ELSEVIER

Journal of Organometallic Chemistry 641 (2002) 220–226

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

An 'Old Hydride' in a new synthesis: a convenient approach to Grubbs-type carbene complexes $(PPh_3)_2Cl_2Ru{=}CH{-}CH{=}CR_2$ and their hexacoordinate acetonitrile adducts

Martin A.O. Volland, Frank Rominger, Frank Eisenträger, Peter Hofmann *

Organisch-Chemisches Institut der Ruprecht-Karls-Universität Heidelberg, Im Neuenheimer Feld 270, D-69120 Heidelberg, Germany

Received 21 September 2001

Dedicated to Professor Rolf Gleiter on the occasion of his 65th birthday

---

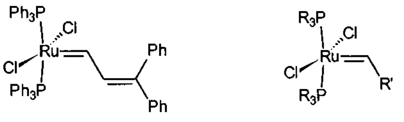
Abstract

A convenient synthetic route to Grubbs-type complexes $(PPh_3)_2Cl_2Ru{=}CH{-}CH{=}CR_2$ by reacting Wilkinson's hydride $(PPh_3)_3Ru(H)Cl$ with propargyl or allenyl chlorides, and the isolation of an adduct complex $(CH_3CN)(PPh_3)_2Cl_2Ru{=}CH{-}CH{=}CMe_2$ (**3**) by treatment of $(PPh_3)_3Ru(H)Cl$ with 3-chloro-3-methyl-1-butyne in the presence of CH_3CN are reported. NMR studies in CD_2Cl_2 show hexacoordinate $(CH_3CN)(PPh_3)_2Cl_2Ru{=}CH{-}CH{=}CMe_2$ (**3**) to be in equilibrium with CH_3CN and pentacoordinate $(PPh_3)_2Cl_2Ru{=}CH{-}CH{=}CMe_2$ (**2**), the solid state structure of which is presented. X-ray characterization of $[(CH_3CN)_3(PPh_3)_2Ru{=}CH{-}CH{=}CMe_2](OTf)_2$ (**6**), the first mononuclear, dicationic complex derived from a Grubbs-type carbene, obtained by treatment of $(CH_3CN)(PPh_3)_2Cl_2Ru{=}CH{-}CH{=}CMe_2$ (**3**) with trimethylsilyl triflate in the presence of an excess of CH_3CN has been performed. This result indicates the possibility of stabilizing such species by labile donor ligands.

Keywords: Ruthenium hydrides; Ruthenium carbenes; Grubbs catalyst; Cationic ruthenium carbenes; Olefin metathesis catalysts

1. Introduction

Since the initial disclosure of the ruthenium(II) carbene olefin metathesis catalyst $(PPh_3)_2Cl_2Ru{=}CH{-}CH{=}CPh_2$ (**1**) by Grubbs [1], such complexes have found many applications in organic synthesis and polymer chemistry due to their stability and functional group tolerance [2] (Fig. 1).



1

Fig. 1. Grubbs-type carbene complexes.

This has led to the rapid development of these systems by rational structure design in the past decade, which has been reviewed thoroughly in recent reports by Fürstner [2d] and Grubbs and coworkers [2e]. Several synthetic routes to the various types of neutral Grubbs-complexes $(PR_3)_2Cl_2Ru{=}CHR$ have been developed [2–4]. In most of these syntheses, trialkyl phosphine ligands PR_3 have been used due to the higher olefin metathesis activity of the resulting complexes. A drawback of some of the available preparative procedures lies in the fact that they involve substrates, which are not readily available or are difficult to handle, such as cyclopropenes [1], diazo compounds [3] or Ru precursors like Ru(η^4-COD)(η^6-COT) [4e]. A convenient, general synthesis of complexes $(PCy_3)_2Cl_2Ru{=}CHR$ (R = alkenyl or alky group) by treatment of the hydride–dihydrogen precursor $Ru(H)Cl(H_2)(PCy_3)_2$ [5] with propargyl and vinyl chlorides was reported by Grubbs and coworkers [4d], and a related one-pot preparation using C_2H_2 or terminal acetylenes as or-

---

* Corresponding author. Tel.: +49-6221-548502; fax: +49-6221-544885.

E-mail address: ph@phindigo.oci.uni-heidelberg.de (P. Hofmann).

0022-328X/02/$ - see front matter © 2002 Published by Elsevier Science B.V.
PII: S0022-328X(01)01361-4

Table 1
Selected bond lengths [Å] and angles [°] for $(PPh_3)_2Cl_2Ru{=}CH{-}CH{=}CMe_2$ (**2**)

Bond lengths	
Ru1–C1	1.844(4)
Ru1–Cl1	2.337(1)
Ru1–Cl2	2.350(1)
Ru1–P2	2.373(1)
Ru1–P1	2.400(1)
C1–C2	1.422(6)
C2–C3	1.367(6)
C3–C5	1.488(6)
C3–C4	1.491(6)
Bong angles	
C1–Ru1–Cl1	106.92(13)
C1–Ru1–Cl2	101.95(13)
Cl1–Ru1–Cl2	151.13(4)
C1–Ru1–P2	91.65(15)
Cl1–Ru1–P2	89.97(4)
Cl2–Ru1–P2	88.69(3)
C1–Ru1–P1	102.07(15)
Cl1–Ru1–P1	87.40(3)
Cl2–Ru1–P1	87.10(3)
P2–Ru1–P1	166.20(4)

ganic substrates has been reported by Werner and coworkers [4a,4b]. This type of synthesis via ruthenium hydride complexes is also applicable to carbene complexes containing bulky chelating diphosphinoalkane ligands [6] and has been extended to allenyl chlorides as substrates [7].

