DOI: 10.1002/ejic.200701324

Reactions of Hydride Complexes of Ruthenium and Osmium with Propargylic Alcohols: Preparation of Chelate Vinyl Derivatives

Gabriele Albertin,*[a] Stefano Antoniutti,[a] Alessia Bacchi,[b] Giancarlo Pelizzi,[b] and Gianluigi Zanardo[a]

Keywords: Hydrides / Alkene ligands / Alcohols / Ruthenium / Osmium / Vinyl complexes

Vinyl complexes $[Ru\{\eta^2\text{-}C(=CH_2)CPh(R)OH(Ru\text{–}O)\}P_4]BPh_4$ (**1**) [P = $P(OEt)_3$; R = Ph, Me] were prepared by allowing the RuH_2P_4 hydride to react first with $HBF_4{\cdot}Et_2O$ and then with propargylic alcohol HC≡CCPh(R)OH at low temperature. The complexes were characterised spectroscopically (IR, NMR) and by X-ray crystal structure determination of the $[Ru\{\eta^2\text{-}C(=CH_2)CPh_2OH(Ru\text{–}O)\}\{P(OEt)_3\}_4]BPh_4$ (**1a**) derivative. Related osmium complexes $[Os\{\eta^2\text{-}C(=CH_2)CPh(R)OH(Os\text{–}O)\}P_4]BPh_4$ (**2**) and $[Os\{\eta^2\text{-}CH=C(H)CPh(R)OH(Os\text{–}O)\}P_4]BPh_4$ (**3**) [P = $P(OEt)_3$; R = Ph, Me] were obtained by treating the OsH_2P_4 hydride first with methyl triflate (MeOTf) and then with propargylic alcohol [HC≡CCPh(R)OH]. Spectroscopic data (^1H, ^{31}P, ^{13}C NMR) suggest the presence of two isomers with four- and five-membered chelate rings of the vinyl ligands. Treatment of vinyl complexes **1** and **2**+**3** with terminal alkynes $R^1C{\equiv}CH$ yielded enynyl derivatives $[M\{\eta^3\text{-}R^1C_3C(H)R^1\}P_4]BPh_4$ (M = Ru, Os). The allenylidene complex $[Os(=C=C=CPh_2)P_5](BPh_4)_2$ was also prepared by allowing the triflate cation $[Os(\kappa^2\text{-}OTf)P_4]^+$ to react with propargylic alcohol in CH_2Cl_2 solution.

Introduction

The insertion reaction of an alkyne into the metal hydride bond, which leads to vinyl derivatives, has been extensively studied in recent years, and this has allowed the exploration of the chemistry of vinyl complexes.[1–5] Interest in this field stems not only from the rich and varied chemistry shown by these σ-carbon ligands, but also because the σ-vinyl metal complexes are important intermediates in the oligomerisation and polymerisation reactions of alkynes.[6]

However, reactions of alkynes with metal hydrides can give vinyl complexes and also different products such as mono- and bis(alkynyl) complexes[7] and hydride–carbyne and hydride–vinylidene metal derivatives.[8] In addition, some years ago we observed that the reaction of terminal alkynes HC≡CR (R = Ph, *p*-tolyl, *tert*-butyl) with hydride–dihydrogen cations $[RuH(\eta^2\text{-}H_2)P_4]^+$ or hydride–triflate complexes $OsH(\kappa^1\text{-}OTf)P_4$ (P = phosphites) leads to butenynyl $[M\{\eta^3\text{-}RC_3C(H)R\}P_4]^+$ derivatives.[9]

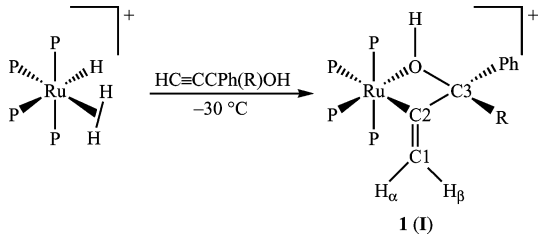
As a continuation of our work on the reactivity of classical and nonclassical hydride complexes with alkynes,[10] we extended our study to propargylic alcohols HC≡CC(OH)R_2 and obtained the first chelate vinyl complexes containing a coordinated hydroxy group. The results of the studies on the synthesis and reactivity of new vinyl complexes of Ru and Os are reported here.

