Hydrido(carbonyl) and Hydrido(carbene) Complexes of Ruthenium

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Dedicated to Professor Dirk Walther on the occasion of his 60th birthday

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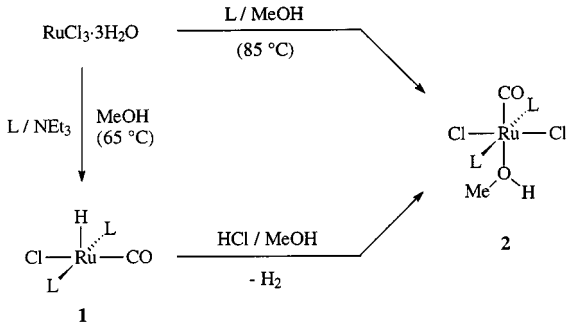
The five-coordinate compound [RuHCl(CO)(P*i*Pr$_2$Ph)$_2$] (**1**), which was prepared from $RuCl_3 \cdot 3\ H_2O$ and P*i*Pr$_2$Ph in methanol in the presence of NEt_3, reacts with CO and with diazoalkanes $RCHN_2$ (R = Ph, H) to give the six-coordinate complexes [RuHCl(CO)$_2$(P*i*Pr$_2$Ph)$_2$] (**4**) and [RuHCl(CO)(=CHR)(P*i*Pr$_2$Ph)$_2$] (**5**, **6**), respectively. If the reaction of **1** with CH_2N_2, which at –78 °C affords **6**, is carried out at room temperature, the ionic compound [MeP*i*Pr$_2$Ph][RuHCl$_2$(CO)(P*i*Pr$_2$Ph)$_2$] (**7**) is formed. The corresponding PPN salt was obtained from **1** and [PPN]Cl. The X-ray crystal structure analysis of **7** revealed, that the anionic species [RuHCl$_2$(CO)(P*i*Pr$_2$Ph)$_2$]$^-$ contains the chloro ligands in *cis* and the phosphanes in *trans* disposition. The Ru=CH$_2$ bond of compound **6** is quite labile and, therefore, the CH$_2$ unit is easily displaced by CO or pyridine. From **1** and pyridine, an isomeric mixture of [RuHCl(CO)(py)(P*i*Pr$_2$Ph)$_2$] (**9a**, **b**) is formed. Treatment of **1** with HC≡CR (R = H, Ph) yields the five-coordinate vinylruthenium(II) complexes [Ru(CH=CHR)Cl(CO)(P*i*Pr$_2$Ph)$_2$] (**12**, **13**) by insertion of the alkyne into the Ru–H bond. The preparation of [RuHX(CO)(P*i*Pr$_2$Ph)$_2$] (X = CF_3CO_2, I) is also reported.

In the search for coordinatively unsaturated complexes with M(P*i*Pr$_3$)$_2$ as a molecular unit, we previously found that treatment of $RuCl_3 \cdot 3\ H_2O$ and $OsCl_3 \cdot 3\ H_2O$ with triisopropylphosphane in methanol leads to the formation of the five-coordinate hydrido(carbonyl)metal compounds [MHCl(CO)(P*i*Pr$_3$)$_2$] (M = Ru, Os) in good to excellent yields.[1] Owing to the free coordination site, these complexes react smoothly with CO, PMe_3, and $P(OMe)_3$ to give the corresponding six-coordinate hydridoruthenium(II) and -osmium derivatives. Further studies revealed that the starting materials [MHCl(CO)(P*i*Pr$_3$)$_2$] are also highly reactive toward terminal acetylenes; however, in this case instead of the anticipated alkyne(hydrido) compounds [MHCl(CO)(HC≡CR)(P*i*Pr$_3$)$_2$] the isomeric insertion products [M(CH=CHR)Cl(CO)(P*i*Pr$_3$)$_2$] are formed.[2]

When we attempted to insert *carbenes* into the M–H bond of the five-coordinate precursors [MHCl(CO)(P*i*Pr$_3$)$_2$], we recently discovered that the complex with M = Os reacts not only with CH_2N_2 but also with substituted diazomethanes $RCHN_2$ by addition of the respective carbene CHR (R = Ph, CO_2Et, $SiMe_3$) to the metal affording the octahedral carbene(hydrido)osmium(II) compounds [OsHCl(CO)(=CHR)(P*i*Pr$_3$)$_2$].[3] In contrast, the ruthenium complex [RuHCl(CO)(P*i*Pr$_3$)$_2$] catalyses the decomposition of diazoalkanes $RCHN_2$ to give olefins RCH=CHR and N_2.[4] Since we knew from our recent work in rhodium chemistry,[5] that both the bulkiness *and* the donor/acceptor capabilities of tertiary phosphanes influences the stability of a carbene-metal bond, we set out to prepare complexes of the general composition [RuHCl(CO)(PR$_3$)$_2$] with phosphanes other than P*i*Pr$_3$. In this paper we report the synthesis of both five-coordinate [RuHCl(CO)(P*i*Pr$_2$Ph)$_2$] and a series of 1:1 adducts including those with CH_2 and CHPh as the additional ligand.

Results and Discussion

Following the procedure used for the preparation of [RuHCl(CO)(P*i*Pr$_3$)$_2$],[1] treatment of a solution of $RuCl_3 \cdot 3\ H_2O$ in methanol with a sixfold excess of P*i*Pr$_2$Ph in the presence of NEt_3 at 65 °C leads to the formation of the analogous chloro(hydrido)ruthenium(II) derivative [RuHCl(CO)(P*i*Pr$_2$Ph)$_2$] (**1**). The yellow, only slightly air-sensitive solid precipitates from the solution in analytically pure form. The ^{1}H-NMR spectrum of **1** displays for each of the four diastereotopic methyl groups of the phosphane ligands a doublet of virtual triplets which is in agreement with the proposed structure. The presence of the hydrido ligand is indicated by the high-field resonance at δ = –24.67 which is split into a triplet due to P-H coupling.



Scheme 1. L = P*i*Pr$_2$Ph

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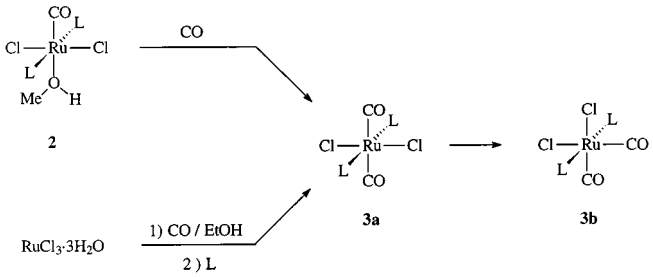
When we changed the reaction conditions in order to increase the yield of compound **1**, we discovered that from $RuCl_3 \cdot 3\,H_2O$, P*i*Pr_2Ph and methanol a by-product is formed besides **1**, which is the six-coordinate dichlororuthenium(II) complex **2** (Scheme 1). After raising the temperature to 85 °C and the time of reaction to 70 h, the isolated yield of **2** was improved to 41%. Moreover, compound **2** is obtained quantitatively upon treatment of the hydrido complex **1** with gaseous HCl in CH_2Cl_2/CH_3OH (1:1). Hereby, the evolution of H_2 is observed. Although it is known that the related hydridoosmium compound $[OsHCl(CO)(P\textit{i}Pr_3)_2]$ reacts with HCl to afford the rather stable dihydrogen complex $[OsCl_2(H_2)(CO)(P\textit{i}Pr_3)_2]$,[6] our attempts to isolate or detect spectroscopically the corresponding 1:1 adduct of **1** and H_2 failed.

