Vinylidene Transition-Metal Complexes, 47[◇]

Synthesis and Molecular Structure of Six-Coordinate Dichlorodihydridoruthenium(IV) and Five-Coordinate Vinylideneruthenium(II) Complexes☆

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The dichlorodihydridoruthenium(IV) compound $[RuH_2Cl_2(PiPr_3)_2]$ (**4**) was prepared from $[RuCl_2(C_8H_{12})]_n$ (**3**), $PiPr_3$, and H_2 in 2-butanol via the chlorohydridoruthenium(II) derivative $[RuHCl(H_2)(PiPr_3)_2]$ (**5**) as an intermediate. The synthesis of **5** was achieved under similar conditions from **3**, $PiPr_3$, H_2, and 2-butanol in the presence of NEt_3. Compound **4**, which was characterized by X-ray crystal structure analysis, reacts with excess phenylacetylene to give the phenylvinylidene complex $[RuCl_2(=C=CHPh)(PiPr_3)_2]$ (**7**) and with propargylic alcohols or derivatives thereof to afford the vinylcarbene complexes $[RuCl_2(=CHCH=CR_2)(PiPr_3)_2]$ (**9**, **10**), respectively. From **5** and terminal alkynes RC≡CH the chlorohydridovinylidene compounds $[RuHCl(=C=CHR)(PiPr_3)_2]$ (**11**, **12**) were obtained. The phenylvinylidene complex $[RuCl_2(=C=CHPh)(PCy_3)_2]$ (**15**) was prepared from phenylacetylene and either $[RuH_2Cl_2(PCy_3)_2]$ (**14**) or one of the carbene derivatives $[RuCl_2(=CHR)(PCy_3)_2]$ (**16**, **17**) as starting materials. The X-ray crystal structure analysis of **15** confirms a distorted square-pyramidal geometry with the vinylidene ligand in the apical position. The interconversion of **4** to **5** and of the tricyclohexylphosphane counterparts **14** to **13** was achieved by hydrogen transfer from 2-propanol in the presence of PR_3. The reverse reaction occurs upon treatment of **5** or **13** with the corresponding phosphonium salt $[HPR_3]Cl$ or HCl, respectively.

In the course of our investigations aimed to prepare bis(trialkylphosphane) transition-metal complexes containing *coordinatively unsaturated* metal centers, we recently described the synthesis of the dichlorodihydridoosmium(IV) compounds $[OsH_2Cl_2(PiPr_3)_2]$ (**1**) and $[OsH_2Cl_2(PtBu_2Me)_2]$ (**2**), in which osmium, although six-coordinate, has 16 electrons in its valence shell.[1] These compounds, in particular **1**, have a rich chemistry which has opened the gate not only to carbyne- but also to vinylideneosmium complexes.[2][3]

Since it was known from our work on the reactivity of compounds such as $[MCl_2\{\kappa^2(P,O)\text{-}iPr_2PCH_2CH_2OMe\}_2]$ and $[MCl_2\{\kappa^2(P,O)\text{-}iPr_2PCH_2CO_2R\}_2]$ (M = Ru, Os) that the ruthenium derivatives react more readily with terminal alkynes and propargylic alcohols to give the corresponding vinylidene and allenylidene complexes,[4] we set out to prepare the hitherto unknown ruthenium(IV) compound $[RuH_2Cl_2(PiPr_3)_2]$ (**4**). After initial attempts with $RuCl_3 \cdot aq$ as starting material failed, we found that the reaction of $[RuCl_2(C_8H_{12})]_n$ (**3**) with triisopropylphosphane in 2-butanol under H_2 gave the dichlorodihydrido complex **4**.[5] Most recently, Caulton and coworkers reported the synthesis of the analogous compound $[RuH_2Cl_2(PtBu_2Me)_2]$ using our methodology with the cycloocta-1,5-diene derivative **3** as the starting material.[6]

In this article we describe the preparation and characterization of **4** and its PCy_3 counterpart **13**, and the use of these dichlorodihydridoruthenium(IV) compounds as well as of the related chlorohydrido(dihydrogen)ruthenium(II) derivatives to obtain five-coordinate vinylideneruthenium(II) complexes. Part of these studies has been communicated.[5]

Results and Discussion

As was mentioned above, instead of $RuCl_3 \cdot aq$, which reacts with $PiPr_3$ in boiling methanol to give $[RuHCl(CO)(PiPr_3)_2]$,[7] compound **3** has to be used as starting material for the preparation of **4** (Scheme 1). On treatment of a suspension of **3** in 2-butanol with 3 equiv. of $PiPr_3$ in the presence of H_2 a red solution is formed which, due to the ^1H- and ^{31}P-NMR spectra, contains the dihydrogen complex **5**. This compound was originally prepared by Chaudret et al. from $[Ru(\eta^4\text{-}C_8H_{12})(\eta^6\text{-}C_8H_{10})]$, $PiPr_3$, and $CHCl_3$ under 4 atm of dihydrogen.[8] If the red solution obtained from **3** was brought to dryness in vacuo and the oily residue recrystallized from ether, orange crystals of **4** (but not **5**) were

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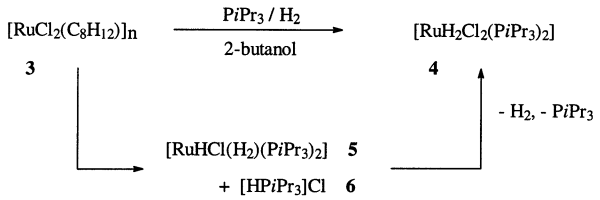
Scheme 1