Although Grubbs-type complexes $(PPh_3)_2Cl_2Ru{=}CHR$, containing two PPh_3 ligands, are less active catalysts, they are especially useful as precursors for ligand exchange reactions, since aryl phosphines are often more easily substituted than alkyl phosphines.

Here we report a facile synthesis of triphenylphosphine containing complexes $(PPh_3)_2Cl_2Ru{=}CH{-}CH{=}CR_2$ by treatment of the easily accessible and easy-to-handle hydride $(PPh_3)_3Ru(H)Cl$, first prepared by Wilkinson more than 30 years ago [9], with propargyl or allenyl chlorides [8]. The triphenylphosphine bearing complexes obtained by this synthesis provide access to a variety of further Grubbs-type and other ruthenium carbenes. Furthermore, the hexacoordinate adduct complex $(CH_3CN)(PPh_3)_2Cl_2Ru{=}CH{-}CH{=}CMe_2$ (**3**) as well as the X-ray structure of $[(CH_3CN)_3(PPh_3)_2Ru{=}CH{-}CH{=}CMe_2](OTf)_2$ (**4**), the first dicationic derivative of a Grubbs-type carbene complex, are presented.

2. Results and discussion

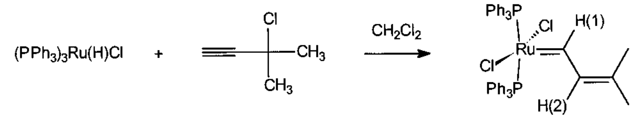
2.1. A convenient approach to $(PPh_3)_2Cl_2Ru{=}CH{-}CH{=}CR_2$

In the course of screening suitable ruthenium precursors for carbene complexes containing chelating diphosphinoalkane ligands, it was found that the readily available Wilkinson hydride $(PPh_3)_3Ru(H)Cl$ [9], upon treatment with 3-chloro-3-methyl-1-butyne, reacts to form $(PPh_3)_2Cl_2Ru{=}CH{-}CH{=}CMe_2$ (**2**) (Scheme 1).

The brownish red complex **2** can be isolated in 75% yield (93% purity) and is obtained analytically pure upon recrystallization from $CH_2Cl_2{-}Et_2O$ at −30 °C.

Alternatively, treatment of $(PPh_3)_3Ru(H)Cl$ with 3-chloro-3-methyl-1-butyne and subsequent addition of other ligands, e.g. 1,2-bis(di-*t*-butylphosphino)ethane ($^tBu_2PCH_2CH_2P^tBu_2$, dtbpe) or PCy_3, to the reaction mixture establishes one-pot syntheses of related ruthenium carbene complexes by phosphine exchange [17].

In the ^1H-NMR spectrum of **2** in CD_2Cl_2, the characteristic pseudo quartet of H(1) is detected at $\delta = 18.10$ ('q', $^3J(H,H) = 9.8$ Hz, $^3J(H,P) = 9.8$ Hz). In the $^{13}C\{^1H\}$-NMR spectrum, a weak signal is observed for Ru=*C*H at $\delta = 291.1$, while the $^{31}P\{^1H\}$-NMR spectrum shows a singlet at $\delta = 27.1$. Recrystallization of **2** from $CH_2Cl_2{-}Et_2O$ at −30 °C yielded single crystals suitable for a high quality X-ray structural determination. This structure, containing an unsaturated carbene moiety, was determined for comparison with related species [10]. An ORTEP diagram is given in Fig. 2 and important bond lengths and angles are collected in Table 1. Complex **2** has the usual distorted square-pyramidal geometry about Ru in the solid state, as has been previously found for related complexes with a different carbene moiety [1,11,12].



2

Scheme 1.

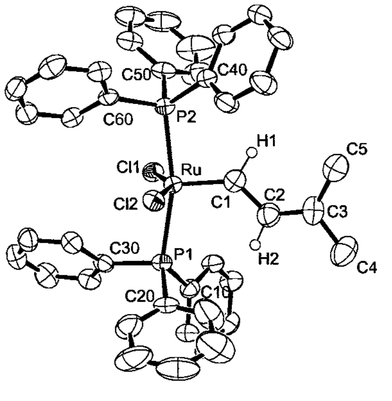


Fig. 2. ORTEP diagram of $(PPh_3)_2Cl_2Ru{=}CH{-}CH{=}CMe_2$ (**2**); H atoms except for H1 and H2 of the carbene moiety are omitted for clarity. The thermal ellipsoids are drawn at the 50% probability level.