With regard to the mechanism of formation of compound **2** from $RuCl_3 \cdot 3\,H_2O$, P*i*Pr_2Ph, and methanol, we assume that initially the chloro(hydrido)ruthenium(II) derivative **1** is generated as an intermediate which, subsequently, reacts with the phosphonium chloride [HP*i*Pr_2Ph]Cl (formed from an excess of P*i*Pr_2Ph) to give **2**. The coordination of methanol to the ruthenium center in **2** is indicated by the appearance of a strong $\tilde{\nu}$(OH) band at 3563 cm^{-1} in the IR spectrum and of a broad singlet (with a relative intensity of 3 H) at $\delta = 2.48$ in the ^{1}H-NMR spectrum. Since the ^{1}H-NMR spectrum of **2** displays only two signals for the PCHC*H*$_3$ protons instead of four as in the case of **1**, we conclude that not only the two phosphanes but also the two chloro ligands are *trans* disposed. A structurally related 1:1 adduct of a dichlororuthenium(II) complex with a weakly bound solvent molecule of the composition $[RuCl_2(H_2O)(CO)(PEt_3)_2]$ was recently isolated by Carty et al. and characterized by an X-ray crystal structure analysis.[7]

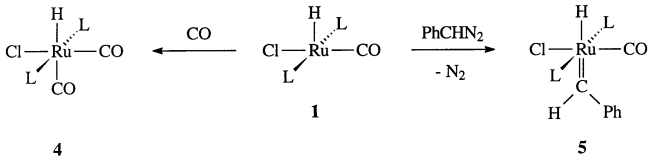
The labile methanol ligand of compound **2** is easily displaced by CO to give the six-coordinate dicarbonyl complex $[RuCl_2(CO)_2(P\textit{i}Pr_2Ph)_2]$ (see Scheme 2). The orange product **3a** initially formed is relatively stable in the solid state but rearranges in solution to the thermodynamically preferred yellow isomer **3b**. An independent synthesis of **3a** consists of the reduction of $RuCl_3 \cdot 3\,H_2O$ by CO in the presence of ethanol, followed by addition of P*i*Pr_2Ph. Since the IR spectrum of **3a** exhibits *one* and that of **3b two** CO stretching frequencies, we assume that **3a** is the *all-trans* and **3b** the *cis,cis,trans* isomer. A similar conclusion was drawn by Nelson et al. who prepared, also from $RuCl_3 \cdot 3\,H_2O$ as the starting material, two isomeric forms of the ruthenium(II) compound $[RuCl_2(CO)_2(PPh_3)_2]$.[8]

The five-coordinate chloro(hydrido) complex **1** is also highly reactive toward CO and affords in the presence of carbonmonoxide in ether the dicarbonyl derivative **4** in quantitative yield (Scheme 3). The open coordination site of the precursor compound **1**, however, cannot only be occupied by CO but also by phenylcarbene. If a solution of **1** in toluene is treated dropwise with a solution of $PhCHN_2$ in hexane, a change of color from yellow to orange occurs and the evolution of gas (N_2) is observed. After removal of the solvent and recrystallization from toluene an orange



Scheme 2. L = P*i*Pr_2Ph

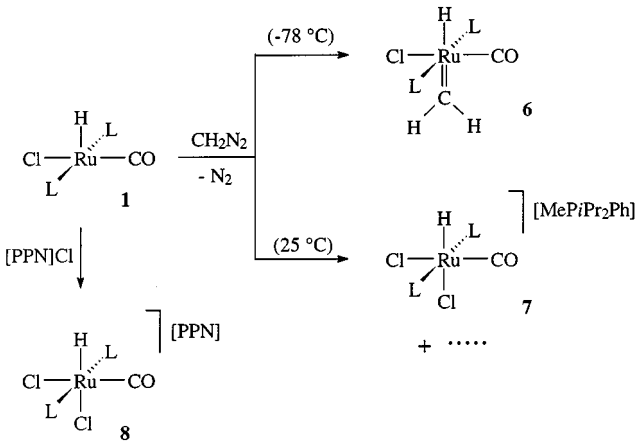
solid is isolated which according to the elemental analysis and the spectroscopic data represents the six-coordinate ruthenium(II) complex **5**. The fact, that the carbene(hydrido) and not the isomeric benzyl compound $[Ru(CH_2Ph)Cl(CO)(P\textit{i}Pr_2Ph)_2]$ is formed, is clearly indicated by the ^{1}H-NMR spectrum, which displays besides the signals for the two phosphanes a doublet of triplets for the hydrido ligand at high field ($\delta = -2.77$) as well as a broadened singlet for the carbene C*H*Ph proton at low field ($\delta = 18.22$). The ^{13}C-NMR spectrum of **5** exhibits resonances at $\delta = 343.4$ and 203.3 which are assigned to the Ru=*C*HPh and Ru-*C*O carbon atoms, respectively.



Scheme 3. L = P*i*Pr_2Ph

The parent diazoalkane CH_2N_2 behaves similarly to $PhCHN_2$ and reacts with the starting material **1** to yield the hydrido(methylene) complex **6** (Scheme 4). However, while the phenylcarbene derivative **5** is thermally stable as a solid up to 138 °C and can be stored under argon at room temperature for weeks, the $RuH(CH_2)$ compound **7** decomposes above −50 °C. Thus it could not be characterized by elemental analysis but only by spectroscopic means. Similarly to **5**, the ^{1}H-NMR spectrum of **6** displays a hydride resonance at $\delta = -2.60$ and two signals for the nonequivalent Ru=CH_2 protons at $\delta = 17.38$ and 16.36. The chemical shifts for these signals differ only slightly to those of the related osmium complex $[OsHCl(=CH_2)(CO)(P\textit{i}Pr_3)_2]$, which is, however, in contrast to **6** significantly more stable.[3]

At room temperature, the reaction of **1** with CH_2N_2 led to a different result. If the solution of the two reacting substrates in toluene/ether is stirred for ca. 12 h, a white precipitate is formed which is easily soluble in dichloromethane but almost insoluble in benzene and ether. These properties, together with the analytical data, indicate that an ionic complex of the composition [MeP*i*Pr_2Ph][$RuHCl_2$(CO)(P*i*Pr_2Ph)$_2$] (**7**) is formed. Based on control measurements (in CD_2Cl_2) in an NMR tube we assume that initially the methylene compound **6** is formed as an intermediate which rapidly decomposes to give inter alia the starting material **1** and [MeP*i*Pr_2Ph]Cl. Both compounds then react to afford



Scheme 4. L = P*i*Pr_2Ph

7. The most typical spectroscopic features of **7** are the two resonances in the ^{31}P-NMR spectrum (in CD_2Cl_2) at δ = 40.6 (sharp singlet) and 47.0 (broad singlet) which are assigned to the phosphorus nuclei of the cation and anion, respectively. Since the hydride signal in the ^{1}H-NMR spectrum at 28 °C is also rather broad (but sharpens in CD_2Cl_2 at −50 °C to a triplet with a P-H coupling of 22.4 Hz), we suppose that at room temperature the anion $[RuHCl_2(CO)(PiPr_2Ph)_2]$ partially dissociates in $[RuHCl(CO)(PiPr_2Ph)_2]$ (**1**) and Cl^-. This proposal is in agreement with the observation that upon cooling at −50 °C the ^{31}P-NMR resonance of the anion of **7**, although still relatively broad, is shifted from δ = 47.0 to 43.5, this process being reversible. A similar phenomenon was observed by measuring the ^{31}P-NMR spectrum of $[OsHCl_2(CO)(PiPr_3)_2]^-$ at different temperatures.[4] We note (see Scheme 4) that the PPN-salt **8** of the anion $[RuHCl_2(CO)(PiPr_2Ph)_2]^-$ is obtained as a white solid from **1** and [PPN]Cl in nearly quantitative yield. The IR as well as the ^{1}H-, ^{13}C-, and ^{31}P-NMR spectra of **8** differ only slightly to those of **7** and thus deserves no further comment.