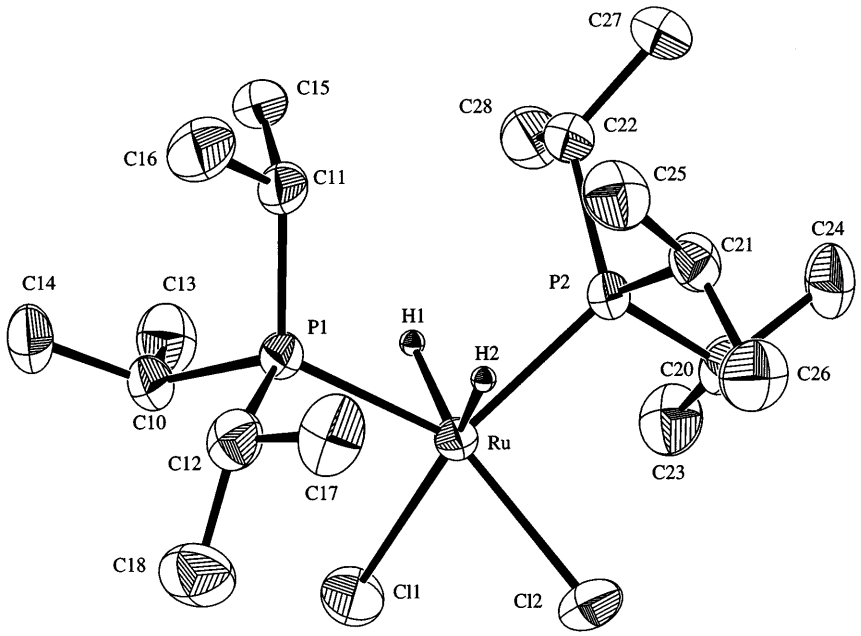
isolated in 92% yield. The conversion of **5** to **4** is promoted by the phosphonium salt **6** which is generated as a byproduct in the reaction of **3**, P*i*Pr$_3$, 2-butanol, and H_2.

In order to confirm the proposal that the initial product in the reaction of **3** with triisopropylphosphane under the conditions used is indeed the dihydrogen complex **5**, a suspension of the oligo- or polymeric cycloocta-1,5-diene compound **3** was treated with P*i*Pr$_3$/H_2 in 2-butanol in the presence of NEt_3 as a base. After removal of the solvent and extraction of the residue with pentane, a red oil was obtained which by comparison of the NMR data with those published by Chaudret is the dihydrogenruthenium(II) derivative **5**.[8] This compound reacts with the phosphonium salt [HP*i*Pr$_3$]Cl (**6**) in CH_2Cl_2 to afford, by evolution of gas (H_2), quantitatively P*i*Pr$_3$ and the dichlorodihydrido complex **4**. The latter is an orange solid which is readily soluble in CH_2Cl_2 and $CHCl_3$, but almost insoluble in hydrocarbons. The characteristic feature in the ^{1}H-NMR spectrum of **4** is the triplet resonance for the two hydrido ligands in the high-field region at $\delta = -12.30$.

The result of the X-ray crystal structure analysis of **4** is shown in Figure 1. The coordination geometry around the six-coordinate metal center is very similar to that of the osmium analogue **1**.[1a] It is best described as a somewhat distorted variant of a D_{4d} square antiprism with the two vacant coordination sites in alternate positions at one square base of this polyhedron. The other square base is made up by the two phosphorus atoms and the two hydrido ligands, the positions of which could be located in a difference Fourier synthesis. The Ru−P and Ru−Cl distances of **4** are almost identical to the corresponding bond lengths in **1**, and this is also true for the P−M−P, P−M−Cl, and Cl−M−Cl bond angles (M = Ru, Os). The distances Ru−H1 and Ru−H2 of 1.46(5) and 1.56(5) Å are in the range found for other hydridoruthenium(II) and -ruthenium(IV) complexes.[9] We note that recently Gusev, Berke, Eisenstein, Caulton et al. observed that the molecules [OsH_2X_2(P*i*Pr$_3$)$_2$] (X = Cl, Br, I) exist *in solution* as two rapidly interconverting isomers, one having C_2 symmetry (as seen in the crystal) and the other having no symmetry.[10] In contrast, the tricyclohexylphosphane derivative **13** which was prepared independently by Chaudret and coworkers[11] and by us (see below), shows a fluxional process attributed to the interconversion of two *symmetrical* isomers.

The dichlorodihydridoruthenium(IV) compound **4** does not only react with phenylacetylene[5] but also with propargylic alcohols and derivatives thereof. The results are summarized in Scheme 2. The reaction of **4** with PhC≡CH in CH_2Cl_2 yields a mixture of two products **7** and **8** of which the first is by far the most dominating species. Compound **7** is exclusively formed if the initially generated mixture, after removal of the solvent, is treated again with phenylacetylene and heated to 80°C for a short period of time. The isolated yield of **7** is then ca. 70%. The minor component

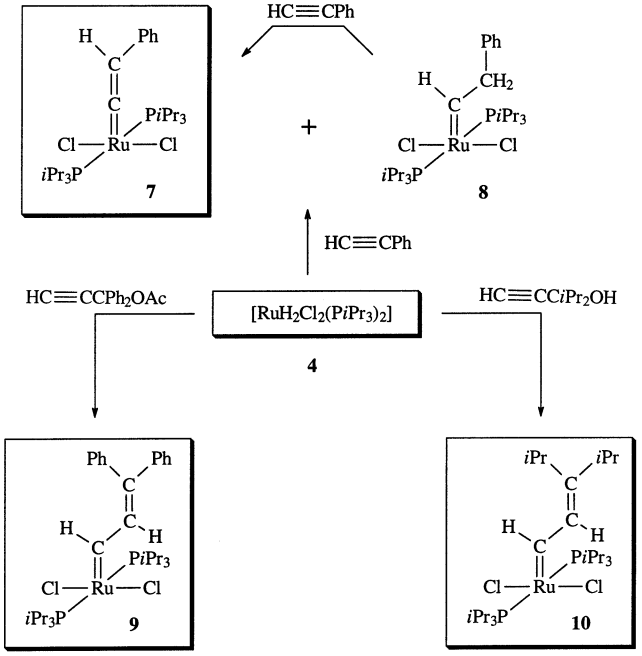
Figure 1. Molecular structure (ORTEP plot) of **4**;[a] the hydrogen atoms besides H1 and H2 are omitted for clarity