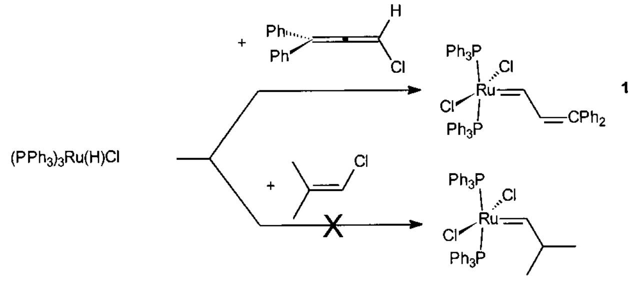
Treatment of the hydride $(PPh_3)_3Ru(H)Cl$ in CD_2Cl_2 in an NMR tube with the allenyl chloride 3-chloro-1,1-diphenyl-1,2-propadiene at ambient temperature leads to the formation of $(PPh_3)_2Cl_2Ru{=}CH{-}CH{=}CPh_2$ (**1**), the compound initially disclosed by Grubbs [1]. However, $(PPh_3)_3Ru(H)Cl$ in CD_2Cl_2 does not react with vinyl chlorides as e.g. 1-chloro-2-methylpropene to form the desired carbene complex within 8 days at ambient temperature (Scheme 2).

Thus, the facile accessibilty of Wilkinson's hydride $(PPh_3)_3Ru(H)Cl$, its clean reaction with alkynyl and allenyl halide substrates and the readiness of PPh_3 substitution reactions provide a novel, convenient two-step procedure for a wide variety of metathesis catalysts with monodentate or chelating ligands.

2.2. Hexacoordinate acetonitrile adducts of Grubbs-type complexes

Different reaction conditions for the synthetic procedure of $(PPh_3)_2Cl_2Ru{=}CH{-}CH{=}CMe_2$ using propargyl chlorides were tested. Wikinson has shown that the complex $[(PPh_3)_3(CH_3CN)_2RuH][Cl]$ is formed in the presence of CH_3CN as shown in Fig. 3 [13].

Thus, it seemed interesting to investigate how $[(PPh_3)_3(CH_3CN)_2RuH][Cl]$ reacts with 3-chloro-3-methyl-1-butyne. Accordingly, the solvents CH_2Cl_2 and CH_3CN were used in a 3:1 ratio to treat $(PPh_3)_3Ru(H)Cl$ with 3-chloro-3-methyl-1-butyne at ambient temperature in order to synthesize $(PPh_3)_2Cl_2Ru{=}CH{-}CH{=}CMe_2$ (**2**). Instead of the expected product **2**, a yellow–green powder is obtained. On the basis of NMR and IR analysis (vide infra), the product has been identified as the hexacoordinate adduct complex $(CH_3CN)(PPh_3)_2Cl_2Ru{=}CH{-}CH{=}CMe_2$ (**3**) with a *trans*-coordination of the carbene and the acetonitrile ligand (Scheme 3). In an alternative procedure for the synthesis of $(PPh_3)_2Cl_2Ru{=}CH{-}CH{=}CPh_2$ by Harlow et al., the formation of an analogous CH_3CN adduct is not described [8].



Scheme 2.

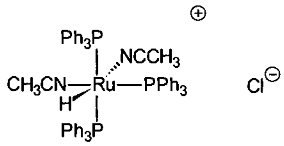
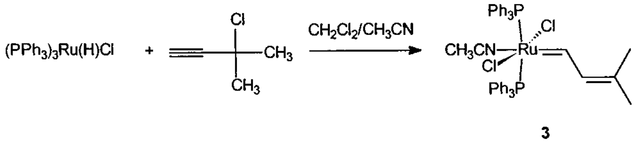


Fig. 3. Cationic hydride complex $[(PPh_3)_3(CH_3CN)_2RuH][Cl]$.

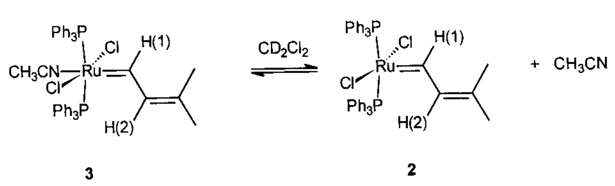
Complex **3** is very soluble in CH_2Cl_2, but sparingly soluble in THF or toluene. Interestingly, the ^1H-NMR spectrum of the yellow–green powder in CD_2Cl_2 at 298 K contains resonances of both **3** and **2** as well as of non-coordinated CH_3CN. Upon addition of an excess of CH_3CN the equilibrium is shifted towards **3** (Scheme 4).

The existence of this equilibrium was confirmed independently by treating complex **2**, synthesized by the procedure described in the first section of this report, with an excess of CH_3CN in CD_2Cl_2.

Compound **3** displays a characteristic doublet of triplets at $\delta = 17.74$ ($^3J(H, H) = 13.5$ Hz, $^3J(H, P) = 3.6$ Hz) in the ^1H-NMR spectrum in CD_2Cl_2 at 298 K, corresponding to a slight upfield shift of 0.3 ppm for the H(1) of **3** in comparison to the H(1) of **2**. For the coordinated acetonitrile $C\mathit{H}_3CN$ a singlet at $\delta = 1.31$ is detected. This represents an upfield shift of 0.66 ppm compared to non-coordinated $C\mathit{H}_3CN$ at $\delta = 1.97$. The $^{31}P\{^1H\}$-NMR spectrum contains a singlet at $\delta = 20.8$, which is 6.8 ppm upfield of the signal for **2**. In contrast, in the $^{13}C\{^1H\}$-NMR spectrum the $Ru{=}\mathit{C}H$ is shifted downfield by 27 ppm to $\delta = 318.1$ upon CH_3CN coordination. The GIAO magnetic shielding values calculated by DFT (B3LYP/LANL2DZ) [14,15] for the fully geometry optimized, simplified model systems $(CH_3CN)(PH_3)_2Cl_2Ru{=}CH_2$ (**4**) and $(PH_3)_2Cl_2Ru{=}CH_2$ (**5**) are in agreement with these spectroscopic data (Fig. 4).