In order to substantiate the exact composition of **7**, a single-crystal X-ray structure analysis was carried out. As Figure 1 reveals, the coordination geometry around the metal center of the anion is distorted octahedral, with the two phosphanes in *trans* and the two chloro ligands in *cis* disposition. The P1−Ru−P2 axis is considerably bent, the bond angle of 163.49(3)° being comparable to that in the related neutral osmium complex $[OsCl_2(=CHPh)(CO)(PiPr_3)_2]$ [167.5(2)°].[3] The most notable detail of the structure of the anion, however, is the significant difference of the Ru−Cl bond lengths. While the bond length between ruthenium and the chloride *trans* to CO is 2.499(1) Å, that between the metal and the chloride *trans* to hydride is 2.618(1) Å. This difference (which is hard to understand owing to the similar *trans* influence of CO and hydride) could be used as an argument to explain the assumed dissociation of the anion $[RuHCl_2(CO)(PiPr_2Ph)_2]$ into **1** and Cl^-. We note that for the two carbonyl(hydrido)iridium(III) complexes $[IrHCl_2(CO)(PiPr_3)_2]$ and $[IrHCl_2(CO)(PPh_3)\{PPh_2(o\text{-}C_6H_4OH)\}]$, both containing a planar $IrHCl_2(CO)$ unit with *cis*-disposed chloro ligands, a similar difference in the Ir−Cl bond lengths of about 0.10 and 0.18 Å, respectively, has been observed.[9][10]

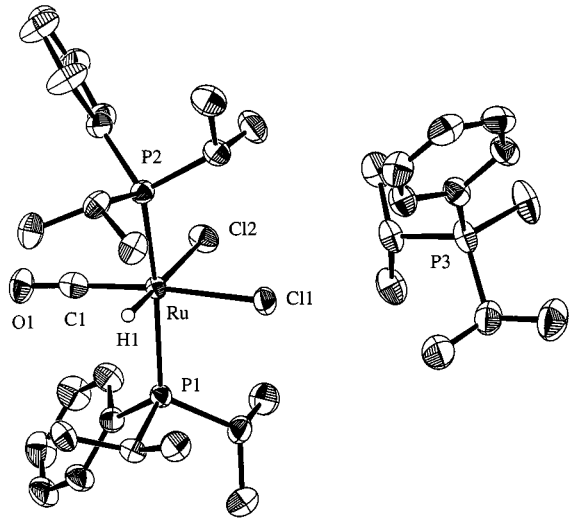
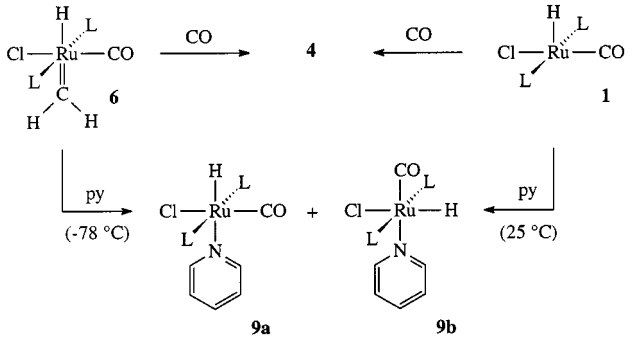


Figure 1. Molecular structure (ORTEP plot) of **7**; the hydrogen atoms besides H1 are omitted for clarity; selected bond lengths [Å] and angles [°]: Ru−P1 2.351(1), Ru−P2 2.358(1), Ru−Cl1 2.499(1), Ru−Cl2 2.618(1), Ru−H1 1.53(2), Ru−C1 1.806(3), C1−O1 1.137(3); P1−Ru−P2 163.49(3), C1−Ru−Cl1 172.71(8), P2−Ru−Cl1 90.81(4), P2−Ru−Cl2 98.41(4), P2−Ru−C1 90.2(1), Cl2−Ru−Cl1 90.31(4), Cl2−Ru−C1 96.67(9), Cl2−Ru−P1 97.97(4), Cl1−Ru−P1 87.04(4), C1−Ru−P1 89.9(1), H1−Ru−P1 84.0(1), H1−Ru−P2 79.5(1), H1−Ru−C1 88.5(1), H1−Ru−Cl1 84.6(1), H1−Ru−Cl2 174.5(1), Ru−C1−O1 176.1(2)

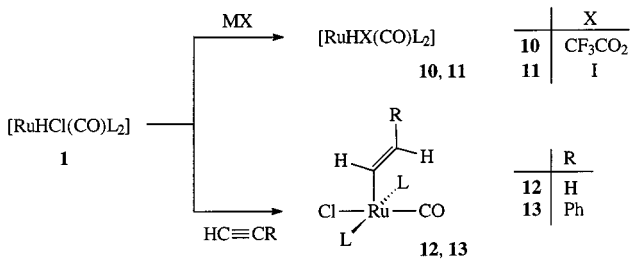
Attempts to initiate an insertion of the carbene ligand into the Ru−H bond of compound **6** by treatment of **6** with Lewis bases such as CO or pyridine led to a displacement of the CH_2 unit. This finding differs with ab initio calculations which predict that for the model system $RuH(=CH_2)Cl$ the conversion into $Ru(CH_3)Cl$ proceeds with a rather low barrier of 11.5 kcal/mol and is exothermic by 7.1 kcal/mol.[11] The model system, however, is coordinatively unsaturated while compound **6** is not. As shown in Scheme 5, the reaction of **6** with CO affords the dicarbonyl complex **4** together with traces of ethene. In contrast, treatment of **6** with pyridine gives a mixture of two isomers **9a** and **9b**, which are also obtained from the five-coordinate starting material **1** and pyridine. Regarding the ligand arrangement of **9a** and **9b**, a plausible assumption is that in one isomer the pyridine is *trans* to hydride and in the other *trans* to CO. The fact, that both the chemical shifts of the hydride signals in the ^{1}H NMR (at δ = −13.54 and −14.41) and of the two resonances in the ^{31}P-NMR spectrum (at δ = 48.9 and 43.8) differ only slightly, seems to be in agreement with this proposal. The alternative, that the hydride and the carbonyl ligands are *trans* to each other, is less likely since in this case, which corresponds to the situation in compound **4**, the hydride signal should be observed at considerably lower field (for **4**: δ = −5.23). In this context we note that Caulton and co-workers recently reported that treatment of $[RuH(OR_F)(CO)(PtBu_2Me)_2]$ (R_F = CH_2CF_3) with pyridine

also produces a mixture of two isomers of the composition $[RuH(OR_F)(CO)(py)(PtBu_2Me)_2]$.[12]