[a] Selected bond lengths [Å] and angles [°]: Ru−P1 2.270(1), Ru−P2 2.297(1), Ru−Cl1 2.400(1), Ru−Cl2 2.401(1), Ru−H1 1.46(5), Ru−H2 1.56(5); P1−Ru−P2 111.69(3), Cl1−Ru−Cl2 84.29(3), P1−Ru−Cl1 92.18(3), P1−Ru−Cl2 139.14(3), P2−Ru−Cl1 145.07(3), P2−Ru−Cl2 92.60(3).

of the reaction mixture is the benzylcarbene complex **8** which has already been characterized by X-ray crystal structure analysis.[5] Compound **8** belongs to the class of Grubbs-type carbene complexes $[RuCl_2(=CHR)(PR'_3)_2]$ that were originally prepared from $[RuCl_2(PPh_3)_3]$ and cyclopropene or diazoalkane derivatives[12] and are now widely used as highly active catalysts for olefin metathesis including ROMP and RCM.[13]

Scheme 2



The vinylideneruthenium(II) compound **7** is a brown, only moderately air-sensitive solid that has been characterized by elemental analysis and spectroscopic techniques. The ^{13}C-NMR spectrum displays two triplets at δ = 341.1 and 109.3, which by comparison[4][14] are assigned to the α- and β-carbon atoms of the vinylidene ligand. In the ^{31}P-NMR spectrum a singlet resonance appears at δ = 29.0, the chemical shift of which is similar to that observed at δ = 27.2 for the PPh_3 ligands in $[RuCl_2(=C=CHtBu)(PPh_3)_2]$.[15] With regard to the mechanism of formation of **7**, we assume that the starting material **4**, containing a metal center with a 16-electron configuration, affords in the initial step of the reaction a 1:1 adduct with the alkyne. This seven-coordinate species could react by insertion of the alkyne into one of the Ru−H bonds to generate a hydrido(vinyl) intermediate (also with a 16-electron configuration at the metal center). This compound could then give upon addition of a second molecule of PhC≡CH, followed by reductive elimination of styrene, the alkyne complex $[RuCl_2(PhC{\equiv}CH)(PiPr_3)_2]$. The conversion of this species to the isomer **7** possibly occurs by a slippage of the π-bonded alkyne to an η^2-CH-coordinated complex which undergoes a 1,2-hydrogen migration to yield the final product. Quite recently, Wakatsuki et al. showed by ab initio MO calculations that the reaction of $[RuX_2(PPh_3)_3]$ with *t*BuC≡CH, which gives the compounds $[RuX_2(=C=CHtBu)(PPh_3)_2]$ (X = Cl, Br), follows a similar route.[16] It should be mentioned that the formation of styrene from **4** and phenylacetylene was confirmed by GC/MS analysis.

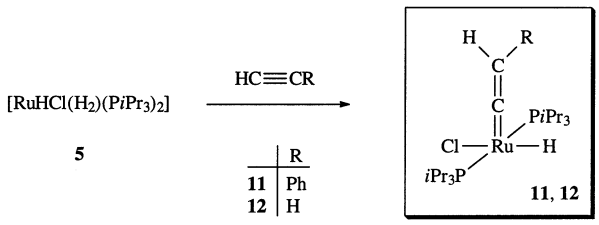
The synthesis of the vinylcarbene complexes **9** and **10** (Scheme 2) from **4** is a somewhat surprising result. Taking earlier work by Selegue,[17] Dixneuf,[18] and by some of us[4b][4c][19] into consideration, we anticipated that on treatment of **4** with propargylic alcohols $HC{\equiv}CCR_2OH$, in particular for R = Ph, allenylidenemetal derivatives $[RuCl_2(=C=C=CR_2)(PiPr_3)_2]$ would be formed. However, instead of these species the related vinylcarbene complexes **9** and **10** were obtained. We found that the reaction of **4** with $HC{\equiv}CCPh_2OH$ in CH_2Cl_2 leads to a mixture of products among which **9** could be detected as a major component by ^{1}H-NMR spectroscopy. In contrast, by using the corresponding acetate $HC{\equiv}CCPh_2OAc$ as a carbene source, compound **9** has been isolated in excellent yield. This (vinylcarbene)ruthenium(II) derivative was originally prepared by Grubbs and coworkers from $[RuCl_2(PPh_3)_3]$ and 1,1-diphenylcyclopropene followed by ligand exchange of PPh_3 for $PiPr_3$.[12c]

The formerly unknown complex **10**, which was isolated as a violet solid in 70% yield, resembles in its properties the diphenyl analogue **9**. The ^{1}H-NMR spectrum of **10** displays in the low-field region two doublets at δ = 19.56 and 8.06 with an H−H coupling of 11.2 Hz which is typical for an $M{=}CH{-}CH{=}CR_2$ unit.[12][14] In the ^{13}C-NMR spectrum of **10** the signal for the carbene-C atom appears at δ = 288.3 and is split into a triplet due to P−C coupling. Mechanistically, the formation of **9** and **10** from **4** is best understood if we assume that in analogy to the course of the reaction of **4** with phenylacetylene a functionalized hydrido(vinyl) species $[RuH(CH{=}CHCR_2OR')Cl_2(PiPr_3)_2]$ (R′ = H, Ac) is generated as an intermediate which yields the product by elimination of HOR′.