[a] Dipartimento di Chimica, Università Ca' Foscari Venezia, Dorsoduro 2137, 30123 Venezia, Italy
[b] Dipartimento di Chimica Generale ed Inorganica, Chimica Analitica, Chimica Fisica, Università di Parma, Parco Area delle Scienze, 17/a, 43100 Parma, Italy

Results and Discussion

Vinyl Complexes

Hydride–dihydrogen cations $[RuH(\eta^2\text{-}H_2)P_4]^+$ react with propargylic alcohols HC≡CCPh(R)OH to give the vinyl chelate complexes $[Ru\{\eta^2\text{-}C(=CH_2)CPh(R)OH(Ru\text{–}O)\}P_4]^+$ (**1**), which were isolated as BPh_4 salts and characterised (Scheme 1).



Scheme 1. P = $P(OEt)_3$; R = Ph (**a**), Me (**b**).

Crucial for the success of the synthesis is carrying out the reaction at a temperature below –30 °C, otherwise only decomposition products are obtained. However, even at low temperature, the $\eta^2\text{-}H_2$ ligand in the $[RuH(\eta^2\text{-}H_2)P_4]^+$ cation is labile[11] and may be replaced by the alkyne, which would allow coordination of HC≡CCPh(R)OH prior to insertion. The need for a vacant site to accommodate the alkyne seems to be an essential requirement in obtaining vinyl complexes **1**, and this is in agreement with the proposed mechanism[12] for the insertion of an alkyne into the M–H bond. The hydride complexes[13,14] RuH_2P_4 and $RuHClP_4$

[P = $P(OEt)_3$], which do not contain any labile ligands, are unreactive towards the propargylic alcohol and do not yield any vinyl complex.

Propargylic alcohols are reported to react with metal hydrides to give vinyl derivatives,[2,3] but in only one case[3m] has the coordination of the OH group to give a five-membered chelate ring been proposed in an osmium complex. In our case, the use of the $Ru[P(OEt)_3]_4$ fragment allows the stabilisation of an unusual four-membered chelate ring that involves the coordination of both the carbon and oxygen atoms of the $C(=CH_2)C(Ph)ROH$ vinyl group. Some examples of vinyl complexes with both four- and five-chelate rings have been reported[3f,9b,15] for ruthenium and osmium, but they contained a carboxylate O-bonded $C(=CH_2)CO(OR)$ ligand. In our case, the use of propargylic alcohol yielded the first example of a vinyl ligand containing an O-bonded OH group.