Scheme 5. L = P*i*Pr$_2$Ph

Similarly to $[RuHCl(CO)(PiPr_3)_2]$ and $[OsHCl(CO)(PiPr_3)_2]$, which react with MX by salt metathesis to give the ruthenium(II) and osmium(II) derivatives $[MHX(CO)(PiPr_3)_2]$ (X = Br, I, N_3, OR, SR),[13] the five-coordinate compound **1** can be converted with CF_3CO_2Tl and KJ to the related hydrido(trifluoracetato) and hydrido(iodo) complexes **10** and **11**, respectively (see Scheme 6). While the orange-yellow $RuH(O_2CCF_3)$ species **10**, in analogy to the starting material **1,** is only slightly air-sensitive, the brown hydrido(iodo) compound **11** smoothly decomposes (in solution as well as in the solid state) in the presence of air. Despite the different behavior of **1** and **11** toward O_2, the spectroscopic data of both complexes are quite similar. This is illustrated by the chemical shifts both of the hydride signal (**1**: $\delta = -24.67$; **11**: $\delta = -25.0$) in the ^{1}H-NMR and of the CO resonance (**1**: $\delta = 197.7$; **11**: $\delta = 198.7$) in the ^{13}C-NMR spectra. In contrast, the corresponding NMR spectra of **10** exhibit the signal for the RuH moiety at $\delta = -18.23$ and that for the CO ligand at $\delta = 205.1$. Owing to these data we assume that the CF_3CO_2 unit of **10** is coordinated in a chelating fashion, which increases the coordination number for ruthenium(II) from five (in **1**) to six (in **10**). This structural proposal is supported by the IR spectrum of **10**, in which the symmetrical and the antisymmetrical OCO stretching vibrations appear at 1597 and 1410 cm^{-1}, respectively. According to extensive studies, particularly by Robinson et al.,[14][15] the observed difference of 187 cm^{-1} clearly points to a bidentate, not a monodentate, linkage of the trifluoracetate to the ruthenium center.



Scheme 6. L = P*i*Pr$_2$Ph

As mentioned above, the chloro compound **1** reacts readily with $PhCHN_2$ at room temperature to give the phenylcarbene complex **5** in 42% isolated yield. Contrary to this result, the trifluoracetato and iodo derivatives **10** and **11** are less reactive toward $PhCHN_2$ and upon stirring a solution of the two respective substrates in toluene for 2−4 h a complex mixture of products is formed. We not only failed to separate the mixture but also found no evidence for the presence of a Ru=CHPh species among the various components.

Completely inert toward $PhCHN_2$ are the vinyl complexes **12** and **13**, which have been obtained likewise to the corresponding ruthenium and osmium compounds $[M(CH=CHR)Cl(CO)(PiPr_3)_2]$ (M = Ru, Os; R = H, Ph)[2] from the starting material **1** and acetylene or phenylacetylene, respectively (Scheme 6). Both complexes, **12** and **13**, are moderately air-sensitive solids which are easily soluble in common organic solvents (with the exception of hexane and pentane). The *trans* stereochemistry at the C=C bond of **13** is strongly supported by the large H−H coupling constant for the vinyl protons, which is 14.0 Hz.[16] The ^{13}C-NMR resonances for the $CH=CH_2$ carbon atoms of **12** appear at $\delta = 152.5$ and 120.5, the chemical shifts being quite similar to those of $[Ru(CH=CH_2)Cl(CO)(PiPr_3)_2]$.[2] Attempts to convert compound **12** to the π-allyl complex $[RuCl(\eta^3\text{-}C_3H_5)(CO)(PiPr_2Ph)_2]$ by treatment with CH_2N_2, in analogy to the preparation of $[RuCl(\eta^3\text{-}C_3H_5)(CO)(PPh_3)_2]$ by Hill and co-workers,[17] remained unsuccessful.

In summary, the present investigations have shown that in contrast to $[RuHCl(CO)(PiPr_3)_2]$ the related five-coordinate bis(diisopropylphenylphosphane) complex **1** reacts with CH_2N_2 and $PhCHN_2$ to generate the six-coordinate carbeneruthenium(II) derivatives **5** and **6**. Although theoretical calculations reveal that an insertion of the carbene unit into the Ru−H bond is conceivable, attempts to prepare alkylruthenium compounds from **5** or **6** as a precursor failed. As recent studies by Caulton and Eisenstein indicate,[18] the conversion of a $RuH(CH_2)$ to a $RuCH_3$ unit could be strongly influenced by the phosphane ligands linked to the ruthenium center, the more bulky P*t*Bu$_2$Me being more suitable than P*i*Pr$_3$. We finally note that despite the lability of the carbene−ruthenium bond, which is most obvious in **6,** the complexes **5** and **6** are catalytically inactive in olefin metathesis. Whether this is due to the octahedral geometry, that hinders the addition of an olefin, or to the presence of a Ru−H bond, is open to speculation.

Experimental Section

All operations were carried out under argon using Schlenk techniques. The diazoalkanes CH_2N_2 and $PhCHN_2$[19] were prepared as reported in the literature. All other starting materials 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 $^1J(PC) + {}^3J(PC)$, respectively]. − Melting points determined by DTA.

1. Preparation of [RuHCl(CO)(P*i*Pr$_2$Ph)$_2$] (1): A solution of 1.00 g (3.98 mmol) of $RuCl_3 \cdot 3\,H_2O$ in 35 mL of methanol was treated dropwise with 4.63 g (23.8 mmol) of P*i*Pr$_2$Ph. After the solution was stirred for 10 min at room temperature, 1.09 mL (7.88 mmol)

of NEt_3 were added and the mixture was heated for 5 h at 65 °C. After the solution was cooled to room temperature, a yellow precipitate was formed which was filtered, washed twice with 5 mL of methanol, then with 10 mL of pentane and dried in vacuo; yield 1.43 g (65%); m.p. 194 °C (dec.). − IR (KBr): $\tilde{\nu}$ = 2100 cm^{-1} (RuH), 1900 (CO). − ^1H NMR (400 MHz, C_6D_6): δ = 7.72 (m, 4 H, C_6H_5), 7.11 (m, 6 H, C_6H_5), 3.22, 2.62 (both m, 2 H each, PC*H*CH_3), 1.33 [dvt, *N* = 14.4, *J*(HH) = 6.8 Hz, 6 H, PCHC*H*$_3$], 1.25 [dvt, *N* = 16.0, *J*(HH) = 6.8 Hz, 6 H, PCHC*H*$_3$], 1.15 [dvt, *N* = 15.2, *J*(HH) = 7.2 Hz, 6 H, PCHC*H*$_3$], 0.87 [dvt, *N* = 13.2, *J*(HH) = 6.6 Hz, 6 H, PCHC*H*$_3$], −24.67 [t, *J*(PH) = 20 Hz, 1 H, RuH]. − ^{13}C NMR (100.6 MHz, C_6D_6): δ = 197.7 [t, *J*(PC) = 10 Hz, CO], 135.0, 127.9 (both vt, *N* = 11 and 8 Hz, *ortho*- and *meta*-C of C_6H_5), 130.5 (s, *para*-C of C_6H_5), 129.4 (vt, *N* = 35 Hz, *ipso*-C of C_6H_5), 22.5, 20.8 (both vt, *N* = 23 and 22 Hz, P*C*HCH$_3$), 18.5, 18.3, 17.8, 15.5 (all s, PCH*C*H$_3$). − ^{31}P NMR (162.0 MHz, C_6D_6): δ = 55.5 (s). − $C_{25}H_{39}ClOP_2Ru$ (554.1): calcd. C 54.20, H 7.10, Ru 18.24; found C 53.92, H 7.00, Ru 18.45.