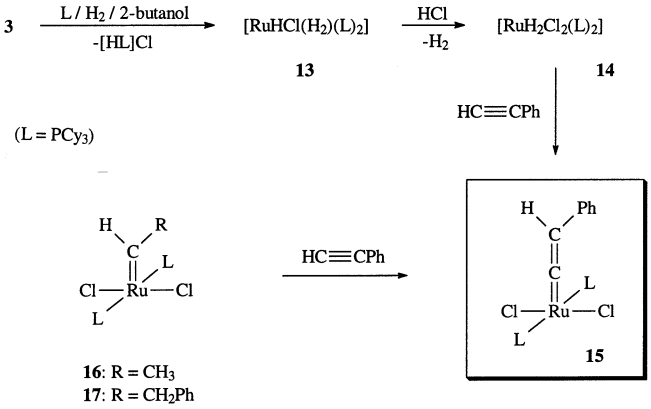
In a similar way to the dihydridoruthenium(IV) compound **4,** the hydridoruthenium(II) derivative **5** reacts with phenylacetylene to give the hydrido(phenylvinylidene) complex **11** (Scheme 3). Moreover, the parent hydrido(vinylidene) compound **12** was obtained from **5** and acetylene. Although a clean reaction between **5** and the terminal alkynes occurs, the isolated yields of **11** and **12** is only moderate (ca. 40%) mainly due to the good solubility of the products in pentane. Quite recently, Olivan, Eisenstein, and Caulton reported that on treatment of $[RuHCl(H_2)(PtBu_2Me)_2]$ with terminal alkynes RC≡CH the analogous hydrido(vinylidene) compounds $[RuHCl(=C=CHR)(PtBu_2Me)_2]$ (R = Ph, $SiMe_3$) are formed which, according to ab initio DFT calculations, possess a distorted trigonal-bipyramidal geometry with the phosphanes in the apical positions.[20] The osmium analogue of **11** was recently prepared by Esteruelas et al. by a different route, namely from the six-coordinate carbyne(hydrido) complex $[OsHCl_2(\equiv CCH_2Ph)(PiPr_3)_2]$ by elimination of HCl with NaOMe.[21]

The ^{13}C-NMR spectra of both **11** and **12** display in the low-field region the typical signals for the vinylidene α- and β-carbon atoms at δ = 329.3 and 109.7 (for **11**) and at δ =

Scheme 3



Scheme 4



326.3 and 87.1 (for **12**) which are all split into triplets due to P−C coupling. In the ^{1}H-NMR spectrum the hydride resonance also appears as a triplet at $\delta = -12.48$ (for **11**) and −15.03 (for **12**). In contrast to **7**, the methyl groups of the triisopropylphosphane ligands in **11** and **12** are diastereotopic and thus two sets of signals are observed for the CH_3 protons and carbon nuclei in the NMR spectra. It should be mentioned that in agreement with recent work from our laboratory[22][23] compounds **11** and **12** react with the phosphonium chloride [HP*i*Pr$_3$]Cl to give the carbene complexes [RuCl$_2$(=CHCH$_2$R)(P*i*Pr$_3$)$_2$] (R = Ph, H) in excellent yield.

The analogues of the chlorohydrido and dichlorodihydrido compounds **5** and **4** with two PCy$_3$ instead of two P*i*Pr$_3$ ligands, **13** and **14**, are also accessible from the cycloocta-1,5-diene derivative **3** as the starting material. Like **5**, the corresponding ruthenium(II) complex **13** was first prepared by Chaudret and coworkers from the ruthenium(0) compound [Ru(η^4-C$_8$H$_{12}$)(η^6-C$_8$H$_{10}$)].[8] While this work was in progress,[24] Grubbs et al. published an experimental procedure for **13** that followed our methodology using the (cycloocta-1,5-diene)ruthenium(II) derivative **3** as the precursor.[25] Regarding the dichlorodihydridoruthenium(IV) complex **14**, very recently Chaudret and coworkers reported a synthesis which is different to that one described in this work and based on the reaction of the "polyhydride" [RuH$_2$(H$_2$)$_2$(PCy$_3$)$_2$] with aqueous HCl in ether.[11] The same authors also confirmed by VT NMR measurements that **14** shows a fluxional process in solution which is attributed to the interconversion between two stereoisomers having C_{2v} symmetry.[11] Our observations are in agreement with these results.[23]

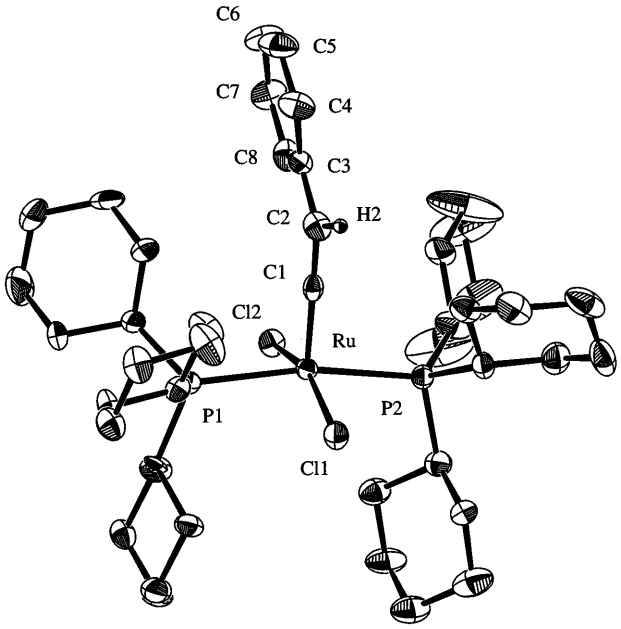
Compound **14** does not only react with CO to give [RuHCl(CO)$_2$(PCy$_3$)$_2$][11] but also with phenylacetylene in the molar ratio of 1:10 to yield the vinylidene complex **15** (Scheme 4). Alternatively, **15** can be prepared upon treatment of the carbene derivatives **16** and **17** with PhC≡CH. In both cases the isolated yield is 60−70%. To the best of our knowledge, there has been only one other compound of the general composition [RuCl$_2$(=C=CHR)(PCy$_3$)$_2$] (with R = H) reported in the literature which was obtained from [RuCl$_2$(=CHPh)(PCy$_3$)$_2$] and a tenfold excess of allene.[12d][12e] The phenylvinylidene complex **15** (which is an almost air-stable solid) is only sparingly soluble in common organic solvents at room temperature and thus the ^{1}H-, ^{13}C-, and ^{31}P-NMR spectra were measured in CDCl$_3$ at 40°C. The NMR data for **15** and the related bis(triisopropylphosphane) complex are quite similar and therefore deserve no further comment.