Scheme 3.



Scheme 4.

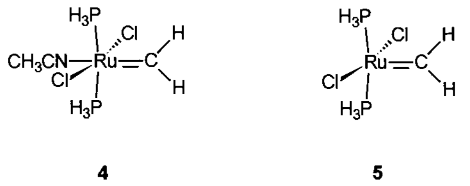


Fig. 4. Model systems for calculating GIAO magnetic sheilding values.

The computed downfield shift ($\Delta\delta$) for the carbene carbon Ru=CH_2 of **4** relative to **5** is 35.1 ppm, in qualitative accord with the experimental observation.

In the IR spectrum of **3**, a characteristic, albeit weak CN vibration is observed at $\tilde{\nu} = 2281$ cm^{-1} both in Nujol and as a KBr pellet. This absorption is shifted by 27 cm^{-1} to higher wave numbers compared to free CH_3CN [16]. The frequency calculations (DFT) for **4** and **5** predict a change ($\Delta\tilde{\nu}$(CN)) of 47 cm^{-1} in the same direction and are thus also in agreement with experiment.

Upon treatment with dtbpe (1,2-bis(di-*t*-butylphosphino)ethane), complexes **2** and **3** both yield (dtbpe-κ_2P)Cl_2Ru=CH–CH=CMe_2 [17]. The similar behavior of **2** and **3** may easily be rationalized by the solution equilibrium between **2** and **3**, which means that **2** is always present in low concentrations. Thus, **3** should undergo the same reactions as **2**, provided that the displaced CH_3CN does not react with the product. Therefore, complex **3**, which can be isolated in 69% yield in the synthesis outlined above, is also a suitable precursor for phosphine ligand substitution reactions. To the best of our knowledge, **3** is the first Grubbs-type bis phosphine carbene complex containing a sixth ligand which is monodentate and labile *trans* to the carbene moiety [18].

Our experimental observation that a donor ligand binds to **2** may be of importance with respect to the possible associative pathway that has been proposed as a minor kinetic channel in olefin metathesis catalysis using Grubbs-type systems [19]. Therefore, the influence of the phosphine ligand upon CH_3CN coordination was examined in NMR experiments by treating the typical Grubbs systems $(PCy_3)_2Cl_2$Ru=CH–CH=CMe_2 [4e] as well as $(PCy_3)_2Cl_2$Ru=CHPh [3] with a fourfold excess of CH_3CN in CD_2Cl_2. Remarkably, in both cases neither ^{1}H- nor $^{31}P\{^1H\}$-NMR spectra indicate any coordination of CH_3CN to the Ru centers at 298 and 230 K; only the five-coordinate compounds $(PCy_3)_2Cl_2$Ru=CH–CH=CMe_2 and $(PCy_3)_2Cl_2$Ru=CHPh are observable under the given conditions. This underlines the importance of the increased steric bulk and higher donor strength of PCy_3 relative to PPh_3 ligands in these systems. The binding of olefins to the five coordinate Grubbs-type complexes bearing bulky ligands should be even less favorable than of CH_3CN, because the olefinic substrates are much more bulky than the 'linear' CH_3CN.

2.3. The first mononuclear dicationic derivative of a Grubbs-type complex

From the spectroscopic data in CD_2Cl_2, it cannot be excluded that neutral **3** may dissociate in solution to form pentacoordinate $[(CH_3CN)(PPh_3)_2ClRu{=}CH{-}CH{=}CMe_2]^+$ with chloride as the counter ion. In that case, coordination of a second CH_3CN would be expected, leading to the hexacoordinate complex ion $[(CH_3CN)_2(PPh_3)_2ClRu{=}CH{-}CH{=}CMe_2]^+$. This complex formally would be a carbene isomer of the hydrido carbyne complexes reported by Werner and coworkers [20]. In the Werner systems, the carbene isomer is not detectable.

Under the conditions described above, integration of the NMR signals for compound **3** does not provide any indication of the formation of $[(CH_3CN)_2(PPh_3)_2ClRu{=}CH{-}CH{=}CMe_2]^+$ by chloride dissociation and subsequent CH_3CN binding. However, the halide ligands of **3** are sufficiently labilized by CH_3CN coordination to allow abstraction by suitable reagents.

In order to test the possibility of chloride abstraction, a solution of **3** in CH_2Cl_2 containing CH_3CN was treated with a fourfold excess of trimethylsilyl triflate at ambient temperature. This led to an immediate color change of the solution from bright yellow–green to deep green. Slowly condensing Et_2O into this solution led to the formation of a few crystals of a new compound suitable for X-ray diffraction. The structural analysis shows formation of the novel mononuclear dicationic derivative **6** of the Grubbs-type complex holding three CH_3CN ligands within its coordination sphere in a *mer*-arrangement [12,21] (Fig. 5).

