46.4 (d), 26.5 (q), 25.6 (t), 24.4 (q), 22.9 (t), 18.9 (t); MS (EI 70 eV): *m/z* (%): 246 (3), 228 (20), 185 (10), 155 (36), 135 (28), 112 (29), 95 (100), 91 (52); HR-MS calcd for $C_{16}H_{20}O_2$: 246.1620; found: 246.1621.

1,2,3,3a,4,9,10,10a-Octahydro-3a,10-dimethyl-4,10-epoxybenz[*f*]azulene (**2a**): A solution of **1a** (0.30 g, 1.22 mmol) in CH_2Cl_2 (50 mL) at $-78\,^\circ C$ was treated with $SnCl_4$ (0.29 mL, 2.44 mmol) and then stirred at that temperature for 105 min. The mixture was poured onto ice (10 g), and the solution extracted with CH_2Cl_2 (3×50 mL). The combined organic extracts were washed with brine (50 mL) and dried ($MgSO_4$). Evaporation gave an oil, which was purified by column chromatography (silica gel, petroleum ether/ethyl acetate 94/6) to give **2a** (0.22 g, 80%) as a white solid. M.p. 37 °C. IR (KBr): $\tilde{\nu}=3950$, 1450, 1000 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): $\delta=7.18-7.07$ (2H, m), 7.02 (1H, t, $J=8$ Hz), 6.92 (1H, d, $J=8$ Hz), 4.46 (1H, s), 2.93 (1H, d, $J=17$ Hz), 2.78 (1H, d, $J=17$ Hz), 2.10 (1H, m), 1.65–0.90 (6H, m), 1.48 (3H, s), 1.38 (3H, s); ^{13}C NMR (68.8 MHz, $CDCl_3$): $\delta=138.5$ (s), 134.2 (s), 127.9 (d), 127.0 (d), 126.1 (d), 125.0 (d), 86.6 (d), 83.0 (s), 63.8 (d), 59.7 (s), 36.9 (t), 35.5 (t), 30.8 (q), 29.0 (t), 29.0 (q), 27.9 (t); MS (EI 70 eV): *m/z* (%): 228 (M, 10), 145 (100), 131 (27), 109 (55); HR-MS calcd for $C_{16}H_{20}O$: 228.3370; found: 228.3365.

1,2,3,3a,4,9,10,10a-Octahydro-3a,10-dimethyl-4,10-epoxybenz[*f*]azulene (**2b**): A solution of **1b** (0.30 g, 1.22 mmol) in CH_2Cl_2 (50 mL) at $-78\,^\circ C$ was treated with $SnCl_4$ (0.29 mL, 2.44 mmol) and then stirred at that temperature for 75 min. The mixture was poured onto ice (10 g), and the solution extracted with CH_2Cl_2 (3×50 mL). The combined organic extracts were washed with brine (50 mL) and dried ($MgSO_4$). Evaporation gave an oil, which was purified by column chromatography (silica gel, petroleum ether/ethyl acetate 94/6) to give **2b** (0.19 g, 69%) as an oil; IR (KBr): $\tilde{\nu}=3950$, 1450, 1370, 1000 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): $\delta=7.15-7.05$ (2H, m), 7.00 (1H, t, $J=8$ Hz), 6.88 (1H, d, $J=8$ Hz), 4.47 (1H, s), 2.96 (1H, d, $J=17$ Hz), 2.54 (1H, d, $J=17$ Hz), 1.90–1.45 (7H, m), 1.32 (3H, s), 0.63 (3H, s); ^{13}C NMR (68.8 MHz, $CDCl_3$): $\delta=138.9$ (s), 132.6 (s), 128.8 (d), 126.8 (d), 125.6 (d), 125.0 (d), 86.2 (d), 81.6 (s), 59.3 (s), 58.5 (d), 43.7 (t), 41.7 (t), 29.7 (t), 27.3 (t), 24.6 (q), 23.0 (q); HR-MS calcd for $C_{16}H_{20}O$: 228.3370; found: 228.3377.