The molecular structure of **15** is shown in Figure 2. The ORTEP plot reveals that the configuration around the metal center is distorted square-pyramidal with the vinylidene unit in the apical position. In the basal plane the two chloro and the two phosphane ligands are *trans* disposed. Although according to ab initio calculations this geometry represents the energy minimum on the potential surface,[16] it was found that in contrast to **15** the analogous compound [RuBr$_2$(=C=CH*t*Bu)(PPh$_3$)$_2$] possesses a trigonal-bipyramidal structure with the PPh$_3$ groups in the apical positions.[16] Therefore it seems that for the preferred configuration of the five-coordinate complexes steric requirements play a dominant role. The Ru−C1−C2 axis is nearly linear with an Ru−C1 distance that is slightly shorter than in [RuBr$_2$(=C=CH*t*Bu)(PPh$_3$)$_2$] [1.77(2) Å][16] and in the six-coordinate compound [RuCl$_2$(=C=CHPh){κ^1(*P*)-Me$_2$PCH$_2$CH$_2$OMe}{κ^2(*P,O*)-Me$_2$PCH$_2$CH$_2$OMe}] [1.815(2) Å][26] but almost identical to that in [RuCl$_2$(=C=CHPh)-{κ^1(*P*)-*i*Pr$_2$PCH$_2$CH$_2$OMe}{κ^2(*P,O*)-*i*Pr$_2$PCH$_2$CH$_2$OMe}] [1.749(7) Å].[4a] The P1−Ru−P2 axis is somewhat bent [169.82(7)°] and this is even more so for the Cl1−Ru−Cl2 unit [158.31(7)°]. The C1−C2 distance is in the expected range and this is true also for the Ru−Cl and Ru−P bond lengths.

Finally, a special comment is appropriate concerning the interconversion of the ruthenium(II) and ruthenium(IV) complexes **5** and **4** (see Scheme 5). In the context of the preparation of **4** from **3** it has already been mentioned that in this process compound **5** is generated as an intermediate which reacts with the byproduct **6**, after removal of 2-butanol, to give **4**. However, the surprising observation is that the red solution, which is initially formed from **3**, P*i*Pr$_3$, and H$_2$ in 2-butanol, is quite stable and can be stored for days without the conversion of the two components **5** and **6** to the ruthenium(IV) complex **4**.

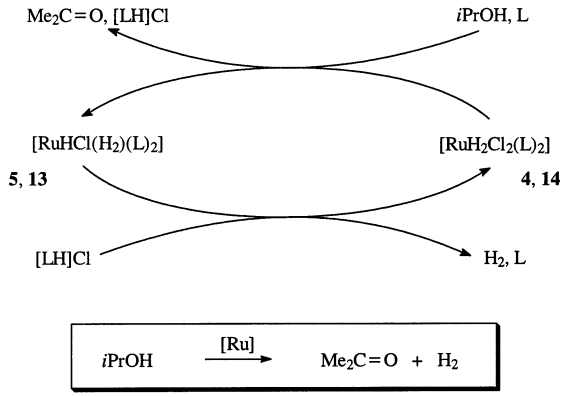
In order to explain this seeming inconsistency it should be emphasized that although **5** and **6** react by elimination of H$_2$ to give **4** and P*i*Pr$_3$, in the presence of a secondary alcohol such as 2-butanol, or even better 2-propanol, the

Figure 2. Molecular structure (ORTEP plot) of **15**;[a] the hydrogen atoms are omitted for clarity



[a] Selected bond lengths [Å] and angles [°]: Ru−C1 1.747(7), Ru−P1 2.429(2), Ru−P2 2.410(2), Ru−Cl1 2.342(2), Ru−Cl2 2.355(2), C1−C2 1.33(1), C2−C3 1.45(1); C1−Ru−Cl1 102.8(2), C1−Ru−Cl2 98.9(2), C1−Ru−P1 94.6(2), C1−Ru−P2 94.9(2), P1−Ru−P2 169.82(7), P1−Ru−Cl1 88.97(7), P1−Ru−Cl2 88.42(6), P2−Ru−Cl1 85.47(7), P2−Ru−Cl2 93.59(7), Cl1−Ru−Cl2 158.31(7), Ru−C1−C2 178.2(6), C1−C2−C3 129.4(7).

Scheme 5



mixture of **4** and triisopropylphosphane is reconverted to **5** and **6**. The formation of acetone as a byproduct has been confirmed by GC/MS analysis which indicates that 2-propanol serves as the hydrogen source. An analogous but significantly slower reaction takes place between compound **14** and PCy_3 in 2-propanol. In this case the chlorohydrido complex **13** precipitates due to its lower solubility (compared with **5**) in the alcohol. The ^{31}P-NMR spectrum of the mother liquor indicates that besides **13** a small quantity of a sideproduct is formed which has not been identified as yet. For the conversion of **13** to **14** it is preferable to use instead of the phosphonium salt $[HPCy_3]Cl$ aqueous HCl as a proton source which yields the ruthenium(IV) compound almost quantitatively.

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Experimental Section

All operations were carried out under argon using Schlenk techniques. The starting materials **3**,[27] and **16**, **17**[22] were prepared as described in the literature. The alkynes were commercial products from Aldrich, Strem, and ABCR. − NMR: Bruker AC 200 and AMX 400 [dvt = doublet of virtual triplets; $N = {}^3J(PH) + {}^5J(PH)$ or ${}^2J(PC) + {}^4J(PC)$, respectively]. − Melting points determined by DTA.

