A 14-electron ruthenium hydride: the key intermediate in the synthesis of ruthenium carbene complexes; X-ray structure of [RuHCl(PPr$^i_3$)$_2$]

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A simple one-pot procedure for the synthesis of ruthenium benzylidenes (Grubbs' catalyst) has been developed in which a novel, highly reactive 14-electron ruthenium mono-hydride, prepared from [RuCl$_2$(cod)] and two bulky phosphines in boiling propan-2-ol without the use of hydrogen gas, is reacted with hydrogen chloride, an alkyne and styrene.

The discovery and isolation of the first well-defined ruthenium carbenes of the type [RuCl$_2$(=CH–CH=CPh$_2$)(PR$_3$)$_2$][1] by Grubbs and coworkers in 1992 followed by the second generation of the type [RuCl$_2$(=CHPh)(PR$_3$)$_2$][2] have changed the impact of the olefin metathesis reaction in many chemical applications dramatically.[3] Because of our long standing interest in metathesis chemistry,[4] we, as did many others, investigated the use of these well-defined ruthenium carbene catalysts intensively. We found that with these ruthenium carbenes the total catalyst loading in, for example, the polymerization of dicyclopentadiene (DCPD) dropped significantly compared with our recently published method using an arene ruthenium catalyst, such as [(*p*-cymene)RuCl$_2$(PCy$_3$)] (Cy = cyclohexyl).[5] However, the existing syntheses for these ruthenium carbenes rely on barely accessible or unstable and toxic organic compounds which act as the carbene source, *e.g.* phenyl diazomethane for the synthesis of ruthenium benzylidenes. Therefore, for successful commercial applications, new synthetic routes have to be developed which can be scaled-up more easily. Parallel to our efforts, Werner and coworkers developed a new route to benzyl substituted ruthenium carbenes,[6] whereas Grubbs and coworkers developed novel routes to vinyl and phenyl substituted ruthenium carbenes.[7] In both synthetic routes the key intermediate is the ruthenium monohydride dihydrogen species [RuHCl(H$_2$)(PCy$_3$)$_2$], prepared from [RuCl$_2$(cod)] (cod = cycloocta-1,5-diene) and PCy$_3$ in an atmosphere of dihydrogen, which is subsequently reacted with phenyl acetylene or a propargylic chloride, respectively. We now report a simple one-pot procedure for the synthesis of ruthenium carbenes in which the key intermediate, a novel 14-electron species, is prepared starting from [RuCl$_2$(cod)], 2 equivalents of a bulky phosphine, and an appropriate base, but *without* the use of dihydrogen.[8]

Recently, Werner and coworkers published their results on treating a 'red solution' formed upon heating [RuCl$_2$(cod)] with an excess of PPr$^i_3$ in butan-2-ol under an atmosphere of dihydrogen with phenyl acetylene.[6] This reaction led to the formation of [RuCl$_2$(=CHCH$_2$Ph)(PPr$^i_3$)$_2$] in *ca.* 65% yield. The active ruthenium species in the 'magic' red solution, however, was unknown. Addition of diethyl ether to this red solution led to the isolation of the ruthenium(IV) complex [RuH$_2$Cl$_2$(PPr$^i_3$)$_2$]. It was reported that this ruthenium(IV) dihydride species reacts with phenyl acetylene predominantly yielding the five-coordinate vinylidene complex [RuCl$_2$(=C=CHPh)(PPr$^i_3$)$_2$] with the above mentioned benzyl substituted ruthenium carbene [RuCl$_2$(=CCH$_2$Ph)(PPr$^i_3$)$_2$] only as the side product. It was speculated that the active species in the red solution which led to the ruthenium carbene complex was the monohydride–dihydrogen complex [RuHCl(H$_2$)(PPr$^i_3$)$_2$]. Surprisingly, when we carried out the reaction *without* the use of dihydrogen, the reaction worked as well. We prepared a 'red solution' by boiling [RuCl$_2$(cod)] for 3 h with 2 equiv. of PPr$^i_3$ and 1 equiv. of NEt$_3$ in propan-2-ol under an argon atmosphere. ^{1}H NMR investigations on this solution showed a broad triplet at δ −17, indeed indicating the possible presence of the above mentioned ruthenium monohydride dihydrogen species [RuHCl(H$_2$)(PPr$^i_3$)$_2$].[9] By slowly cooling this red solution from 80 °C to room temperature we could isolate the hydride as blocky, orange crystals. Surprisingly, an X-ray structure determination on these crystals revealed the hydride species to be a tetracoordinate, 14-electron d^6 species with formula [RuHCl(PPr$^i_3$)$_2$] **1**.† Fig. 1 shows the molecular geometry of **1** which can be best described as a square-planar structure with the bulky triisopropylphosphines in *trans* positions.‡