Disorder in the crystal leads to a crystallographic center of inversion that a single molecule cannot have, thus preventing an accurate determination of bond lengths and angles for this complex and a detailed discussion of structural features on the basis of the present data.

Undoubtedly, the ease of subsequently abstracting both chloride ligands from **3** with trimethylsilyl triflate is related to the additional electron density provided to the metal center by acetonitrile coordination in **3**. This situation strongly resembles that found for ruthenium(II) carbenes ($^tBu_2P(CH_2)_nP^tBu_2$-κ_2P)Cl_2Ru=CHR with *cis*-chelating, electron-rich bisphosphines as dtbpm

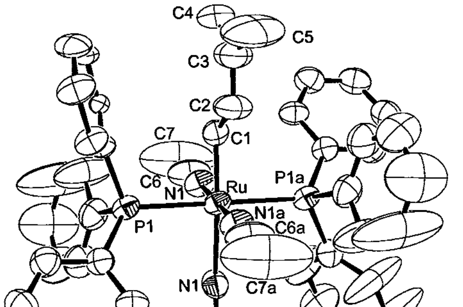


Fig. 5. ORTEP diagram of $[(CH_3CN)_3(PPh_3)_2Ru{=}CH{-}CH{=}CMe_2](OTf)_2$ (**6**); H atoms and triflate counter ions are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

or dtbpe ($n = 1$, 2) with a *trans* P–Cl arrangement [7,22].

Our preliminary result for **6** requires further substantiation for related systems and a closer inspection of these ionic species. Our current attempts are also aimed at removal of only one chloride ligand by addition of an appropriate Lewis acid, as well as towards a detailed investigation of olefin metathesis activity of these compounds.

3. Conclusion

A convenient synthetic route to Grubbs-type complexes $(PPh_3)_2Cl_2Ru{=}CH{-}CH{=}CR_2$ with unsaturated carbene ligands by treatment of Wilkinson's chlorides $(PPh_3)_3Ru(H)Cl$ with propargyl or allenyl hydrides has been developed. Their PPh_3 ligand substitution chemistry makes a wide variety of ruthenium carbene derivatives accessible. The solid state structure of $(PPh_3)_2Cl_2Ru{=}CH{-}CH{=}CMe_2$ has been determined. Futhermore, the hexacoordinate adduct complex $(CH_3CN)(PPh_3)_2Cl_2Ru{=}CH{-}CH{=}CMe_2$ has been isolated and spectroscopically characterized. This compound, the first Grubbs-type bis phosphine carbene complex containing a sixth ligand, which is monodentate and labile in a *trans* arrangement to the carbene, is a convenient alternative precursor for phosphine exchange reactions. X-ray characterization of $[(CH_3CN)_3(PPh_3)_2Ru{=}CH{-}CH{=}CMe_2](OTf)_2$, the first mononuclear dicationic, halide free derivative of a Grubbs-type carbene complex, shows the possibility of stabilizing these species by labile CH_3CN coordination.

4. Experimental

All reactions were carried out under an atmosphere of dry argon using standard Schlenk techniques. Solvents were dried according to standard procedures and saturated with argon prior to use. Chemicals used were purchased or prepared according to published procedures: $(PPh_3)_3Ru(H)Cl$ [9], $(PCy_3)_2Cl_2Ru{=}CH{-}CH{=}CMe_2$ [4e], $(PCy_3)_2Cl_2Ru{=}CHPh$ (Strem), 3-chloro-3-methyl-1-butyne, 1-chloro-2-methylpropene, trimethylsilyl triflate (Aldrich), 3-chloro-1,1-diphenyl-1,2-propadiene [23]. NMR spectra were recorded using a Bruker DRX 300 or DRX 500 spectrometer. ^{31}P-NMR spectra were calibrated to an external standard (85% H_3PO_4). Abbreviations used are: s = singlet, d = doublet, t = triplet, dt = doublet of triplet, ‘q’ = pseudoquartet.

4.1. Synthesis of $(PPh_3)_2Cl_2Ru{=}CH{-}CH{=}CMe_2$ (2)

To a violet solution of 1.0 g (1.08 mmol) of $(PPh_3)_3Ru(H)Cl$ in 15 ml CH_2Cl_2 in a Schlenk tube, 134 μl (1.19 mmol, 1.1 equivalents) 3-chloro-3-methyl-1-butyne in 5 ml CH_2Cl_2 were added at −15 °C within 5 min with stirring. The reaction mixture was allowed to warm to ambient temperature over 1.5 h and then reduced in volume to 1.5 ml in vacuo. Addition of 20 ml hexane led to precipitation of a red–brown microcrystalline powder. The suspension was stirred vigorously for 20 min, and the mother liquor was separated by cannula filtration. The remaining powder was dissolved in 1.5 ml CH_2Cl_2 and again precipitated with 20 ml hexane. After removal of the mother liquor, the remaining powder was dried in vacuo and then washed thrice with a mixture of 2 ml MeOH–15 ml pentane. In every step, the suspension was stirred for at least 30 min. The remaining microcrystalline solid was dried in vacuo yielding 650 mg (75%) of the desired product in 93% purity based on NMR. Further purification was achieved by slowly condensing Et_2O to a solution of the crude product in CH_2Cl_2 at −30 °C.