2. Preparation of [$RuCl_2$(CO)(MeOH)(P*i*Pr_2Ph)$_2$] (2): a) A solution of 1.00 g (3.98 mmol) of $RuCl_3 \cdot 3\,H_2O$ in 10 mL of methanol was treated dropwise with 1.95 g (10.0 mmol) of P*i*Pr_2Ph and heated for 70 h at 85 °C. After the reaction mixture was cooled to room temperature, the resulting pale yellow precipitate was filtered, washed twice with 10 mL of methanol, and dried in vacuo; yield: 1.01 g (41%). − b) A slow stream of dried HCl was passed through a solution of 83 mg (0.15 mmol) of **1** in 4 mL of dichloromethane-methanol (1:1) for ca. 1 min. The solvent was removed and the resulting yellow solid was dried in vacuo; yield: 92 mg (99%); m.p. 138 °C (dec.). − IR (KBr): $\tilde{\nu}$ = 3563 cm^{-1} (OH), 1918 (CO). − ^1H NMR (400 MHz, C_6D_6): δ = 7.58 (m, 4 H, C_6H_5), 7.20−6.82 (m, 6 H, C_6H_5), 3.50 (m, 4 H, PC*H*CH_3), 2.48 (s, 3 H, C*H*$_3$OH), 1.72 [dvt, *N* = 15.6, *J*(HH) = 7.6 Hz, 12 H, PCHC*H*$_3$], 1.09 [dvt, *N* = 12.8, *J*(HH) = 6.4 Hz, 12 H, PCHC*H*$_3$], signal of CH_3OH not observed. − ^{31}P NMR (162.0 MHz, C_6D_6): δ = 36.7 (s). − $C_{26}H_{42}Cl_2O_2RuP_2$ (620.5): calcd. C 50.32, H 6.82; found C 50.38, H 6.88.

3. Preparation of *trans,trans,trans*-[$RuCl_2$(CO)$_2$(P*i*Pr_2Ph)$_2$] (3a): A solution of 100 mg (0.40 mmol) of $RuCl_3 \cdot 3\,H_2O$ in 5 mL of ethanol was stirred in a pressure bottle under CO atmosphere (1 bar) for 5 h at 65 °C. After the reaction mixture was cooled to 0 °C, it was treated under CO dropwise with a solution of 155 mg (0.80 mmol) of P*i*Pr_2Ph in 1.3 mL of chloroform. The solution was stirred for 15 h at room temperature, the resulting orange precipitate was filtered, washed with 5 mL of ethanol and dried in vacuo; yield: 186 mg (79%). − IR (KBr): $\tilde{\nu}$ = 1975 cm^{-1} (CO). − ^{31}P NMR (81.0 MHz, $CDCl_3$): δ = 32.7 (s).

4. Preparation of *cis,cis,trans*-[$RuCl_2$(CO)$_2$(P*i*Pr_2Ph)$_2$] (3b): A solution of 186 mg (0.30 mmol) of **3a** in 5 mL of chloroform was heated for 15 min at 80 °C. After the reaction mixture was cooled to room temperature, the solvent was removed and the yellow solid was dried in vacuo; yield: 186 mg, (99%); m.p. 69 °C (dec.). − IR (KBr): $\tilde{\nu}$ = 2020 cm^{-1} (CO), 1960 (CO). − ^1H NMR (400 MHz, $CDCl_3$): δ = 8.12 (m, 4 H, C_6H_5), 7.45 (m, 6 H, C_6H_5), 3.25 (m, 4 H, PC*H*CH_3), 1.36 [dvt, *N* = 15.2, *J*(HH) = 7.2 Hz, 12 H, PCHC*H*$_3$], 1.19 [dvt, *N* = 14.4, *J*(HH) = 7.2 Hz, 12 H, PCHC*H*$_3$]. − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 195.2 [t, *J*(PC) = 11 Hz, CO], 134.2, 128.1 both vt, *N* = 7 and 8 Hz, *ortho*-C and *meta*-C of C_6H_5), 130.4 (s, *para*-C of C_6H_5), 127.7 (vt, *N* = 36 Hz, *ipso*-C of C_6H_5), 23.4 (vt, *N* = 24 Hz, P*C*HCH$_3$), 18.5, 17.7 (both s, PCH*C*H$_3$). − ^{31}P NMR (162.0 MHz, $CDCl_3$): δ = 30.6 (s). − $C_{26}H_{38}Cl_2O_2RuP_2$ (616.5): calcd. C 50.65, H 6.21; found C 50.56, H 6.01.

5. Preparation of [$RuHCl(CO)_2$(P*i*Pr_2Ph)$_2$] (4): A slow stream of CO was passed at room temperature through a suspension of 124 mg (0.22 mmol) of **1** in 5 mL of ether until a clear, almost colorless solution was formed. The solvent was removed and the remaining white solid was dried in vacuo; yield 130 mg (99%); m.p. 161 °C (dec.). − IR (KBr): $\tilde{\nu}$ = 2010 cm^{-1} (RuH), 1950, 1900 (CO). − ^1H NMR (400 MHz, CD_2Cl_2): δ = 7.85 (m, 4 H, C_6H_5), 7.50 (m, 6 H, C_6H_5), 2.99, 2.89 (both m, 2 H each, PC*H*CH_3), 1.28 [dvt, *N* = 16.1, *J*(HH) = 7.1 Hz, 6 H, PCHC*H*$_3$], 1.22 [dvt, *N* = 16.8, *J*(HH) = 7.2 Hz, 6 H, PCHC*H*$_3$], 1.12 [dvt, *N* = 13.8, *J*(HH) = 7.1 Hz, 6 H, PCHC*H*$_3$], 1.01 [dvt, *N* = 15.9, *J*(HH) = 7.2 Hz, 6 H, PCHC*H*$_3$], −5.23 [t, *J*(PH) = 20 Hz, 1 H, RuH]. − ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ = 200.8, [t, *J*(PC) = 8 Hz, CO], 198.3 [t, *J*(PC) = 11 Hz, CO], 134.9, 128.2 (both vt, *N* = 10 and 9 Hz, *ortho*-C and *meta*-C of C_6H_5), 130.5 (s, *para*-C of C_6H_5), 128.8 (vt, *N* = 35 Hz, *ipso*-C of C_6H_5), 23.3, 22.5 (both vt, *N* = 29 and 23 Hz, P*C*HCH$_3$), 18.3, 17.8, 17.4, 16.8 (all s, PCH*C*H$_3$). − ^{31}P NMR (162.0 MHz, CD_2Cl_2): δ = 59.6 (s). − $C_{26}H_{39}ClO_2P_2Ru$ (582.1): calcd. C 53.65, H 6.75; found C 53.74, H 7.06.

6. Preparation of [RuHCl(CO)(=CHPh)(P*i*Pr_2Ph)$_2$] (5): A solution of 156 mg (0.28 mmol) of **1** in 10 mL of toluene was treated dropwise with 0.27 mL of a 1.5 M solution of $PhCHN_2$ (0.42 mmol) in hexane. A change of color from yellow to orange occurred and the evolution of gas was observed. After the reaction mixture was stirred for 30 min at room temperature, the solvent was removed in vacuo, and pentane was added to the oily residue. Ultrasonic irradiation of this mixture gave an orange precipitate, which was filtered, washed three times with 2 mL of pentane and dried in vacuo. The crude product (yield ca. 80%) still contained ca. 5% of compound **1**. After recrystallization from toluene at −20 °C, a pure orange solid was obtained; yield 76 mg (42%); m.p. 138 °C (dec.). − IR (KBr): $\tilde{\nu}$ = 1930 cm^{-1} (CO). − ^1H NMR (400 MHz, C_6D_6): δ = 18.22 (m, 1 H, Ru=C*H*Ph), 8.22 (m, 2 H, C_6H_5), 7.74 (m, 4 H, C_6H_5), 7.12 (m, 9 H, C_6H_5), 3.14, 2.81 (both m, 2 H each, PC*H*CH_3), 1.49 [dvt, *N* = 16.8, *J*(HH) = 7.2 Hz, 6 H, PCHC*H*$_3$], 0.99 [dvt, *N* = 14.8, *J*(HH) = 7.2 Hz, 6 H, PCHC*H*$_3$], 0.96 [dvt, *N* = 16.8, *J*(HH) = 7.2 Hz, 6 H, PCHC*H*$_3$], 0.95 [dvt, *N* = 14.8, *J*(HH) = 7.2 Hz, 6 H, PCHC*H*$_3$], −2.77 [dt, *J*(PH) = 21, *J*(HH) = 2 Hz, RuH]. − ^{13}C NMR (100.6 MHz, C_6D_6): δ = 343.4 (s, Ru=*C*HPh), 203.3 [t, *J*(PC) = 12 Hz, CO], 154.3 [s, *ipso*-C of Ru=CH(*C*$_6$H$_5$)], 135.0 (vt, *N* = 9 Hz, C_6H_5), 133.2, 132.1, 130.0, 129.6, 127.6, 125.6 (all s, C_6H_5), 23.8, 23.6 (both vt, *N* = 22 and 31 Hz, P*C*HCH$_3$), 18.5, 17.1, 17.0, 16.8 (all s, PCH*C*H$_3$). − ^{31}P NMR (162.0 MHz, C_6D_6): δ = 75.2 (s). − $C_{32}H_{45}ClORuP_2$ (644.2): calcd. C 59.67, H 7.04; found C 59.23, H 6.80.