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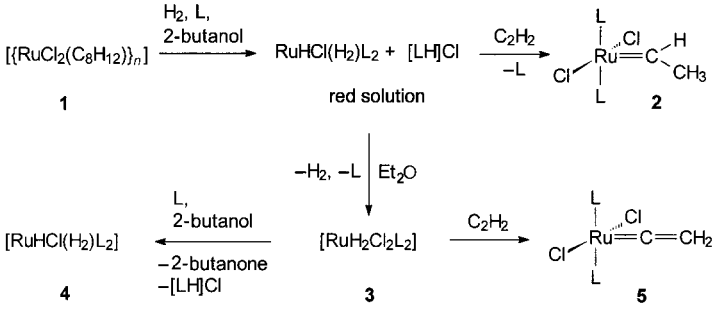
Ruthenium Trichloride, Tricyclohexylphosphane, 1-Alkynes, Magnesium, Hydrogen, and Water—Ingredients of an Efficient One-Pot Synthesis of Ruthenium Catalysts for Olefin Metathesis

Justin Wolf, Wolfram Stüer, Claus Grünwald, Helmut Werner,* Peter Schwab, Michael Schulz

Ruthenium carbene complexes of the type $[RuCl_2(=CHR)(PR'_3)_2]$, are highly efficient catalysts for olefin metathesis. On account of their unique properties, for example, their stability to oxygen and their tolerance of diverse functional groups, they have been increasingly used in organic synthesis, since their discovery by Grubbs and coworkers.[1] The extreme demand and the manifold applications of these catalysts have inevitably initiated the search for alternative synthetic routes that avoid the use of carbene precursors such as diphenylcyclopropenes or diazoalkanes utilized in the established routes. These carbene precursors are either difficult to access or problematic in their handling.[2] The goal set by these demands is fulfilled by a synthetic route recently established in our laboratory that starts from hydrido complexes of ruthenium and 1-alkynes.[3] We found that on reaction of $[\{RuCl_2(C_8H_{12})\}_n]$ (**1**) with hydrogen and P*i*Pr$_3$ in 2-butanol at 80 °C a red solution is formed, which reacts with ethyne (at 25 °C) to afford the carbene complex $[RuCl_2(=CHCH_3)(PiPr_3)_2]$ (**2**). After workup of the red solution with ether, the dihydridoruthenium(IV) compound **3** is obtained in nearly quantitative yield (based on **1**). Complex **3**, however, does not give the carbene complex **2** on reaction with ethyne but rather the vinylidene complex **5** (see Scheme 1).[3, 4]



Scheme 1. L = P*i*Pr$_3$.

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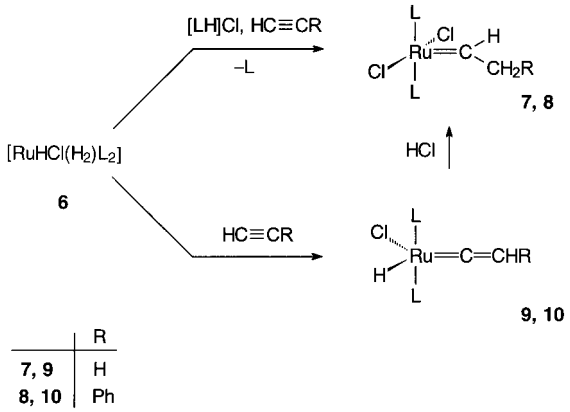
In the course of our efforts to reveal the mechanism of formation of the compounds **2** and **5** we developed a simple and efficient one-pot synthesis of the carbene complexes $[RuCl_2(=CHR)(PCy_3)_2]$. The rationale of our approach was based on the perception that the red solution initially formed from **1**, hydrogen, and P*i*Pr$_3$ contains $[HP{i}Pr_3]Cl$ and the monohydrido dihydrogen compound **4**.[5] The formation of **2** from this solution and the conversion into **3** requires the presence of chloride ions and a proton source. Moreover, we noted that complex **3** in solutions of 2-butanol gives **4** even in the absence of hydrogen at room temperature. Thus the stoichiometrically required equivalent of hydrogen is supplied by dehydration of the secondary alcohol.