1. *Preparation of [$RuH_2Cl_2(PiPr_3)_2$]* (**4**): A suspension of 220 mg (0.79 mmol for $n = 1$) of **3** in 20 ml of 2-butanol was treated with 463 µl (2.37 mmol) of $PiPr_3$ and heated under hydrogen (1.5 bar) for 6 h at 80°C. Upon cooling the resulting red solution to room temperature, the solvent was removed in vacuo and 5 ml of diethyl ether was added to the oily residue. After 2 h, an orange solid crystallized, which was washed with 5 ml of diethyl ether and dried in vacuo; yield 359 mg (92%); m. p. 60°C (dec.). − ^1H NMR (200 MHz, CD_2Cl_2): δ = 2.30 (m, 6 H, $PCHCH_3$), 1.22 [dd, $J(PH) = 14.9$, $J(HH) = 7.1$ Hz, 36 H, $PCHCH_3$], −12.30 [t, $J(PH) = 19.0$ Hz, 2 H, RuH_2]. − ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ = 29.7 (m, $PCHCH_3$), 19.6 (s, $PCHCH_3$). − ^{31}P NMR (162.0 MHz, CD_2Cl_2): δ = 103.2 (s). − $C_{18}H_{44}Cl_2P_2Ru$ (494.5): calcd. C 43.72, H 8.97, Ru 20.44; found C 43.41, H 8.83, Ru 19.85.

2. *Preparation of [$RuHCl(H_2)(PiPr_3)_2$]* (**5**) *from* **3**: A suspension of 119 mg (0.42 mmol für $n = 1$) of **3** in 15 ml of 2-butanol was treated with 200 µl (1.02 mmol) of $PiPr_3$ and 117 µl (0.84 mmol) of NEt_3 and then heated for 6 h under hydrogen (1.5 bar) at 80°C. Upon cooling to room temperature, the solvent was removed in vacuo and the orange residue was extracted with 15 ml of pentane. After the extract was brought to dryness in vacuo, a red oil was obtained which by comparison of the NMR data was identified as **5**.[8] Yield almost quantitative.

3. *Reaction of Compound* **5** *with [$HPiPr_3$]Cl* (**6**): A solution of compound **5**, prepared from 25 mg (0.09 mmol) of **3**, 45 µl (0.23 mmol) of $PiPr_3$ and 25 µl (0.18 mmol) of NEt_3 in 5 ml of 2-butanol, was brought to dryness in vacuo. The oily residue was extracted with 10 ml of pentane and, after removal of the solvent, was dissolved in 3 ml of CH_2Cl_2. The red solution was treated with 37 mg (0.19 mmol) of **6**, which led to a rapid evolution of gas (H_2). After the solution was stirred for 5 min, the solvent was removed and the remaining orange solid identified as **4** by comparison of the NMR data with those of an authentic sample. Yield almost quantitative.

4. *Preparation of [$RuCl_2(=C=CHPh)(PiPr_3)_2$]* (**7**): A solution of 142 mg (0.29 mmol) of **4** in 10 ml of CH_2Cl_2 was treated with 63 µl (0.57 mmol) of phenylacetylene and stirred for 5 min at room temperature. The solvent was removed in vacuo to give a red oil which according to the ^1H- and ^{31}P-NMR spectra consisted of a mixture of **7** (90%) and **8** (10%). The oily material was dissolved in 5 ml of benzene, the solution was treated with 30 µl (0.27 mmol)

of phenylacetylene and heated for 10 min at 80°C. After cooling to room temperature, the solvent was removed in vacuo and 3 ml of methanol were added to the brownish residue. Upon storing the mixture for 2 h, a brown microcrystalline solid was obtained which was separated from the mother liquor and dried in vacuo; yield 113 mg (66%); m. p. 97°C (dec.). – ^{1}H NMR (400 MHz, C_6D_6): δ = 7.23–7.02 (m, 5 H, C_6H_5), 4.71 [t, *J*(PH) = 3.6 Hz, 1 H, =C=C*H*Ph], 2.79 (m, 6 H, PC*H*CH$_3$), 1.29 [dvt, *N* = 13.2, *J*(HH) = 6.6 Hz, 36 H, PCHC*H*$_3$]. – ^{13}C NMR (100.6 MHz, C_6D_6): δ = 341.1 [t, *J*(PC) = 15.1 Hz, =*C*=CHPh], 133.8 [t, *J*(PC) = 2.5 Hz, *ipso*-C of C_6H_5], 128.5, 125.6, 124.4 (each s, C_6H_5), 109.3 [t, *J*(PC) = 4.3 Hz, =C=*C*HPh], 23.7 [vt, *N* = 19.0 Hz, P*C*HCH$_3$], 20.1 (s, PCH*C*H$_3$). – ^{31}P NMR (162.0 MHz, C_6D_6): δ = 29.0 (s). – $C_{26}H_{48}Cl_2P_2Ru$ (594.6): calcd. C 52.52, H 8.14; found C 52.85, H 7.86.

5. *Preparation of [RuCl$_2$(=CHCH=CPh$_2$)(PiPr$_3$)$_2$]* (**9**) *from* **4**: A solution of 116 mg (0.23 mmol) of **4** in 10 ml of CH_2Cl_2 was treated with 121 mg (0.48 mmol) of HC≡CCPh$_2$OAc and stirred for 1 h at room temperature. The solvent was removed in vacuo and 5 ml of pentane was added to the oily residue. After the mixture was stored for 2 h, a red solid precipitated which was filtered and dried in vacuo. It was identified by comparison of the ^{1}H- and ^{13}C-NMR data with those reported by Grubbs et al. for compound **9**.[12b]