The complexes $[Ru\{\eta^2\text{-}C(=CH_2)CPh(R)OH(Ru–O)\}\{P(OEt)_3\}_4]BPh_4$ (**1**) were obtained as white microcrystals, stable in air and in solution of polar organic solvents, where they behave as 1:1 electrolytes.[16] The formulation is supported by analytical and spectroscopic (IR, ^1H, ^{31}P, ^{13}C NMR) data and by the X-ray crystal structure determination of $[Ru\{\eta^2\text{-}C(=CH_2)CPh_2OH(Ru–O)\}\{P(OEt)_3\}_4]BPh_4$ (**1a**). Figure 1 shows the molecular structure of the octahedral $[Ru\{\eta^2\text{-}C(=CH_2)CPh_2OH(Ru–O)\}\{P(OEt)_3\}_4]^+$ cation, together with the labelling scheme, and Table 1 lists significant geometric features. A tetraphenylborate anion (not shown) completes the structure. Coordination of the ruthenium atom to the vinyl ligand occurs by chelation through the oxhydryl group and the alkyne sp carbon atom, which, as a consequence, transforms into an sp^2 geometry. The resulting four-membered chelation ring is perfectly coplanar with the two phosphorus atoms, which are, respectively, *trans* to the oxygen and carbon ligands (maximum deviation from planarity = 0.06 Å). This forms the equatorial plane of the coordination octahedron, and it is completed by the two remaining apical phosphite ligands. Coordination of 1,1-diphenyl-2-propyl-1-ol to transition metals has already been reported,[17,18] but this is the first-known instance where the alkyne carbon atom acts as a η^1 donor and C,O chelation is observed; all other cases involve η^2 coordination of the triple bond. The four-membered chelation ring is characterised by two very compressed bond angles on the C,O donor atoms: C26–C39–Ru 98.8(2)° and C26–O13–Ru 94.7(1)°. Correspondingly, the bond angle C26–C39–C25 bends from 177 to 125.3(3)°. This results in a lower bond order in the vinyl ligand relative to that in the crystal structure of 1,1-diphenyl-2-propyl-1-ol alone[19] and that which is cocrystallised with a Ru^{II} complex:[20] the C26–O13 bond is stretched from 1.430 Å in the free ligand (1.426 Å in the cocrystal) to 1.500(3) Å in **1a**; C26–C39 changes from 1.476 (1.490) to 1.535(4) Å and C39–C25 from 1.168 (1.169) to 1.318(4) Å; C26–C27 and C26–33 are less affected and measure 1.530 and 1.530 Å in the free molecule (1.536, 1.537 Å cocrystal) and 1.544(3) and 1.539(4) Å in **1a**. The Ru–O bond [2.232(2) Å] is also slightly longer than expected when compared with the bond length observed for a coordinated water molecule *trans* to a $P(OEt_3)_3$ ligand (2.218 Å).[15] The Ru–P1 bond opposite the Ru–O13 bond [Ru–P1 2.2033(7) Å] is considerably shorter than the other ones in **1a**, which range between 2.3292(7) and 2.3434(7) Å. The hydrogen atom of the OH donor points towards the oxygen atom of one of the phosphite ligands by forming the intramolecular hydrogen bond O13–H···O11 [O···O 2.691(3) Å, O–H···O 143(3)°].

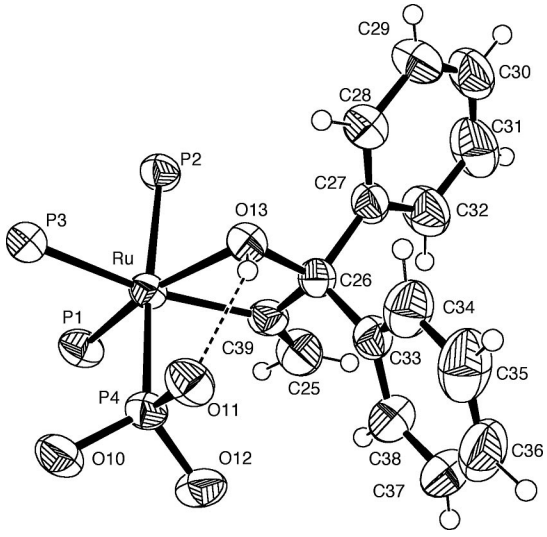


Figure 1. Perspective view of the molecular structure of $[Ru\{\eta^2\text{-}C(=CH_2)CPh_2OH\}\{P(OEt)_3\}_4]^+$ in compound **1a**. Displacement ellipsoids drawn at the 50% level; ethoxy groups omitted for clarity; dashed line represents an intramolecular hydrogen bond.

Table 1. Relevant bond lengths and angles for **1a**.

Lengths [Å]			
Ru–C39	2.107(3)	O13–C26	1.500(3)
Ru–P1	2.2034(7)	C25–C39	1.318(4)
Ru–O13	2.2322(18)	C26–C39	1.535(4)
Ru–P3	2.3292(7)	C26–C33	1.539(4)
Ru–P2	2.3304(7)	C26–C27	1.544(3)
Ru–P4	2.3433(7)		
Angles [°]			
C39–Ru–P1	101.64(8)	C39–Ru–P2	87.84(7)
C39–Ru–O13	65.33(9)	P1–Ru–P2	92.37(3)
P1–Ru–O13	166.88(5)	O13–Ru–P2	88.80(5)
C39–Ru–P3	164.03(8)	P3–Ru–P2	92.10(3)
P1–Ru–P3	94.32(3)	C39–Ru–P4	90.11(7)
O13–Ru–P3	98.70(5)	P1–Ru–P4	95.13(3)