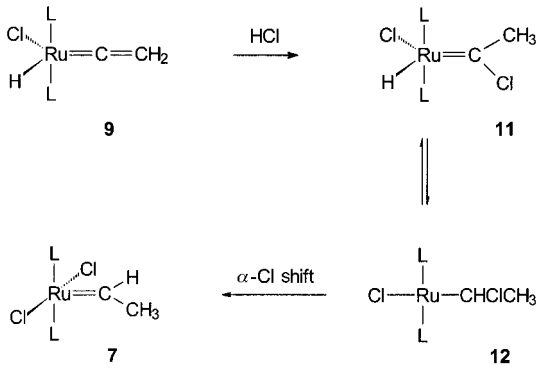
In view of the straightforward preparation and isolation of the tricyclohexylphosphane compound **6**[5] (Scheme 2), structurally related to **4**, we used **6** for further mechanistic



Scheme 2. L = PCy$_3$.

investigations. Like **4** complex **6** reacts with ethyne or phenylacetylene in the presence of one equivalent of $[HPCy_3]Cl$ to give the carbene complexes **7**[2d] and **8** in almost quantitative yield. In contrast, in the absence of the phosphonium salt the hydrido vinylidene compounds **9** and **10** are formed. These complexes are less stable than the corresponding triisopropylphosphane derivatives $[RuHCl(=C=CHR)(P{i}Pr_3)_2]$ that were also prepared in our laboratory[4] and decompose in benzene or CH_2Cl_2 at room temperature within a few hours. Analogous compounds with P*t*Bu$_2$Me as phosphane ligand have been recently described by Caulton and co-workers.[6]

As expected, compounds **9** and **10** react with $[HPCy_3]Cl$ to give the carbene complexes **7** and **8**. Hydrogen chloride (in benzene) can also be used as the proton source. With regard to the mechanism of this reaction, we assume that HCl initially attacks the C=C double bond of the vinylidene ligand. From the resulting intermediate **11** (Scheme 3) the 14-electron species **12** is formed by carbene insertion into the Ru–H bond. Such α-chloroalkyl compounds were also proposed by Grubbs et al. as intermediates in the recently described synthesis of $[RuCl_2(=CHCH_2R)(PCy_3)_2]$ (R = H, Me) from **6** and vinyl chlorides RCH=CHCl.[7] The complex $[RuCl_2(=CHCH_2D)(PCy_3)_2]$ ($[D_1]$**7**) is obtained exclusively from the reaction of **9** with DCl and has been characterized by ^{2}H NMR spectroscopy; this result is in agreement with the mechanism discussed above.



Scheme 3. L = PCy$_3$.

As the relatively weak acid $[HPCy_3]Cl$ is sufficient as a source of HCl for the conversion of **9** and **10** into the carbene complexes **7** and **8**, respectively, we investigated whether the first step of the reaction is a nucleophilic attack of the chloride at the α-C-atom of the vinylidene ligand or at the metal center. The reaction of compound **9** with $[Ph_3PNPPh_3]Cl$ ([PPN]Cl) or $MgCl_2$ in THF was carried out. Whereas in the first case no reaction was observed, small amounts of **7** were formed on treatment of **9** with $MgCl_2$. That the residual content of water in the $MgCl_2$ is responsible for this reaction was shown by addition of extra water to the reaction mixture of **9** and $MgCl_2$, which afforded complete conversion into the carbene complex **7** within seconds. On the other hand, the reaction of **9** with [PPN]Cl and H_2O is significantly slower and only completed after about 5 hours. The active role of $MgCl_2$ in the formation of **7** is also supported by the fact that in the presence of $MgCl_2$ but not of [PPN]Cl acetylene can serve as the proton source instead of water.