Very recently, Caulton and coworkers also described a 14-electron ruthenium monohydride as the intermediate in the synthesis of heteroatom substituted ruthenium carbene complexes using vinyl ethers as the carbene source.[10] However, this hydride, prepared by dehydrohalogenation of [Ru(H)$_2$Cl$_2$(PR$_3$)$_2$] with lithium 2,2,6,6-tetramethylpiperidide, appears to be a halide bridged dimer.[11]

Subsequent addition of phenyl acetylene and styrene to the red solution containing **1** resulted in the isolation of the 'Grubbs' catalyst' [RuCl$_2$(=CHPh)(PPr$^i_3$)$_2$] in moderate yields. However, when we first added an extra equivalent of hydrogen chloride to the hydride solution at −20 °C, subsequently added the acetylene and styrene, warmed the reaction mixture to room temperature and stirred it for an additional hour, the yield could be increased to 75%.§

In the first step of the reaction, the preparation of monohydride **1**, the formation of 3 equivalents of acetone were detected by gas chromatography; 1 equivalent is the result of the hydride formation whereas the other 2 equivalents originate from the reduction of cod to cyclooctane, which was detected by gas chromatography. Upon addition of the HCl solution in diethyl ether the typical sharp ^{1}H NMR hydride signal at δ −17 disappeared and a very broad signal at δ −5 could be observed. Unfortunately, we were unable to isolate a distinct compound. However, in analogy to the previously described HCl addition
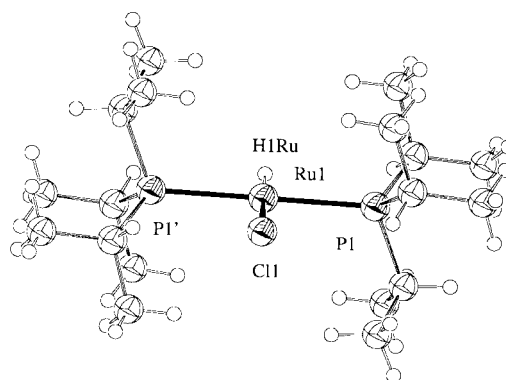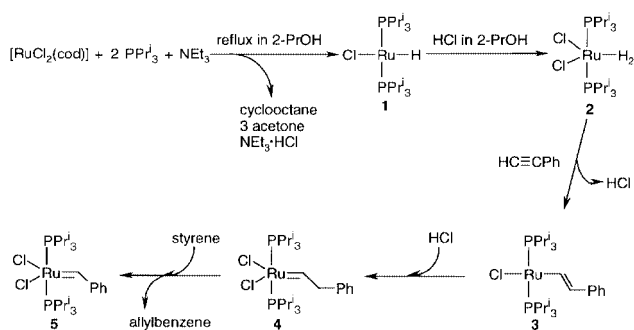

Fig. 1 ORTEP drawing of **1**. Selected bond distances (Å) and angles (°): Ru(1)–P(1) 2.3704(9), Ru(1)–Cl(1) 2.434(3), Ru(1)–H(1Ru) 1.5983; P(1)–Ru(1)–H(1Ru) 90.3, P(1′)–Ru(1)–H(1Ru) 89.7, P(1)–Ru(1)–Cl(1) 89.47(5), P(1′)–Ru(1)–Cl(1) 90.53(5).

Scheme 1

to a similar osmium carbonyl complex,[12] we propose that the intermediate is the ruthenium(II) dichloride dihydrogen complex **2**. This dihydrogen complex reacts upon addition of phenyl acetylene to generate a short-lived 14-eletron alkenyl complex **3** along with the formation of a molecule HCl. **3** immediately reacts with HCl to form the more stable benzyl substituted ruthenium carbene **4**. A simple metathesis reaction with styrene then gives the Grubbs ruthenium benzylidene catalyst **5** which can be easily isolated by filtration and purified by washing with cold methanol. The complete postulated reaction mechanism is depicted in Scheme 1.

These results demonstrate a very simple one-pot synthesis procedure for the preparation of multigram quantities of the Grubbs catalyst without the use of dihydrogen gas, and utilizing only commercially available starting materials. The novel intermediate monohydride complex was isolated and fully characterized and appeared to be a mononuclear, square-planar, 14-electron species. The reactivity of this monohydride species in other reactions, *e.g.* hydrogen transfer reactions, is currently under investigation.

Notes and references

† An X-ray structure determination of the deuterium analog of **1**, *i.e.* [RuDCl(PPr$^i_3$)$_2$] **1D** prepared in propan-2-ol-d$_8$, revealed exactly the same structure. To have absolute proof of this unexpected result we also determined the structure of the tricyclohexylphosphine analogue [RuHCl(PCy$_3$)$_2$] **1Cy**, prepared using DBU as base instead of NEt$_3$. This complex also has a square-planar geometry with the two bulky phosphines in *trans* positions.