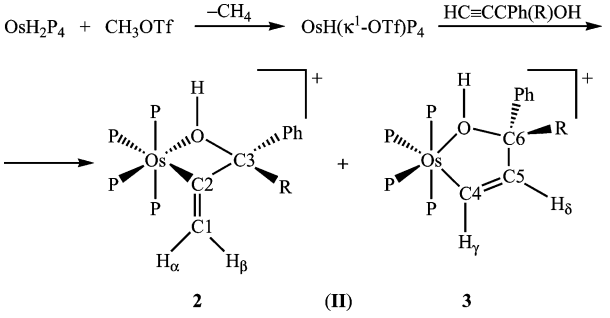
Besides the signals of the phosphite and phenyl groups, the ^1H NMR spectra of the $[Ru\{\eta^2\text{-}C(=CH_2)CPh(R)OH(Ru–O)\}\{P(OEt)_3\}_4]BPh_4$ (**1**) complexes show two sets of multiplets between 6.31 and 5.43 ppm, which are attributed to the vinyl α-H and β-H protons of the chelate ligands.

As the ^{31}P NMR spectra are ABC_2 (**1a**) and ABCD (**1b**) multiplets, the vinyl pattern can be simulated by using ABC_2XY and ABCDXY (X = α-H, Y = β-H) as models, respectively, and the parameters are reported in the Experimental Section. The good fit between the experimental and

calculated spectra supports the proposed formulation for the complexes and indicates that geometry **I**, like that observed in the solid state for **1a**, is also present in solution. In addition, the ^{1}H NMR spectra of complexes **1** show a multiplet at 3.82 ppm for **1a** and at 3.02 ppm for **1b**, which can be attributed to the hydrogen resonance of the OH group. Support for this attribution comes from the HMBC experiments, which show the correlation between the ^{1}H signal of the OH multiplet at 3.82 and 3.02 ppm with the ^{13}C signal at 109.4 (**1a**) and 109.2 ppm (**1b**), respectively, of the C3 carbon resonance. It may also be noted that the ^{1}H and ^{31}P NMR spectra of the complex [Ru{η^2-C(=CH$_2$)-CPh(Me)OH(Ru–O)}{P(OEt)$_3$}$_4$]BPh$_4$ (**1b**) show some peculiarities. The resonance of the methyl substituent is present as a singlet at 1.67 ppm, whereas the ^{31}P NMR spectrum of the complex appears as an ABCD multiplet due to the presence of two different substituents at the C3 carbon atom, which are located under and on the plane of the chelate ring; thus, all four phosphorus atoms of the phosphite are inequivalent.

Besides the signals of the phosphite and BPh$_4$ anion, the ^{13}C NMR spectra of vinyl derivatives **1a** and **1b** show the characteristic C1, C2 and C3 carbon resonances of the vinyl ligand, whose attribution is supported by HMQC, HMBC and NOESY experiments and in agreement with the proposed formulation.

The hydride–dihydrogen complex of osmium [OsH(η^2-H$_2$){P(OEt)$_3$}$_4$]BPh$_4$ does not react with propargylic alcohols, and the starting complex can be recovered unchanged after 24 h of reaction. This unreactivity of the Os complex is due to the high stability of the η^2-H$_2$ ligand towards substitution,[11] which prevents coordination of the alkyne prior to insertion. However, vinyl complexes may be prepared by following a different strategy involving the reaction of the OsH$_2$P$_4$ dihydride first with methyl triflate and then with the appropriate propargylic alcohol, as shown in Scheme 2.



Scheme 2. P = P(OEt)$_3$; R = Ph (**a**), Me (**b**).

The reaction of OsH$_2$P$_4$ with methyltriflate proceeds with the evolution of methane and formation of the triflate complex OsH(κ^1-OTf)P$_4$,[9b] which reacts with propargylic alcohol to give vinyl chelate derivative **2**+**3**. Surprisingly, in this case, the reaction produces a mixture of two species that are both characterised as vinyl complexes containing either a four-membered (as in **2**) or a five-membered (as in **3**) chelate ring. Insertion of the alkyne into the Os–H bond is followed by O-coordination of the propargylic alcohol through the OH group, which yields two different vinyl ligands, and which is in contrast with ruthenium. We attempted to separate the two isomers by fractional crystallisation, but only enriched fractions in one of the two compounds were obtained.