^{1}H-NMR (500.1 MHz, CD_2Cl_2, 298 K): δ 0.99 (s, 3H, $C\mathit{H}_3$), 1.25 (s, 3H, $C\mathit{H}_3$), 7.33–7.61 (m, 31H, Ar–*H* and $C\mathit{H}{=}C(CH_3)_2$), 18.10 (‘q’, $^{3}J(H, H) = 9.8$ Hz, $^{3}J(H, P) = 9.8$ Hz, 1H, $Ru{=}C\mathit{H}$). $^{31}P\{^{1}H\}$-NMR (202.5 MHz, CD_2Cl_2, 298 K): δ 27.1 (s). $^{13}C\{^{1}H\}$-NMR (125.8 MHz, CD_2Cl_2, 298 K) [DEPT-135]: δ 20.6 (s, $C(\mathit{C}H_3)_2$, [CH, CH_3]), 26.9 (s, $C(\mathit{C}H_3)_2$, [CH, CH_3]), 128.2 (t, $J(P, C) = 4.5$ Hz, Ar–*C*, [CH, CH_3]), 130.1 (s, Ar–*C*, [CH, CH_3]), 131.9 (t, $J(P, C) = 21$ Hz, Ar–*C*, [C_q]), 134.6 (t, $J(P, C) = 5$ Hz, Ar–*C*, [CH, CH_3]), 151.8 (t, $J(P, C) = 0.8$ Hz, $\mathit{C}H{=}C(CH_3)_2$, [CH, CH_3]), 291.1 (s, weak, $Ru{=}\mathit{C}H$, [CH, CH_3]). m.p. 165 °C (dec.). Anal. Calc.: for $C_{41}H_{38}Cl_2P_2Ru$: C, 64.40; H, 5.01; P, 8.10. Found: C, 64.12; H, 5.27; P, 8.13%.

4.2. Synthesis of $(CH_3CN)(PPh_3)_2Cl_2Ru{=}CH{-}CH{=}CMe_2$ (3)

To a violet solution of 400 mg (0.43 mmol) of $(PPh_3)_3Ru(H)Cl$ in 10 ml CH_2Cl_2, 3 ml CH_3CN were added, leading to a clear, pale yellow solution. Upon addition of 60 μl (0.53 mmol, 1.2 equivalents) 3-chloro-3-methyl-1-butyne at ambient temperature the mixture immediately turned brown and was stirred for 1.25 h at ambient temperature. After removal of volatiles in vacuo, the remaining brown solid was dissolved in 1 ml CH_2Cl_2. Addition of 10 ml Et_2O led to precipitation of a yellow–green powder. The brown mother liquor was removed via cannula filtration and discarded. The remaining powder was reprecipitated again from 1 ml CH_2Cl_2 with 10 ml Et_2O and after removal of the mother liquor once again precipitated from 1 ml CH_2Cl_2 with 10 ml hexane, followed by removal of the mother liquor. The remaining microcrystalline powder was washed thrice with hexane (10 ml each) and dried in vacuo to yield 240 mg (69%) of a yellow–green powder.

Compound **3** + 5 Äq. CH_3CN: ^{1}H-NMR (300.1 MHz, CD_2Cl_2, 298 K): δ 1.05 (s, 3H, $C(CH_3)_2$), 1.10 (s, 3H, $C(CH_3)_2$), 1.31 (s, 3H, coord. CH_3CN), 1.97 (s, non-coord. CH_3CN), 7.02 (d, 1H, $^3J(H,H) = 13.5$ Hz, $CH{=}C(CH_3)_2$), 7.27–7.34 (m, 20H, Ar–H), 7.74–7.80 (m, 10H, Ar–H), 17.74 (dt, $^3J(H,H) = 13.5$ Hz, $^3J(H,P) = 3.6$ Hz, 1H, Ru=CH). $^{31}P\{^1H\}$-NMR (121.5 MHz, CD_2Cl_2 298 K) δ 20.3 (s). $^{13}C\{^1H\}$-NMR (75.5 MHz, CD_2Cl_2, 298 K) [DEPT-135]: δ 1.7 (s, non-coord. CH_3CN, [CH, CH_3]), 3.3 (s, coord. CH_3CN, [CH, CH_3]), 20.9 (s, $C(CH_3)_2$, [CH, CH_3]), 27.8 (s, $C(CH_3)_2$, [CH, CH_3]), 116.7 (s, non-coord. CH_3CN, [C_q]), 120.9 (s, coord. CH_3CN, [C_q]), 127.5 (t, $J(P,C) = 4.6$ Hz, Ar–C, [CH, CH_3]), 129.0 (s, Ar–C, [CH, CH_3]), 133.5 (t, $J(P,C) = 21$ Hz, Ar–C, [C_q]), 134.6 (t, $J(P,C) = 5$ Hz, Ar–C, [CH, CH_3]), 145.3 (s, $CH{=}C(CH_3)_2$, [CH, CH_3]), 146.3 (s, $C(CH_3)_2$, [C_q]), 318.1 (s, weak, Ru=CH, [CH, CH_3]). IR (KBr): $\tilde{\nu}$ (cm^{-1}) 2281 (w, CN). IR (Nujol): $\tilde{\nu}$ (cm^{-1}) = 2281 (very w, CN). m.p. 160 °C (dec.). Anal. Calc. for $C_{43}H_{41}Cl_2NP_2Ru$: C, 64.10; H, 5.13; N, 1.74. Found: C, 63.92; H, 5.21; N, 1.83%.