6. *Preparation of [RuCl$_2$(=CHCH=CiPr$_2$)(PiPr$_3$)$_2$]* (**10**): A solution of 120 mg (0.24 mmol) of **4** in 10 ml of CH_2Cl_2 was treated with 85 µl (0.55 mmol) of HC≡CC*i*Pr$_2$OH and stirred for 10 min at 60°C. After cooling to room temperature, the solvent was removed in vacuo. Upon addition of 5 ml of pentane, a purple solid precipitated which was filtered and dried in vacuo; yield 103 mg (70%); m. p. 124°C (dec.). – ^{1}H NMR (400 MHz, C_6D_6): δ = 19.56 [d, *J*(HH) = 11.2 Hz, 1 H, =C*H*CH=C*i*Pr$_2$], 8.06 [d, *J*(HH) = 11.2 Hz, 1 H, =CHC*H*=C*i*Pr$_2$], 3.87 [sept, *J*(HH) = 6.8 Hz, 1 H, C*H*CH$_3$], 2.82 (m, 6 H, PC*H*CH$_3$), 2.38 [sept, *J*(HH) = 6.8 Hz, 1 H, C*H*CH$_3$], 1.24 [dvt, *N* = 13.2, *J*(HH) = 6.6 Hz, 36 H, PCHC*H*$_3$], 1.04, 0.98 both d, *J*(HH) = 6.8 Hz, 12 H, CHC*H*$_3$]. – ^{13}C NMR (100.6 MHz, C_6D_6): δ = 288.3 [t, *J*(PC) = 7.0 Hz, =*C*HCH=C*i*Pr$_2$], 152.4 [s, =CH*C*H=C*i*Pr$_2$], 143.3 [s, =*Ci*Pr$_2$], 30.8, 29.0 (both s, *C*HCH$_3$), 22.3 [vt, *N* = 19.8 Hz, P*C*HCH$_3$], 21.8, 19.4 (both s, PCH*C*H$_3$), 18.3 (s, CH*C*H$_3$). – ^{31}P NMR (162.0 MHz, C_6D_6): δ = 45.5 (s). – $C_{27}H_{58}Cl_2P_2Ru$ (616.7): calcd. C 52.59, H 9.48; found C 52.13, H 9.13.

7. *Preparation of [RuHCl(=C=CHPh)(PiPr$_3$)$_2$]* (**11**): A solution of compound **5**, prepared from 113 mg (0.40 mmol for *n* = 1) of **3**, 193 µl (0.99 mmol) of P*i*Pr$_3$, and 115 µl (0.83 mmol) of NEt$_3$ in 20 ml of 2-propanol under hydrogen, was brought to dryness in vacuo and the oily residue was extracted with 20 ml of hexane. The extract was treated with 96 µl (0.88 mmol) of phenylacetylene and the solution was stirred for 10 min at room temperature. The solvent was then removed at 0°C in vacuo, the residue was dissolved in 10 ml of pentane, and the solution was filtered through Celite. The filtrate was concentrated to ca. 4 ml and then stored at –78°C. Olive-green crystals precipitated which were separated from the mother liquor, washed with 2 ml of pentane (–20°C) and dried; yield 83 mg (37%); m. p. 78°C (dec.). – ^{1}H NMR (400 MHz, C_6D_6): δ = 7.16–6.87 (m, 5 H, C_6H_5), 4.36 [t, *J*(PH) = 3.4 Hz, 1 H, =C=C*H*Ph], 2.51 (m, 6 H, PC*H*CH$_3$), 1.24, 1.22 both m, in ^{1}H{^{31}P} d, *J*(HH) = 7.7 Hz, 36 H, PCHC*H*$_3$], –12.48 [t, *J*(PH) = 17.2 Hz, 1 H, RuH]. – ^{13}C NMR (100.6 MHz, C_6D_6): δ = 329.3 [t, *J*(PC) = 15.1 Hz, =*C*=CHPh], 133.8 [t, *J*(PC) = 2.5 Hz, *ipso*-C of C_6H_5], 128.5, 123.6, 123.5 (each s, C_6H_5), 109.7 [t, *J*(PC) = 3.5 Hz, =C=*C*HPh], 24.7 [vt, *N* = 19.4 Hz, P*C*HCH$_3$], 20.4, 20.2 (both s, PCH*C*H$_3$). – ^{31}P NMR (162.0 MHz, C_6D_6): δ = 50.4 (s). – $C_{26}H_{49}ClP_2Ru$ (560.2): calcd. C 55.75, H 8.82; found C 55.47, H 8.49.

8. *Preparation of [RuHCl(=C=CH$_2$)(PiPr$_3$)$_2$]* (**12**): A solution of compound **5**, prepared from 122 mg (0.43 mmol for *n* = 1) of **3**, 215 µl (1.10 mmol) of P*i*Pr$_3$, and 120 µl (0.87 mmol) of NEt$_3$ in 20 ml of 2-propanol under hydrogen, was brought to dryness in vacuo and the oily residue was extracted with 20 ml of hexane. A slow stream of acetylene was passed at –78°C through the hexane solution, which led to a rapid change of color from red to brown. The solvent was removed at 0°C in vacuo and the residue was worked up as described for **11**. A brown solid was obtained; yield 85 mg (41%); m. p. 83°C (dec.). – ^{1}H NMR (400 MHz, C_6D_6): δ = 2.64 (m, 8 H, PC*H*CH$_3$ and =C=CH$_2$), 1.28, 1.24 both m, in ^{1}H{^{31}P} d, *J*(HH) = 7.2 Hz, 36 H, PCHC*H*$_3$], –15.03 [t, *J*(PH) = 18.3 Hz, 1 H, RuH], signal of =C=C*H*$_2$ obscured by signal of PC*H*CH$_3$. – ^{13}C NMR (100.6 MHz, C_6D_6): δ = 326.3 [t, *J*(PC) = 14.6 Hz, =*C*=CH$_2$], 87.1 [t, *J*(PC) = 3.7 Hz, =C=*C*H$_2$], 24.4 [vt, *N* = 19.5 Hz, P*C*HCH$_3$], 20.4, 20.3 (each s, PCH*C*H$_3$). – ^{31}P NMR (162.0 MHz, C_6D_6): δ = 51.0 (s). – $C_{20}H_{45}ClP_2Ru$ (484.1): calcd. C 49.63, H 9.37; found C 49.36, H 9.11.

9. *Preparation of [RuHCl(H$_2$)(PCy$_3$)$_2$]* (**13**) *from* **3**: A suspension of 220 mg (0.79 mmol for *n* = 1) of **3** in 20 ml of 2-butanol was treated with 886 mg (3.16 mmol) of PCy$_3$ and heated for 6 h under hydrogen (1.5 bar) at 80°C. After the reaction mixture was cooled to room temperature, the solution was decanted from the precipitate. The orange solid was washed twice with 10 ml of 2-butanol and dried in vacuo. It was characterized by comparison of the ^{1}H- and ^{31}P-NMR data with those found in the literature.[8] Yield 470 mg (85%).