Complexes [Os{η^2-C(=CH$_2$)CPh(R)OH(Os–O)}P$_4$]BPh$_4$ (**2**) and [Os{η^2-CH=C(H)CPh(R)OH(Os–O)}P$_4$]BPh$_4$ (**3**) were obtained as a mixture as a pale-yellow solid that is stable in air and in solution of polar organic solvents, where they behave as 1:1 electrolytes.[16] Analytical and spectroscopic (IR, ^{1}H, ^{13}C, ^{31}P NMR) data support the proposed formulation.

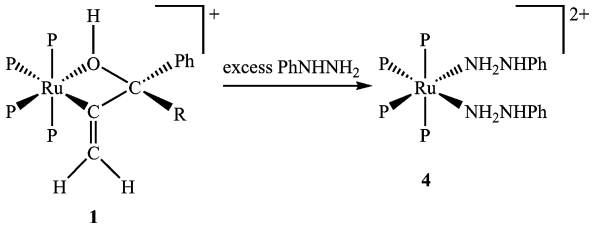
In the vinyl region between 8.28 and 5.56 ppm, the ^{1}H NMR spectra of both complexes **2a**+**3a** and **2b**+**3b** show four multiplets that are two-by-two coupled (COSY experiment) and attributed to the four vinyl α-H, β-H, γ-H and δ-H protons of the two isomers **2** and **3** (Scheme 2).

As the ^{31}P{^{1}H} NMR spectrum of **2a**+**3a** appears as two AB$_2$C multiplets, both vinyl patterns were simulated by using an AB$_2$CXY model (X = α-H or γ-H, Y = β-H or δ-H), and the parameters are reported in the Experimental Section. The good fit between the calculated and experimental spectra strongly support the presence of the two isomeric species **2a** and **3a**. Furthermore, the value of $J_{H,H}$ of the vinyl protons is very low (0.1 Hz) in one case, and results comparable with those of ruthenium species **1**, in agreement with a four-membered chelate ring **2**. In the other case, a value of 10.5 Hz for $J_{H,H}$ fits the mutually *cis* position[21] of the two vinyl protons, as expected for the five-membered chelate vinyl species **3**.

The ^{31}P{^{1}H} NMR spectrum of the related complex **2b**+**3b** also shows two multiplets, but in this case, they could be simulated with an ABCD model. As a result, the two vinyl multiplets of **2b** and **3b** were simulated with an ABCDXY model, and the parameters are reported in the Experimental Section. In this case too, the good fit between the observed and calculated spectra, and the $J_{H,H}$ values support geometries **2** and **3** for the two isomers of the complex. Further support for the formulation of vinyl osmium complexes **2** and **3** came from the ^{13}C NMR spectra, which, besides the signals due to the phosphite ligands and the BPh$_4$ anion, show six signals attributable to carbon atoms C1–C3 and C4–C6 of vinyl isomers **2** and **3**. The results of HMBC and HMQC experiments allowed the attribution of all the vinyl carbon resonances, and their values are reported in the Experimental Section. In the spectrum of compound **2b**+**3b**, two singlets at 34.8 and 29.9 ppm for the methyl substituents at the C3 and C6 carbon atoms were also present, which is in agreement with the geometry proposed for these complexes.