7. Preparation of [RuHCl(CO)(=CH_2)(P*i*Pr_2Ph)$_2$] (6): A suspension of 123 mg (0.22 mmol) of **1** in 5 mL of toluene was treated dropwise at −78 °C with 1.5 mL of a ca. 0.5 M solution of diazomethane (ca. 0.75 mmol) in ether. Almost instantaneously, a pale yellow solid precipitated, the formation of which was facilitated upon addition of 10 mL of pentane (−78 °C). The mother liquor was removed, the remaining residue washed with 5 mL of pentane (−78 °C) and dried at −78 °C in vacuo. Since the pale yellow solid decomposed at −50 °C, it was characterized spectroscopically. − ^1H NMR (400 MHz, [D_8]THF, −53 °C): δ = 17.36, 16.38 (both br s, 1 H each, Ru=CH_2), −2.60 [t, *J*(PH) = 20 Hz, RuH], signals of C_6H_5 and C_3H_7 protons overlap with those of the solvents used for preparation.

8. Preparation of [MeP*i*Pr_2Ph][$RuHCl_2$(CO)(P*i*Pr_2Ph)$_2$] (7): A solution of 100 mg (0.18 mmol) of **1** in 10 mL of toluene was treated dropwise with 1 mL of a ca. 0.5 M solution of diazomethane in ether (ca. 0.5 mmol) at room temperature. The color of the reaction

mixture changed from yellow to dark red and the evolution of gas was observed. After the reaction mixture was stirred for ca. 15 h, a white precipitate was formed, which was filtered, washed twice with 5 mL of pentane, and dried in vacuo; yield 41 mg (30%); m.p. 138 °C (dec.). – IR (KBr): $\tilde{\nu}$ = 2085 cm^{-1} (RuH), 1940 (CO). – ^{1}H NMR (400 MHz, CD_2Cl_2); signals for $[RuHCl_2(CO)(P$-$i Pr_2Ph)_2]^-$: δ = 8.08 (m, 4 H, C_6H_5), 7.70 (m, 2 H, C_6H_5), 7.38 (m, 4 H, C_6H_5), 2.99, 2.82 (both m, 2 H each, PC*H*CH_3), 1.22 [br d, *J*(HH) = 6.7 Hz, 6 H, PCHC*H*$_3$], 1.17 [br d, *J*(HH) = 6.7 Hz, 6 H, PCHC*H*$_3$], 1.08 [dvt, *N* = 11.6, *J*(HH) = 5.8 Hz, 6 H, PCHC*H*$_3$], 1.01 [dvt, *N* = 13.4, *J*(HH) = 6.7 Hz, 6 H, PCHC*H*$_3$], −17.8 (br s, 1 H, RuH); signals for $[MeP$-$i Pr_2Ph]^+$: δ = 7.84−7.59 (m, 5 H, C_6H_5), 3.18 (m, 2 H, PC*H*CH_3), 2.26 [d, *J*(PH) = 12.4 Hz, 3 H, PC*H*$_3$], 1.29 [dd, *J*(HH) = 7.2, *J*(PH) = 10.8 Hz, 6 H, PCHC*H*$_3$], 1.34 [dd, *J*(HH) = 6.8, *J*(PH) = 10.8 Hz, 6 H, PCHC*H*$_3$]. – ^{13}C NMR (100.6 MHz, CD_2Cl_2); signals for $[RuHCl_2(CO)(Pi Pr_2Ph)_2]^-$: δ = 203.0 [t, *J*(PC) = 13.1 Hz, CO], 135.8, 127.3 (both vt, *N* = 10.0 and 8.0 Hz, *ortho*- and *meta*-C of C_6H_5), 132.4 (vt, *N* = 27.3 Hz, *ipso*-C of C_6H_5) 129.2 (s, *para*-C of C_6H_5), 23.9, 22.7 (both vt, *N* = 26.1 and 20.2 Hz, P*C*HCH$_3$), 19.0, 18.3, 18.1, 17.6 (all s, PCH*C*H$_3$); signals for $[MeP$-$i Pr_2Ph]^+$: δ = 135.0 [d, *J*(PC) = 3 Hz, *para*-C of C_6H_5], 133.0, 130.6 both d, *J*(PC) = 8 Hz and 11 Hz, *meta*- and *ortho*-C of C_6H_5], 115.7 [d, *J*(PC) = 78 Hz, *ipso*-C of C_6H_5], 21.5 [d, *J*(PC) = 47 Hz, P*C*HCH$_3$], 15.9, 15.8 both d, *J*(PC) = 2 Hz, PCH*C*H$_3$], −0.5 [d, *J*(PC) = 52 Hz, P*C*H$_3$]. – ^{31}P NMR (162.0 MHz, CD_2Cl_2): δ = 47.0 (s, PiPr$_2$Ph), 40.6 (s, $[MeP$-$i Pr_2Ph]^+$). – $C_{38}H_{61}Cl_2OP_3Ru$ (798.8): calcd. C 57.14, H 7.70; found C 57.32, H 7.70.

9. Preparation of [PPN][$RuHCl_2(CO)(Pi Pr_2Ph)_2$] (8): A solution of 104 mg (0.19 mmol) of **1** in 10 mL of benzene was treated with 108 mg (0.19 mmol) of [PPN]Cl. The color of the solution changed gradually from yellow to pale yellow. After the reaction mixture was stirred for ca. 18 h at room temperature, a white solid precipitated, which was filtered, washed three times with 5 mL of benzene, and dried in vacuo; yield 187 mg (88%); m.p. 125 °C (dec.). – IR (KBr): $\tilde{\nu}$ = 2062 cm^{-1} (RuH), 1890 (CO). – ^{1}H NMR (200 MHz, CD_2Cl_2): δ = 8.32 (m, 4 H, C_6H_5), 7.66−7.36 (m, 36 H, C_6H_5), 3.11, 2.70 (both m, 2 H each, PC*H*CH_3), 1.33 [dvt, *N* = 14.1, *J*(HH) = 7.0 Hz, 6 H, PCHC*H*$_3$], 1.20 [dvt, *N* = 14.9, *J*(HH) = 7.2 Hz, 6 H, PCHC*H*$_3$], 1.03 (m, 12 H, PCHC*H*$_3$), −16.1 (br s, 1 H, RuH). – ^{13}C NMR (50.3 MHz, CD_2Cl_2): δ = 203.3 [t, *J*(PC) = 15.7 Hz, CO], 135.0 (s, PC_6H_5), 134.1 (s, PPN), 132.9, 128.6 both vt, *N* = 26.2 and 25.7 Hz, PC_6H_5), 132.4, 129.7, 128.4, 126.2 (all m, PPN), 127.1 (s, PC_6H_5), 24.0, 22.3 (both vt, *N* = 26.8 and 19.5 Hz, P*C*HCH$_3$), 18.8, 18.3, 18.0, 17.1 (all s, PCH*C*H$_3$). – ^{31}P NMR (81.0 MHz, CD_2Cl_2): δ = 45.7 (br s, PiPr$_2$Ph), 21.6 (s, PPN). – $C_{61}H_{69}Cl_2NOP_4Ru$ (1128.1): calcd. C 64.95, H 6.17, N 1.24; found C 64.73, H 6.11, N 1.20.