In view of these results, it was obvious that **6**, ethyne, $MgCl_2$ and H_2O should give the carbene complex **7** (via the intermediate formation of **9**). This conclusion led to the development of a simple one-pot synthesis of **7**.[8] Commercially available $RuCl_3 \cdot 3H_2O$ in THF was reduced to compound **6** in the presence of PCy$_3$ with Mg/$ClCH_2CH_2Cl$ under a hydrogen atmosphere at 60–85 °C. The activation of magnesium with 1,2-dichloroethane serves not only to accelerate the reduction, but also to increase the concentration of $MgCl_2$. After cooling of the reaction mixture to −40 °C, ethyne (two equivalents) was introduced along with a small excess of water. On warming to room temperature the formation of the carbene complex **7** occurs, which after removal of the solvent in vacuo can be extracted from the crude residue with pentane to give 75% yield of the isolated product. In a similar manner, again by one-pot synthesis, compound **8** is obtained. In this case it is noteworthy that under the reaction conditions the intermediate complex **6** reacts with phenylacetylene by substitution of H_2. Therefore, in contrast to the formation of **7**, only one equivalent of the alkyne is needed for the preparation of **8**.

The method presented here is the most convenient for the preparation of the catalytically active carbeneruthenium(II) compounds $[RuCl_2(=CHCH_2R)(PCy_3)_2]$ developed to date. The principal advantage is that it avoids starting materials which are not easily accessible, such as $[RuCl_2(PPh_3)_3]$,[2]

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$[Ru(\eta_4\text{-}C_8H_{12})(\eta_6\text{-}C_8H_{10})]$,[9] or $[RuH_2(H_2)_2(PCy_3)_2]$,[5, 10] and uses 1-alkynes instead of cyclopropenes, diazoalkanes, vinyl chlorides, or propargylic chlorides as carbene source. The complexes **7** and **8**, which display about the same catalytic activity as the hitherto most commonly used compound $[RuCl_2(=CHPh)(PCy_3)_2]$, can now be prepared on a larger scale. Our method of using 1-alkynes also allows the synthesis of other carbene compounds such as $[RuCl(X)(=CHCH_2R)(PCy_3)_2]$ ($X = CF_3CO_2$, CN), the catalytic properties of which are currently being investigated.[11]

Experimental Section

7: Mg (2 g, 82.3 mmol) in THF (100 mL) was activated with 1,2-dichloroethane (2 mL). Tricyclohexylphosphane (9 g, 32.1 mmol) and $RuCl_3 \cdot 3H_2O$ (2 g, 7.65 mmol) were then added . The mixture was warmed under an atmosphere of hydrogen and vigorously stirred first for 2 h at 65 °C and then for 2 h at 85 °C. A red solution formed and an orange solid precipitated. The reaction mixture was then cooled to −40 °C, and ethyne (380 mL, ca. 15.8 mmol) was introduced by gas burette. The solution was then stirred for 5 min at −40 °C, followed by the addition of H_2O (0.5 mL, 27.8 mmol). After the reaction mixture was warmed to room temperature the solvent was removed, the crude product was transfered to a soxhlet apparatus and extracted with pentane (250 mL) for 12 h. A pink solid was isolated, which was washed with pentane (20 mL) and dried in vacuo. Yield: 4.37 g (75 %). For spectroscopic data see ref. [2d].