Vinyl compounds **1**, **2** and **3** are robust and, at room temperature, do not undergo either substitution of the ligands or protonation of the vinyl group by Brønsted acids to give the corresponding alkene. Instead, in refluxing 1,2-dichloroethane, substitution of the vinyl ligand is easy and

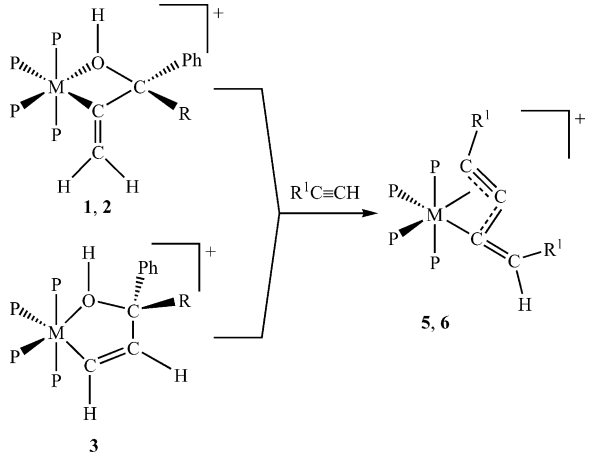
proceeds, for example, with phenylhydrazine to give the bis(hydrazine)[22] $[Ru(PhNHNH_2)P_4](BPh_4)_2$ (**4**) derivatives (Scheme 3).



1 **4**

Scheme 3. P = $P(OEt)_3$.

The reaction of the $[Ru\{\eta^2\text{-}C(=CH_2)CPh(R)OH(Ru–O)\}P_4]BPh_4$ (**1**) complex with terminal alkynes to give enynyl derivatives of the type $[Ru(\eta^3\text{-}R^1C_3CHR^1)P_4]BPh_4$ (**5**) (Scheme 4) in high yields is interesting.

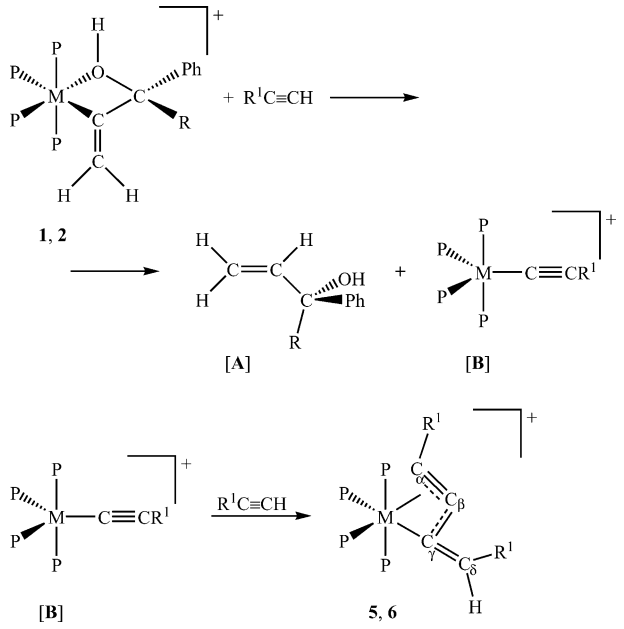


Scheme 4. M = Ru (**5**), Os (**6**); P = $P(OEt)_3$; R^1 = Ph (**a**), *p*-tolyl (**b**).

The related osmium complexes **2** and **3** also react with terminal alkynes, but the reaction is slow in refluxing dichloroethane and yields small quantities of $[Os(\eta^3\text{-}R^1C_3CHR^1)P_4]BPh_4$ (**6**). However, it is worth noting that only phenyl (PhC≡CH) and *p*-tolyl (4-$CH_3C_6H_4C{\equiv}CH$) acetylenes yield butenynyl derivatives **5** and **6**, whereas the reaction of vinyl complexes **1** and **2**+**3** with propargylic alcohols of the type HC≡CCPh(R)OH in refluxing $ClCH_2CH_2Cl$ only yields intractable mixtures of decomposition products.

Both the hydrazine complexes **4** and the enynyl derivatives **5** and **6** were previously prepared by us following a different method,[9,22] and their spectroscopic properties are exactly the same as those of our complexes **4**, **5** and **6**, which thus confirms their formulation.