10. Preparation of [$RuHCl(CO)(py)(Pi Pr_2Ph)_2$] (9a, b): A suspension of 82 mg (0.15 mmol) of **1** in 5 mL of hexane was treated with 0.05 mL (0.62 mmol) of pyridine at room temperature. After the reaction mixture was stirred for ca. 3 min, a white solid precipitated, which was filtered, washed three times with 5 mL of pentane and dried in vacuo; yield 89 mg (95%); m.p. 115 °C (dec.). The same compound was formed upon addition of ca. 0.1 mL of pyridine to a solution of 80 mg (0.14 mmol) of **6** in 1 mL of [D_8]THF at −78 °C. After the solution was warmed to room temperature, the ^{1}H-NMR spectrum indicated the complete conversion of **6** to **9a**, **b**. – ^{1}H NMR (400 MHz, C_6D_6); signals for **9a**: δ = 8.20, 7.07, 6.16 (all m, NC_5H_5 and C_6H_5) 3.19, 2.83 (both m, 2 H each, PC*H*CH_3), 1.41 [dvt, *N* = 13.6, *J*(HH) = 6.8 Hz, 6 H, PCHC*H*$_3$], 1.22 [dvt, *N* = 13.2, *J*(HH) = 6.6 Hz, 6 H, PCHC*H*$_3$], 1.10 [dvt, *N* = 14.0, *J*(HH) = 7.0 Hz, 6 H, PCHC*H*$_3$], 0.89 [dvt, *N* = 15.0, *J*(HH) = 7.2 Hz, 6 H, PCHC*H*$_3$], −13.54 [t, *J*(PH) = 22.0 Hz, 1 H, RuH]; signals for **9b**: δ = 7.57, 7.07, 6.51 (all m, NC_5H_5 and C_6H_5), 2.67, 1.81 (both m, 2 H each, PC*H*CH_3), 1.35 [dvt, *N* = 16.4, *J*(HH) = 7.0 Hz, 6 H, PCHC*H*$_3$], 1.29 [dvt, *N* = 13.6, *J*(HH) = 6.8 Hz, 6 H, PCHC*H*$_3$], 1.21 [dvt, *N* = 13.6, *J*(HH) = 6.8 Hz, 6 H, PCHC*H*$_3$], 0.99 [dvt, *N* = 13.4, *J*(HH) = 6.7 Hz, 6 H, PCHC*H*$_3$], −14.41 [t, *J*(PH) = 21.8 Hz, 1 H, RuH]. – ^{31}P NMR (162.0 MHz, CD_2Cl_2): δ = 48.9, 43.8 (both s). – $C_{30}H_{44}ClONP_2Ru$ (633.2): calcd. C 56.91, H 7.00, N 2.21; found C 56.62, H 7.04, N 2.23.

11. Reaction of Compound 6 with CO: A slow stream of CO was passed through a solution of 80 mg (0.14 mmol) of **6** in 1 mL of [D_8]THF at −80 °C. After the solution was warmed to room temperature, the ^{1}H-NMR spectrum indicated the complete conversion of **6** to **4**.

12. Preparation of [$RuH(CF_3CO_2)(CO)(Pi Pr_2Ph)_2$] (10): A solution of 192 mg (0.35 mmol) of **1** in 10 mL of toluene was treated with 111 mg (0.35 mmol) of CF_3CO_2Tl and stirred for 15 h at room temperature. The solution was decanted from the solid residue and then brought to dryness in vacuo. An orange-yellow microcystalline solid was obtained; yield 188 mg (86%); m.p. 177 °C (dec.). – IR (KBr): $\tilde{\nu}$ = 2090 cm^{-1} (RuH), 1910 (CO), 1597 ($OCO_{as.}$), 1410 ($OCO_{sym.}$). – ^{1}H NMR (400 MHz, C_6D_6): δ = 7.89 (m, 4 H, C_6H_5), 7.31−7.17 (m, 6 H, C_6H_5), 2.54 (m, 4 H, PC*H*CH_3), 1.42 [dvt, *N* = 15.9, *J*(HH) = 7.2 Hz, 6 H, PCHC*H*$_3$], 1.33 [dvt, *N* = 15.0, *J*(HH) = 7.2 Hz, 6 H, PCHC*H*$_3$], 1.24 [dvt, *N* = 14.6, *J*(HH) = 7.1 Hz, 6 H, PCHC*H*$_3$], 1.01 [dvt, *N* = 13.3, *J*(HH) = 6.7 Hz, 6 H, PCHC*H*$_3$], −18.23 [t, *J*(PH) = 20 Hz, 1 H, RuH]. – ^{13}C NMR (100.6 MHz, C_6D_6): δ = 205.1 [t, *J*(PC) = 10 Hz, CO], 164.2 [q, *J*(FC) = 38 Hz, CF_3CO_2] 134.7, 128.1 (both vt, *N* = 10 and 14 Hz, *ortho*-C and *meta*-C of C_6H_5), 130.1 (s, *para*-C of C_6H_5], 128.7 (vt, *N* = 34 Hz, *ipso*-C of C_6H_5), 115.0 [q, *J*(FC) = 287 Hz, CF_3CO_2], 24.5, 24.3, (both vt, *N* = 24 and 23 Hz, P*C*HCH$_3$), 19.1, 18.4, 18.1, 17.2, (all s, PCH*C*H$_3$). – ^{19}F NMR (376.4 MHz, C_6H_6): δ = −75.4 (s). – ^{31}P NMR (162.0 MHz, C_6D_6): δ = 53.7 (s). – $C_{27}H_{39}F_3O_3P_2Ru$ (631.6): calcd. C 51.34, H 6.22; found C 51.03, H 5.98.

