were unsuccessful.



Scheme 2. Ligand exchange reaction of complexes **8** and **9**.

Table 1
Isomerization activity of complex **4**[a]

Entry	*T* (°C)	Conv. (%)	% Selectivity for 2-octene (*cis*:*trans*)	TON
1	23	0	–	–
2	40	4.6	96 (30:70)	4600
3	60	12.2	99 (26:74)	12,200
4	80	36.6	99 (29:31)	36,600
5	100	95.1	92 (28:72)	95,100
6	120	96.4	41 (27:73)	96,400

[a] *Reaction procedure*: After purification of the substrate (alumina column), it was degassed and heated to the desired temperature. The catalyst was then added and samples were taken at different times and analyzed by GC–FID.

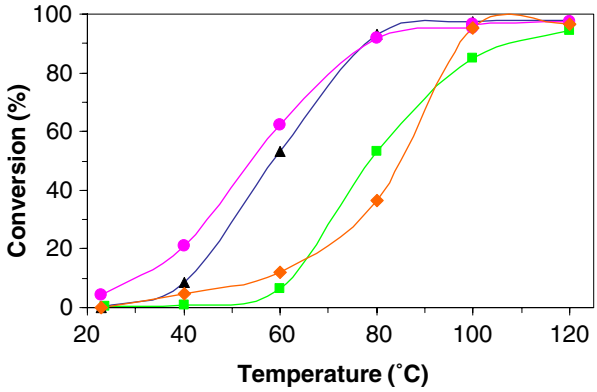


Fig. 1. Conversion as a function of reaction temperature for the double-bond isomerization of neat 1-octene (100,000 equivalents) in the presence of catalysts **4** (◆), **6** (▲), **8** (●) and **9** (■).

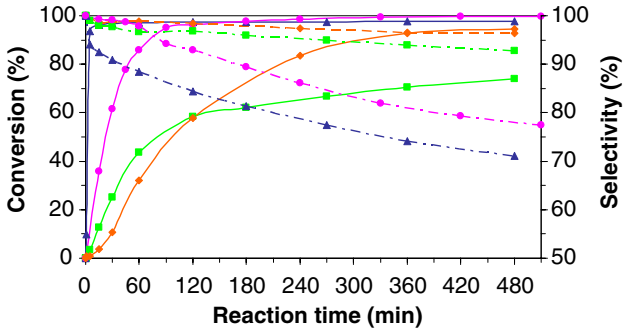


Fig. 2. Conversion (full lines) and selectivity for 2-octene (dotted lines) as functions of reaction time for the isomerization of neat 1-octene (100,000 equivalents) at 100 °C in the presence of catalysts **4** (◆), **6** (▲), **8** (●) and **9** (■).

Table 2
Hydrogenation of 1-octene with hydride **4**[a]

Entry	Equiv.	*T* (°C)	*P* (bar)	*t* (h)	Conv. (%)	TON	Isom. (%)	2-Octene (%)	*cis*:*trans* Ratio
1	100,000	23	4	22	56.0	56,000	2.8	64	56:64
2	100,000	100	4	3	98.1	98,100	19.6	72	31:69
3	250,000	100	1	3	97.0	242,000	67	75	33:67
4	350,000	100	4	2	43.0	151,000	31	72	39:61

[a] Hydrogenation experiments were conducted in an autoclave fitted with a glass liner. The autoclave was filled with the substrate, the catalyst and then quickly set to the desired H_2 pressure and temperature.

The new complex **4** was tested for its hydrogenation and isomerization properties for 1-octene; the results were compared with the literature data [4].

Table 1 shows the isomerization activity of complex **4** and the graphs (Figs. 1 and 2) illustrate comparisons with literature data.

Hydrogenation experiments on 1-octene were conducted in an autoclave that was filled with hydrogen to the desired pressure and subsequently allowed to come to the required temperature.

As is evident from the results reported in Table 2 a significant increase in the percentage of isomerization products was recorded for **4** when compared to the activity of similar catalysts in the literature [4]. This could be due to the additional steric bulk of the carbene ligand in **4** which impedes the hydrogenation of internal olefins (once produced by the isomerization side reaction). In order to ascertain whether the hydrogenation selectivity for α-olefins was 100%, additional tests on an internal olefin were also conducted.

When 2-octene was used a mixture of octane and *cis* and *trans* 2-octene was obtained (conversion: 74%) revealing that the hydrogenation selectivity for α-olefins is not 100% and that the hydrogenation of internal olefins is slower than with previous hydride catalysts [4].

In conclusion, the isopropylidene hydride **4** was isolated and characterized for the first time. Reactivity tests showed it to be a highly active isomerization and hydrogenation catalyst. Such species also represent the main degradation product of catalyst **3** in a basic alcoholic solution, providing therefore a further step forward towards the possibility to perform tandem metathesis/isomerization and metathesis/hydrogenation reactions.

Acknowledgements

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version at doi:10.1016/j.jorganchem.2004.07.033.

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[7] Upon addition of methanol to the toluene reaction mixture the unreacted diphosphine species **8** was precipitated first and quickly cannula filtrated. Then (upon evaporation of ca. 30% of the solvent) the desired hydride species **4** was precipitated, cannula filtrated and isolated as a yellow/greenish solid with 56% yield (based on 95% conversion). [RuClH(CO)(H_2IPr)(PCy_3)] **4:** IR (KBr): 1901 cm^{-1} (vs, C≡O); ^{31}P NMR (CD_2Cl_2; ppm): 47.04 ppm; ^{1}H NMR (CD_2Cl_2; ppm): −24.35 (d, $^2J_{H,P}$ = 21 Hz, 1H, Ru–H), 1.03–1.68 (m, 33H, PCy_3), 1.26 (d, $^3J_{H-H}$ = 7.0 Hz, 6H, $C(CH_3)_2$), 1.29 (d, $^3J_{H-H}$ = 7.0 Hz, 6H, $C(CH_3)_2$), 1.38 (d, $^3J_{H-H}$ = 6.5 Hz, 6H, $C(CH_3)_2$), 1.44 (d, $^3J_{H-H}$ = 6.5 Hz, 6H, $C(CH_3)_2$), 1.95–2.02 (m, 4H, CH_2–CH_2), 3.58 (sept, $^3J_{H-H}$ = 6.5 Hz, 2H, $CH(CH_3)_2$), 3.70 (sept, $^3J_{H-H}$ = 6.5 Hz, 2H, $CH(CH_3)_2$), 7.24–7.27 (m, 4H, *m*-H $C_6(iPr_2)H_3$), 7.36 (t, $^3J_{H-H}$ = 7.0 Hz, 2H, *m*-H $C_6(iPr_2)H_3$)); $C_{46}H_{72}ClN_2OPRu$: calc. C 66.04, H 8.67, N 3.35. Found C 65.87; H 8.68; N 3.26.