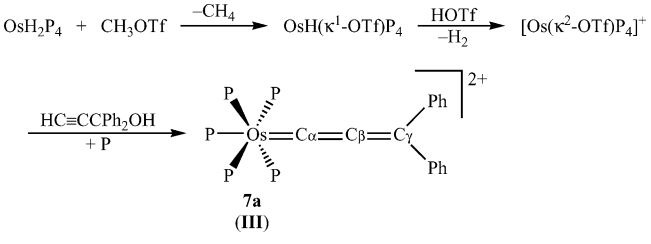
The formation of an enynyl complex from the reaction of vinyl derivatives **1** and **2** with alkynes may be explained on the basis of the reaction path reported in Scheme 5. The vinyl chelate complexes **1** and **2** react with terminal alkynes to give an alkene $C(H_2)=C(H)CPhR(OH)$ [**A**] and an acetylide intermediate [**B**]. Reaction of these pentacoordinate complexes with alkynes gives the final enynyl derivatives **5** and **6**. Support for this reaction path comes both from our previous studies in this field[9,23] and from the presence, in the ^1H NMR spectra of the reaction mixture, of a multiplet between 5.8 and 5.0 ppm, which is characteristic of alkene [**A**]. The reaction therefore indicates that our chelate vinyl ligand $C(=CH_2)CPhR(OH)$ may be removed from the coordination sphere of a metal by reaction with a terminal alkyne to yield enynyl [M]-η^3-$R^1C_3C(H)R^1$ derivatives as a final product.



Scheme 5.

Allenylidene Derivatives

Reactivity studies with propargylic alcohols were also extended to triflate cations $[M(\kappa^2\text{-}OTf)P_4]^+$ prepared in situ by treating the MH_2P_4 dihydride first with methyl triflate and then with triflic acid.[9b] Treatment of the triflate complex with propargylic alcohol results in a colour change of the solution from colourless to dark red. In the case of osmium, the addition of $NaBPh_4$ allows the separation of a purple solid that was characterised as the pentakis(phosphite)allenylidene complex $[Os(=C=C=CPh_2)P_5](BPh_4)_2$ (**7a**) (Scheme 6).



Scheme 6. P = $P(OEt)_3$.

The formation of the allenylidene ligand is not surprising owing to the known properties of propargylic alcohols, which can tautomerise on the central metal to yield a hy-

droxyvinylidene [M]=C=C(H)CPh$_2$(OH) intermediate.[24] Elimination of H_2O gives the final propadienylidene derivative [M]=C=C=CPh$_2$. In the case of osmium, a phosphite exchange reaction between the molecule of the complex must also be present in solution to give the more stable pentakis(phosphite) cation [Os(=C=C=CPh$_2$)P$_5$]$^{2+}$ (**7a**), which was isolated in low yield as the BPh_4 salt and characterised. Allenylidene complexes of osmium have been reported with several supporting ligands,[24] but none with phosphite is known.

The [Os(=C=C=CPh$_2$)P$_5$](BPh$_4$)$_2$ (**7a**) complex is a purple solid that is stable in air and in solution of polar organic solvents, where it behaves as a 2:1 electrolyte.[16] The IR spectrum shows a strong band at 1955 cm^{-1}, which is attributed to the $\nu_{C=C=C}$ of the propadienylidene ligand. Its presence was confirmed by ^{13}C NMR spectroscopy, which revealed characteristic signals for the C-α, C-β and C-γ carbon atoms of the C=C=CPh$_2$ ligand. Thus, a multiplet at 281.5 ppm was attributed to the C-α carbon resonance, and the signals at 195.5 (m) and 162.9 (s) ppm to the C-β and C-γ carbon atoms, respectively, of the allenylidene ligand. The ^{31}P NMR spectrum appears as an A_4B multiplet, which could be simulated with the parameters reported in the Experimental Section, and this is in accord with the presence of four phosphites magnetically equivalent and different from the fifth. On the basis of these data, a geometry of type **III** may be proposed for allenylidene complex **7a**.

Conclusions

In this paper, we report details of the first chelate vinyl complex [M{η^2-C(=CH$_2$)CPh(R)OH(M–O)}P$_4$]BPh$_4$ containing a coordinated hydroxy group that was prepared from propargylic alcohols as reagents. The structural parameters of a four-membered vinyl chelate ring bonded to a ruthenium fragment were described. Reactivity studies with terminal alkynes leading to enynyl derivatives were also reported. Lastly, the use of a triflate complex as a precursor yielded the pentakis(phosphite)allenylidene cation [Os(=C=C=Ph$_2$)P$_5$]$^{2+}$.