10. *Preparation of [RuH$_2$Cl$_2$(PCy$_3$)$_2$]* (**14**) *from* **13**: A solution of 130 mg (0.19 mmol) of **13** in 10 ml of CH_2Cl_2 was treated with 0.5 ml of a 2 M aequous solution of HCl and stirred for 3 h at room temperature. The resulting dark red mixture was cooled to –40°C to remove excess HCl and then filtered. The filtrate was brought to dryness in vacuo and the dark red microcrystalline solid was dried; yield 119 mg (87%); m. p. 74°C (dec.). –The ^{1}H- and ^{31}P-NMR data were identical to those reported by Chaudret et al.[11] – ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ = 38.9 [d, *J*(PC) = 28.6 Hz, *ipso*-C of C_6H_{11}], 29.4 (s, C_6H_{11}), 27.4 [d, *J*(PC) = 11.0 Hz, C_6H_{11}], 26.1 (s, C_6H_{11}).

11. *Preparation of [RuCl$_2$(=C=CHPh)(PCy$_3$)$_2$]* (**15**): a) A solution of 119 mg (0.162 mmol) of **14** in 5 ml of CH_2Cl_2 was treated with 178 µl (1.62 mmol) of PhC≡CH at –78°C. After the solution was warmed to room temperature, it was stirred for 30 min and then concentrated to ca. 2 ml in vacuo. Addition of 10 ml of acetone led to the precipitation of a purple solid, which was filtered, washed twice with 10 ml of acetone, and dried; yield 91 mg (67%). – b) A solution of 172 mg (0.21 mmol) of **16** in 10 ml of benzene was treated with 226 µl (2.10 mmol) of PhC≡CH and the resulting brown solution heated for 15 h at 45°C. After the solution was cooled to room temperature, it was worked up as described for a); yield 103 mg (60%); m. p. 88°C (dec.). If instead of **16** the analogous compound **17** was used as starting material, the yield of the product was about the same. – ^{1}H NMR (200 MHz, $CDCl_3$, 40°C): δ = 7.14–7.07, 6.90–6.80 both m, 5 H, C_6H_5), 4.34 [t, *J*(PH) = 3.1 Hz, 1 H, =C=C*H*Ph], 2.70–2.54, 2.14–2.02, 1.68–1.50 (each m, C_6H_{11}). – ^{13}C NMR (50.3 MHz, $CDCl_3$, 40°C): δ = 342.8 [t, *J*(PC) = 15 Hz, =*C*=CHPh], 133.2, 127.9, 125.1, 123.3, (each s, C_6H_5) 108.6 (br s, =C=*C*HPh), 33.3 (vt, *N* = 22.0 Hz, *ipso*-C of C_6H_{11}), 30.1 (s, C_6H_{11}), 27.9 (vt, *N* = 8.0 Hz, C_6H_{11}). – ^{31}P NMR (81.0 MHz, $CDCl_3$, 40°C): δ = 22.0 (s). –

$C_{44}H_{72}Cl_2P_2Ru$ (834.98): calcd. C 63.29, H 8.69; found C 63.48, H 8.73.

12. *Conversion of Compound* **4** *to* **5** *with PiPr$_3$ and 2-Propanol:* In an NMR tube a suspension of 25 mg (0.05 mmol) of **4** in 0.5 ml of 2-propanol was treated with 20 µl (0.10 mmol) of P*i*Pr$_3$. After 2−3 min, a clear red solution was formed which due to the ^{1}H- and ^{31}P-NMR spectra contained the two compounds **5** and **6** in equimolar amounts. Moreover, the presence of acetone was confirmed by GC/MS analysis.

13. *Conversion of Compound* **14** *to* **13** *with PCy$_3$ and 2-Propanol:* A solution of 50 mg (0.068 mmol) of **14** in 5 ml of 2-propanol was treated with 76 mg (0.272 mmol) of PCy$_3$ at room temperature. Upon stirring for 12 h an orange precipitate was formed, which was filtered, washed with 2 ml of 2-propanol and dried in vacuo; yield 29 mg (61%).

14. *Determination of the X-ray Crystal Structure of* **15**[28] (for data of compound **4** see ref.[5]): Single crystals of **15** were grown upon cooling of a saturated solution of **15** in $CHCl_3$ from 50°C to room temperature. Crystal data (from 25 reflections, $4° < \Theta < 11°$): monoclinic; space group $P2_1/n$ (No. 14); a = 14.505(2), b = 16.816(1), c = 20.057(3) Å, β = 108.438(6)°; V = 4641(1) Å^3, Z = 4; $d_{calcd.}$ = 1.366 gcm^{-3}; μ(Mo-K_α) = 0.720 mm^{-1}; crystal size 0.15 × 0.10 × 0.10 mm; Enraf-Nonius CAD4 diffractometer, Mo-K_α radiation (0.71073 Å), graphite monochromator, zirconium filter (factor 16.4); T = 173(2) K; ω/θ scan, max. 2θ = 48°; 9081 reflections measured, 6500 independent ($R_{int.}$ = 0.0533), 4196 with $I > 2\sigma(I)$. Intensity data were corrected for Lorentz and polarization effects and an empirical absorption correction (Ψ scan method) was applied (min. transmission 98.29%). The structure was solved by the Patterson method (SHELXS-86)[29]. Atomic coordinates and the anisotropic thermal parameters of non-hydrogen atoms were refined by full-matrix least squares on F^2 (SHELXL-93)[30]. The positions of all hydrogen atoms except of H2 were calculated according to ideal geometry and refined by using the riding method. The position of H2 could be located in a final difference Fourier synthesis and refined with fixed U_{eq}. The asymmetric unit includes one molecule of $CHCl_3$ which was refined anisotropically without any restrictions. Conventional R = 0.0588 [for 4196 reflections with $I > 2\sigma(I)$], and weighted wR_2 = 0.1337 for all 6500 located reflections; reflection/parameter ratio 13.51; residual electron density +0.819/−0.685 eÅ^{-3}.

☆ Dedicated to Professor *Bernt Krebs* on the occasion of his 60th birthday.

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