5. Supplementary material

Crystallographic data for the structures reported here has been deposited as supplementary publication nos. CCDC-171304 and 171305 at the Cambridge Crystallographic Data Center. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk).

Acknowledgements

This work has been generously supported by Fonds der Chemischen Industrie and Studienstiftung des deutschen Volkes (Ph.D. Fellowships to M.A.O.V.), by the Deutsche Forschungsgemeinschaft, BASF AG and Heraeus. The authors thank Dr Madeleine Schultz for fruitful discussions.

References

[1] S.T. Nguyen, L.K. Johnson, R.H. Grubbs, J. Am. Chem. Soc. 114 (1992) 3974.

[2] (a) A. Fürstner (Ed.), Topics in Organometallic Chemistry, vol. 1, Springer, Berlin, 1998;
(b) K.J. Ivin, J.C. Mol, in: Olefin Metathesis and Metathesis Polymerization, Academic Press, San Diego, 1997;
(c) F. Zaragoza Dörwald, in: Metal Carbenes in Organic Synthesis, Wiley-VCH, Weinheim, 1999;
(d) A. Fürstner, Angew. Chem. 112 (2000) 3141; Angew. Chem. Int. Ed. 39 (2000) 3012;
(e) T.M. Trnka, R.H. Grubbs, Acc. Chem. Res. 34 (2001) 18.

[3] (a) P. Schwab, M. France, J.W. Ziller, R.H. Grubbs, Angew. Chem. 107 (1995) 2179; Angew. Chem. Int. Ed. 34 (1995) 2039;
(b) P. Schwab, R.H. Grubbs, J.W. Ziller, J. Am. Chem. Soc. 118 (1996) 110.

[4] (a) J. Wolf, W. Stüer, C. Grünwald, H. Werner, P. Schwab, M. Schulz, Angew. Chem. 110 (1998) 1165; Angew. Chem. Int. Ed. 37 (1998) 112;
(b) Verfahren zur Herstellung von Rutheniumkomplexen, BASF AG, O.Z.0050/48279;
(c) M. Oliván, O. Eisenstein, K.G. Caulton, Organometallics 16 (1997) 2227;
(d) T.E. Wilhelm, T.R. Belderrain, S.N. Brown, R.H. Grubbs, Organometallics 16 (1997) 3867;
(e) T.R. Belderrain, R.H. Grubbs, Organometallics 16 (1997) 4001;
(f) K.J. Harlow, A.F. Hill, J.D.E.T. Wilton-Ely, J. Chem. Soc. Dalton Trans. (1999) 285;
(g) L. Jafarpour, H.-J. Schanz, E.D. Stevens, S.P. Nolan, Organometallics 18 (1999) 5416.

[5] (a) M.L. Christ, S. Sabo-Etienne, B. Chaudret, Organometallics 13 (1994) 3800;
(b) R.P. Beatty, R.A. Paciello, U.S. Patent 5,554,778, 1996.

[6] S.M. Hansen, F. Rominger, M. Metz, P. Hofmann, Chem. Eur. J. 5 (1999) 557.

[7] S.M. Hansen, M.A.O. Volland, F. Rominger, F. Eisenträger, P. Hofmann, Angew. Chem. 111 (1999) 1360; Angew. Chem. Int. Ed. 38 (1999) 1273.

[8] The reaction of $(PPh_3)_3Ru(H)Cl$ with 1,1-diphenylprop-2-yne-1-ol has been mentioned, leading to a hexacoordinate, CH_3CN containing vinyl complex, which can be transformed into **1** by treatment with HCl: K.J. Harlow, A.F. Hill, T. Welton, J. Chem. Soc. Dalton Trans. (1999) 1911.

[9] P.S. Hallman, B.R. McGarvey, G. Wilkinson, J. Chem. Soc. Sect. A (1968) 3143 method B was employed and scaled up by a factor of 8.

[10] In Grubbs' structural determination of the closely related compound $(PPh_3)_2Cl_2Ru{=}CH{-}CH{=}CPh_2$ (**1**) [1], determination of the bond lengths and bond angles was not possible due to a disorder in the crystal.

[11] Dark red crystal (needle) with dimensions $0.40 \times 0.16 \times 0.12$ mm^3, $C_{41}H_{38}Cl_2P_2Ru$, crystal system monoclinic, space group $P2_1/c$, $Z = 4$, $a = 22.3226(3)$ Å, $b = 9.3709(1)$ Å, $c = 19.2379(3)$ Å, $\beta = 114.836(1)°$, $V = 3652.1(1)$ Å^3, ρ (calculated) = 1.39 g cm^{-3}, $2\theta_{max} = 51°$, radiation Mo–K_α, $\lambda = 0.71073$ Å, 0.3° ω-scans with CCD area detector, $T = 200(2)$ K, 26718 reflections measured, 6408 unique ($R_{int} = 0.0501$), 4446 observed ($I > 2\sigma(I)$), intensities were corrected for Lorentz and polarization effects, an empirical absorption correction was applied using the SADABS program based on the Laue symmetry of the reciprocal space, $\mu = 0.69$ mm^{-1}, $T_{min} = 0.81$, $T_{max} = 0.94$, structures solved by Patterson method and refined against F^2 with a full matrix least squares algorithm using the SHELXTL-PLUS (5.10) software package, 425 parameters refined, hydrogen atoms were treated using appropriate riding models except for H1 and H2, which were refined isotropically, final residual values $R(F) = 0.042$, $wR(F^2) = 0.089$ for observed reflections, residual electron density -0.36–0.98 e Å^{-3}.