‡ *Crystal data* for **1**: C$_{18}$H$_{43}$ClP$_2$Ru, M = 457.98, monoclinic, space group $P2_1/c$ (no. 14), a = 8.0682(5), b = 8.9506(8), c = 16.6435(12) Å, β = 92.76(1)°, V = 1200.5(2) Å^3, Z = 2, μ(Mo-Kα) = 0.895 mm^{-1}, 9038 reflections measured, 2295 unique (R_{int} = 0.042), observed 1938 [$I > 2\sigma(I)$], Final R_1 = 0.038 (obsd. data), wR_2 = 0.122 (all data).

For **1D**: C$_{18}$H$_{42}$DClP$_2$Ru, M = 457.98, monoclinic, space group $P2_1/c$ (no. 14), a = 8.0641(8), b = 8.9361(6), c = 16.6840(15) Å, β = 92.74(1)°, V = 1200.9(2) Å^3, Z = 2, μ(Mo-Kα) = 0.895 mm^{-1}, reflections measured 8559, independent 2272 (R_{int} = 0.022), observed 1977 [$I > 2\sigma(I)$]. Final R_1 = 0.042 (obsd. data), wR_2 = 0.1421 (all data).

For **1Cy**: C$_{36}$H$_{67}$ClP$_2$Ru, M = 698.36, triclinic, space group $P\bar{1}$ (no. 2), a = 9.8438(8), b = 10.2011(8), c = 10.8356(9) Å, α = 114.29(1), β = 108.48(1), γ = 90.82(1)°, V = 927.4(13) Å^3, Z = 1, μ(Mo-Kα) = 0.603 mm^{-1}, 6747 reflections measured, 3181 independent (R_{int} = 0.025), observed 2953 [$I > 2\sigma(I)$]. Final R_1 = 0.041 (obsd. data), wR_2 = 0.128 (all data). Twinned crystal with 6% overlapped reflections, which were omitted. Full spheres of intensity data were collected at 223 K on a Stoe Image Plate Diffraction system using Mo-Kα graphite monochromated radiation. Image plate distance 70 mm, ϕ oscillation scans 0–200°, step $\Delta\phi$ = 1°, 2θ range 3.27–52.1°, $d_{max}-d_{min}$ = 12.45–0.81 Å.

The structures were solved by direct methods using the program SHELXS-97.[13] The refinements and all further calculations were carried out using SHELXL-97.[14] The alkyl group H-atoms were included in calculated positions and treated as riding atoms using SHELXL-97 default parameters. In all three compounds the hydride (H1Ru) could be located from a final difference map (*ca.* 1.7 e Å^{-3}), at a distance of 1.6–1.8 Å from the Ru atom. In the final refinement cycles it was held fixed with a U_{iso} = 1.5U_{eq}(Ru) Å^2. The non-H atoms were refined anisotropically, using weighted full-matrix least squares on F^2. An empirical absorption correction was applied for all three compounds but a small amount of residual density was still located near the Cl atoms. All three structures are centrosymmetric implying disordered structures with the Cl and hydride sites being 50% occupied.

CCDC 182/1627. See http://www.rsc.org./suppdata/cc/b0/b002298p/ for crystallographic files in .cif formed.

§ *Synthetic procedure*: a suspension of [RuCl$_2$(cod)] (5.00 g, 17.8 mmol) in 125 ml propan-2-ol was treated with PPr$^i_3$ (7.0 ml, 36.6 mmol) and NEt$_3$ (5.0 ml, 36.0 mmol) and refluxed under argon for 3 h. The resulting red coloured, clear solution was cooled to −20 °C and changed to an orange suspension. To this suspension was added dropwise 35 ml of a 1 M HCl solution in diethyl ether over a period of *ca* 15 min keeping the temperature around −20 °C. The reaction mixture was stirred for an additional 10 min, and phenylacetylene (4.0 ml, 36.4 mmol) was added dropwise keeping the reaction mixture below −15 °C. Subsequently, the reaction mixture was stirred for 2 h at between −20 and −15 °C. The resulting purple suspension was treated with styrene (8.0 ml, 70 mmol), the temperature was slowly raised to room temperature and the reaction mixture was allowed to stir for an additional hour. The reaction mixture was partially concentrated and the product filtered off. The purple product was washed with methanol (2 × 10 ml), and dried *in vacuo*. This procedure yielded 7.7 g of [RuCl$_2$(=CHPh)(P-Pr$^i_3$)$_2$] (75%). A similar procedure can be used for the synthesis of [RuCl$_2$(=CHPh)(PCy$_3$)$_2$], except that DBU has to be used as base instead of NEt$_3$.

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