13. Preparation of [$RuHI(CO)(Pi Pr_2Ph)_2$] (11): A solution of 200 mg (0.36 mmol) of **1** in 10 mL of dichloromethane was treated with 600 mg (3.61 mmol) of KI and stirred for 15 h at room temperature. The reaction mixture was filtered and the filtrate was brought to dryness in vacuo. The brown microcrystalline residue was washed with methanol and dried; yield 116 mg (50%); m.p. 122 °C (dec.). – ^{1}H NMR (400 MHz, C_6D_6): δ = 7.70 (m, 4 H, C_6H_5), 7.46 (m, 6 H, C_6H_5), 3.33, 3.02 (both m, 2 H each, PC*H*CH_3), 1.35 [dvt, *N* = 15.2, *J*(HH) = 7.6 Hz, 6 H, PCHC*H*$_3$], 1.19 [dvt, *N* = 15.2, *J*(HH) = 7.2 Hz, 6 H, PCHC*H*$_3$], 1.14 [dvt, *N* = 16.8, *J*(HH) = 8.0 Hz, 6 H, PCHC*H*$_3$], 1.04 [dvt, *N* = 13.2, *J*(HH) = 6.8 Hz, 6 H, PCHC*H*$_3$], −25.0 (br s, 1 H, RuH). – ^{13}C NMR (100.6 MHz, C_6D_6): δ = 198.7 [t, *J*(PC) = 12 Hz, CO], 134.9, 127.8 (both vt, *N* = 10 and 8 Hz, *ortho*-C and *meta*-C of C_6H_5), 130.1 (s, *para*-C of C_6H_5), 130.3 (vt, *N* = 36 Hz, *ipso*-C of C_6H_5), 25.1, 24.4 (both vt, *N* = 27 and 23 Hz, P*C*HCH$_3$), 19.6, 19.5, 19.1, 17.8 (all s, PCH*C*H$_3$). – ^{31}P NMR (162.0 MHz, C_6D_6): δ = 53.3 (s). – $C_{25}H_{39}IOP_2Ru$ (645.5): calcd. C 46.52, H 6.09; found C 46.13, H 5.67.

14. Preparation of [$Ru(CH{=}CH_2)Cl(CO)(Pi Pr_2Ph)_2$] (12): A slow stream of acetylene was passed through a suspension of 129 mg (0.23 mmol) of **1** in 15 mL of pentane until a change of color from yellow to red occurred. After the suspension was stirred for 30 min at room temperature, a red solid precipitated which was filtered, washed with pentane and dried in vacuo; yield 119 mg (90%); m.p.

124 °C (dec.). – IR (KBr): $\tilde{\nu}$ = 1923 cm^{-1} (CO). – $^1H\{^{31}P\}$NMR (200 MHz, $CDCl_3$): δ = 8.15 [dd, *J*(HH) = 14.0 Hz, *J*(HH) = 6.0 Hz, 1 H, C*H*=CH_2], 7.81 (m, 4 H, C_6H_5), 7.38 (m, 6 H, C_6H_5), 5.22 [d, *J*(HH) = 6.0 Hz, 1 H, one H of =CH_2], 4.89 [d, *J*(HH) = 14.0 Hz, 1 H, one H of =CH_2], 3.24, 2.87 (both m, 2 H each, PC*H*CH_3), 1.26 [d, *J*(HH) = 7.0 Hz, 6 H, PCHC*H*$_3$], 1.16 [d, *J*(HH) = 7.2 Hz, 6 H, PCHC*H*$_3$], 1.08 [d, *J*(HH) = 7.2 Hz, 6 H, PCHC*H*$_3$], 1.01 [d, *J*(HH) = 6.8 Hz, 6 H, PCHC*H*$_3$]. – ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 200.7 [t, *J*(PC) = 12 Hz, CO], 152.5 [t, *J*(PC) = 10 Hz, *C*H=CH_2], 133.9, 127.0 (both vt, *N* = 13 and 8 Hz, *ortho*-C and *meta*-C of C_6H_5), 129.6 (s, *para*-C of C_6H_5), 129.6 (vt, *N* = 33 Hz, *ipso*-C of C_6H_5), 120.5 (s, CH=*C*H_2), 23.7, 22.4 (both vt, *N* = 23 and 21 Hz, P*C*HCH$_3$), 20.7, 18.9, 18.3, 17.4 (all s, PCH*C*H$_3$). – ^{31}P NMR (81.0 MHz, $CDCl_3$): δ = 35.6 (s). – $C_{27}H_{41}ClORuP_2$ (580.1): calcd. C 55.90, H 7.12; found C 55.60, H 7.12.

15. Preparation of [Ru(CH=CHPh)Cl(CO)(P*i*Pr$_2$Ph)$_2$] (13): A suspension of 100 mg (0.18 mmol) of **1** in 10 mL of hexane was treated with 19 μL (0.18 mmol) of phenylacetylene and stirred for 1 h at room temperature. A violet solid precipitated which was filtered, washed three times with pentane, and dried in vacuo; yield 74 mg (62%); m.p. 148 °C (dec.). – IR (KBr): $\tilde{\nu}$ = 1916 cm^{-1} (CO). – $^1H\{^{31}P\}$ NMR (400 MHz, CD_2Cl_2): δ = 8.83 [d, *J*(HH) = 13.4 Hz, 1 H, C*H*=CHPh], 7.78 (m, 4 H, C_6H_5), 7.44 (m, 6 H, C_6H_5), 7.25 (m, 4 H, C_6H_5), 7.06 (m, 1 H, C_6H_5), 6.15 [d, *J*(HH) = 13.4 Hz, 1 H, CH=C*H*Ph], 3.27, 2.94 (both m, 2 H each, PC*H*CH_3), 1.33 [d, *J*(HH) = 7.0 Hz, 6 H, PCHC*H*$_3$], 1.27 [d, *J*(HH) = 7.1 Hz, 6 H, PCHC*H*$_3$], 1.16 [d, *J*(HH) = 7.0 Hz, 6 H, PCHC*H*$_3$], 1.04 [d, *J*(HH) = 7.0 Hz, 6 H, PCHC*H*$_3$]. – ^{31}P NMR (162.0 MHz, CD_2Cl_2): δ = 35.0 (s). – $C_{33}H_{45}ClORuP_2$ (656.2): calcd. C 60.40, H 6.91, Ru 15.40; found C 60.15, H 6.98, Ru 15.34.

Determination of the X-ray Crystal Structure of 7:[20] Single crystals were grown upon cooling of a saturated solution of **7** in toluene from 25 °C to −20 °C. Crystal data (from 5000 reflections, 1.95° < Θ < 26.20°): triclinic; space group *P*-1 (No. 2); *a* = 12.237(3), *b* = 14.039(6), *c* = 15.697(4) Å, α = 85.96(4), β = 76.94(3), γ = 70.33(4)°; *V* = 2474(1) Å^3, *Z* = 2; $d_{calc.}$ = 1.258 gcm^{-3}; μ(Mo-K_α) = 0.555 mm^{-1}; crystal size 0.2 × 0.2 × 0.1 mm; IPDS (STOE), Mo-K_α radiation (0.71073 Å), graphite monochromator; *T* = 173(2) K; φ-scans, max. 2θ = 52.40°; 18792 reflections measured, 9434 independent ($R_{int.}$ = 0.0557), 7477 with $I > 2\sigma(I)$. Intensity data were corrected for Lorentz and polarization effects. The structure was solved by the Patterson method (SHELXS-86).[21] Atomic coordinates and the anisotropic thermal parameters of non-hydrogen atoms were refined by full-matrix least squares on F^2 (SHELXL-93).[22] The positions of all hydrogen atoms except of H1 were calculated according to ideal geometry and refined by using the riding method. The position of H1 was located in a final difference Fourier synthesis and refined isotropically without restraints. The asymmetric unit includes one and a half molecules of toluene which were refined anisotropically with restraints. The half molecule was located on the inversion center of the space group. The other molecule of toluene was found disordered and two positions were refined with occupancy factors of 0.646 and 0.354. Conventional $R = 0.0339$ [for 7477 reflections with $I > 2\sigma(I)$], and weighted $wR_2 = 0.0953$ for all 9434 located reflections; reflection/parameter ratio 17.31; residual electron density +0.505/−0.916 eÅ^{-3}.

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[20] Crystallographic data (excluding structure factors) for the structure of **7** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-120117. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: internat. +44 (0)1223/ 336-033; E-mail: deposit@ccdc.cam.ac.uk).
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