[12] G.M. Sheldrick, Bruker Analytical X-ray Division, Madison (WI), Version 5.10, 1995.

[13] R.J. Young, G. Wilkinson, J. Chem. Soc. Dalton Trans. (1976) 719.

[14] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery, Jr., R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q.

Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle, J.A. Pople, GAUSSIAN 98, Revision A.5, Gaussian, Inc., Pittsburgh (PA), 1998.

[15] (a) K. Wolinski, J.F. Hilton, P. Pulay, J. Am. Chem. Soc. 112 (1990) 8251;
(b) J.L. Dodds, R. McWeeny, A.J. Sadlej, Mol. Phys. 41 (1980) 1419;
(c) R. Ditchfield, Mol. Phys. 27 (1974) 789;
(d) R. McWeeny, Phys. Rev. 126 (1962) 1028;
(e) F. London, J. Phys. Radium (Paris) 8 (1937) 397.

[16] Review: (a) B.N. Storhoff, H.C. Lewis, Jr., Coord. Chem. Rev. 23 (1977) 1;
(b) CH_3CN Ru complexes: D.E. Fogg, B.R. James, Inorg. Chem. 36 (1997) 1961;
(c) W.E. Buschmann, J.S. Miller, Chem. Eur. J. 4 (1998) 1731.

[17] P. Hofmann, M.A.O. Volland, manuscript in preparation.

[18] (a) With a tripodal mer-PNP ligand 6 coordinate vinylidene complexes (PNP-$\kappa^3 P,N,P'$)$Cl_2Ru{=}C{=}CHPh$ are known: C. Bianchini, P. Innocenti, M. Peruzzini, A. Romerosa, F. Zanobini, Organometallics 15 (1996) 272;
(b) Carbene complex with a tripodal mer-POP ligand: P. Nieczypor, P.W.N.M. van Leeuwen, J.C. Mol, M. Lutz, A.L. Spek, J. Organomet. Chem. 625 (2001) 58.

[19] (a) E.L. Dias, S.T. Nguyen, R.H. Grubbs, J. Am. Chem. Soc. 119 (1997) 3887;
(b) M. Ulman, R.H. Grubbs, Organometallics 17 (1998) 2484.

[20] (a) W. Stüer, J. Wolf, H. Werner, P. Schwab, M. Schulz, Angew. Chem. 110 (1998) 3603; Angew. Chem. Int. Ed. 37 (1998) 3421;
(b) P. González-Herrero, B. Weberndörfer, K. Ilg, J. Wolf, H. Werner, Angew. Chem. 112 (2000) 3392; Angew. Chem. Int. Ed. (39) 2000 3266.

[21] Brownish crystal (polyhedron) with dimensions $0.30 \times 0.28 \times 0.10$ mm^3, $C_{49}H_{47}F_6N_3O_6P_2RuS_2$, crystal system monoclinic, space group $P2_1/n$, $Z = 2$, $a = 11.0808(2)$, $b = 19.1319(2)$, $c = 12.3841(1)$ Å, $\beta = 99.333(1)°$, $V = 2590.6(1)$ Å^3, $\rho_{calc} = 1.43$ g cm^{-3}, $2\theta_{max} = 50°$, radiation Mo–K$_\alpha$, $\lambda = 0.71073$ Å, 0.3° ω-scans with CCD area detector, $T = 200(2)$ K, 21 811 reflexions measured, 4539 unique ($R_{int} = 0.056$), 3302 observed ($I > 2\sigma(I)$), intensities were corrected for Lorentz and polarization effects, an empirical absorption correction was applied using the SADABS program based on the Laue symmetry of the reciprocal space, $\mu = 0.52$ mm^{-1}, $T_{min} = 0.60$, $T_{max} = 0.96$, structures solved by direct methods and refined against F^2 with a full-matrix-least squares algorithm using the SHELXTL-PLUS (5.10) software package, disordering leads to a crystallographic center of inversion, that a single molecule does not fulfill: carbene and CH_3CN (trans to carbene moiety) are superimposed leading also to a disordering of the phenyl rings, 411 parameters refined, 99 restraints, hydrogen atoms were treated using appropriate riding models, final residual values $R(F) = 0.074$, $wR(F^2) = 0.208$ for observed reflections, residual electron density -0.60–1.12 e Å^{-3}.

[22] M.A.O. Volland, B.F. Straub, I. Gruber, F. Rominger, P. Hofmann, J. Organomet. Chem. 617–618 (2001) 288.

[23] F. Toda, M. Higashi, K. Akagi, Bull. Chem. Soc. Jpn. 42 (1969) 567 conditions were slightly modified: −15 °C reaction temperature and 20 h reaction time.