8: As described for **7**, with $RuCl_3 \cdot 3H_2O$ (0.5 g, 1.91 mmol), THF (25 mL), Mg (0.5 g, 20.6 mmol), $ClCH_2CH_2Cl$ (0.5 mL), and PCy_3 (2.31 g, 8.2 mmol) as starting materials. After the reduction the reaction mixture was cooled to −40 °C and phenylacetylene (0.22 mL, 1.91 mmol) was added dropwise, which caused a vigorous evolution of gas. The solution was stirred for 20 min at −40 °C, and then warmed to 0 °C, and H_2O (0.13 mL, 7.2 mmol) was added. After further warming to room temperature and continuous stirring for another 10 min, the solvent was removed, and the residue extracted with toluene (60 mL). The extract was dried in vacuo, and the purple residue was washed four times with pentane (4 × 10 mL) and twice with methanol (2 × 40 mL). Yield: 1.21 g (76 %). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 19.40$ [t, ^3J(H,H) = 5 Hz, 1H, C*H*CH$_2$Ph], 7.30 – 7.12 (m, 5H, Ph-H), 3.98 [d, ^3J(H,H) = 5 Hz, 2H, CHC*H*$_2$Ph]; ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 316.5$ [t, ^2J(C,P) = 7 Hz, *C*HCH$_2$Ph], 138.9, 128.3, 128.2, 126.3 (je s, C-Ph), 64.5 (s, CH*C*H$_2$Ph); ^{31}P NMR (162 MHz, $CDCl_3$): $\delta = 34.6$ (s).

9: Ethyne was passed through a stirred solution of **6** (102 mg, 0.146 mmol) in CH_2Cl_2 (10 mL) at −78 °C for 30 s. The solvent was removed under reduced pressure, and the brown residue was washed with pentane (5 mL) and dried in vacuo. Yield: 99 mg (94 %). ^{1}H NMR (400 MHz, C_6D_6): $\delta =$ 2.70 [d, ^3J(P,H) = 3 Hz, 2H, RuCC*H*$_2$], −16.17 [t, ^2J(P,H) = 18 Hz, 1H, RuH]; ^{13}C NMR (100.6 MHz, C_6D_6): $\delta = 326.2$ [t, ^2J(P,C) = 15 Hz, Ru*C*CH$_2$], 86.6 [t, ^3J(P,C) = 4 Hz, RuC*C*H$_2$]; ^{31}P NMR (162 MHz, $CDCl_3$): $\delta = 41.5$ (s).

10: To a solution of **6** (96 mg, 0.137 mmol) in CH_2Cl_2 (10 mL) phenylacetylene (28.0 μL, 0.274 mmol) was added at −78 °C. After warming to room temperature, the solution was concentrated under reduced pressure to ca. 2 mL. Upon addition of pentane a green solid precipitated, which was removed by filtration and dried in vacuo. Yield: 80 mg (73 %). ^{1}H NMR (200 MHz, C_6D_6): $\delta = 4.41$ (br s, RuCC*H*Ph), −12.88 [t, ^2J(P,H) = 17 Hz, 1H, RuH]; ^{31}P NMR (162 MHz, C_6D_6): $\delta = 41.3$ (s).

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Exceptionally Simple Enantioselective Syntheses of Chiral Hexa- and Tetracyclic Polyprenoids of Sedimentary Origin**

Elias J. Corey,* Guanglin Luo, and Linus Shouzhong Lin

A recent publication described the isolation of a series of four novel chiral polycyclic hydrocarbons from Eocene Messel shale (Germany), which appear to be remnants of an ancient family of cyclopolyprenoids.[1] This series includes the hexacyclic and tetracyclic hydrocarbons **1** and **2** as well as their pentacyclic analogue. In addition, GC-MS evidence was obtained for the occurrence in other sediments of the hepta- and octacyclic homologues of **1** and **2** in small amounts.[1] We report here the first syntheses of **1** and **2** by relatively short routes that take advantage of several recently introduced synthetic methods, especially regio- and enantioselective catalytic dihydroxylation of polyprenol esters,[2–4] stereospecific two-component synthesis of tri- and tetrasubstituted olefins,[3–5] and stereoselective Lewis acid catalyzed polycyclization of chiral polyunsaturated oxiranes.[3, 4, 6, 7]

The synthesis of the benzoperhydropicene derivative **1** is outlined in Scheme 1. α-Deprotonation of sulfone **3** with *n*BuLi generated the corresponding α-lithio derivative, which upon treatment with chiral acylsilane **4**[4] provided stereospecifically the coupling product **5** in a reaction that proceeds

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