Experimental Section

General: All synthetic work was carried out under an appropriate atmosphere (Ar, N_2) by using standard Schlenk techniques or a vacuum atmosphere dry box. All solvents were dried with appropriate drying agents, degassed on a vacuum line and distilled into vacuum-tight storage flasks. RuCl$_3$·3H$_2$O and (NH$_4$)$_2$OsCl$_6$ salts were Pressure Chemical Co. (USA) products and used as received. Other reagents were purchased from commercial sources in the highest available purity and used as received. Infrared spectra were recorded with a Perkin–Elmer Spectrum One FTIR spectrophotometer. NMR spectra (^1H, ^{31}P, ^{13}C) were obtained with AC200 or AVANCE 300 Bruker spectrometers at temperatures between –80 and +30 °C, unless otherwise noted. ^1H and ^{13}C spectra are referred to internal tetramethylsilane; $^{31}P\{^1H\}$ chemical shifts are reported with respect to 85% H_3PO_4, with downfield shifts considered positive. The COSY, HMQC and HMBC NMR experiments were performed by using their standard programs. The SwaN-MR software package[25] was used to treat NMR spectroscopic data. The conductivity of 10^{-3} mol L^{-1} solutions of the complexes in CH_3NO_2 at 25 °C were measured with a Radiometer CDM 83. Elemental analyses were determined in the Microanalytical Laboratory of the Dipartimento di Scienze Farmaceutiche of the University of Padua, Italy.

Synthesis of Complexes: The hydride and dihydrogen complexes MH$_2$P$_4$, [MH(η^2-H$_2$)P$_4$]BF$_4$ and MH(κ^1-OTf)P$_4$ [M = Ru, Os; P = P(OEt)$_3$; OTf = CF$_3$SO$_3$] were prepared following the methods previously reported.[9b,11,13,26]

[Ru{η^2-C(=CH$_2$)CPh(R)OH(Ru–O)}{P(OEt)$_3$}$_4$]BPh$_4$ (1) [R = Ph (a), Me (b)]: An equimolar amount of HBF$_4$·Et$_2$O (0.26 mmol, 37 μL) was added to a solution of RuH$_2$P$_4$ (0.26 mmol, 200 mg) in CH$_2$Cl$_2$ (8 mL) allowed to stand under an H_2 atmosphere and then cooled to –196 °C. The reaction mixture was left to reach –50 °C and stirred at this temperature for 30 min. An excess amount of the appropriate propargylic alcohol HC≡CCPh(R)OH (R = Ph, Me; 0.78 mmol) in CH$_2$Cl$_2$ solution (2 mL) was added to the reaction mixture, and the resulting solution was brought to –30 °C. After stirring for 1 h, the reaction mixture was left to reach room temperature and stirred for another 3 h. The solvent was removed under reduced pressure to give an oil that was triturated with ethanol (3 mL) containing an excess amount of NaBPh$_4$ (0.52 mmol, 178 mg). A white solid slowly separated out, which was filtered and crystallised from ethanol. Yield: 289 mg for **1a** (86%), 269 mg for **1b** (84%). Data for **1a**: Λ_M = 55.4 S cm^2 mol^{-1}. ^1H NMR [300 MHz, (CD$_3$)$_2$CO, 20 °C]: δ = 7.65–6.74 (m, 30 H, Ph), 5.59 and 6.31 (ABC$_2$XY, X = α-H, Y = β-H; $J_{A,X}$ = 11.3 Hz, $J_{A,Y}$ = 21.7 Hz, $J_{B,X}$ = 0.50 Hz, $J_{B,Y}$ = 0.95 Hz, $J_{C,X}$ = 2.80 Hz, $J_{C,Y}$ = 2.80 Hz, $J_{X,Y}$ = 0.90 Hz; 2 H; CH$_2$ vinyl), 3.82 (m, 1 H, OH), 4.08, 3.87 (m, 24 H, CH$_2$ phos), 1.35, 1.29, 1.18 (t, J = 7.0 Hz, 36 H, CH$_3$ phos) ppm. $^{31}P\{^1H\}$ NMR [121.52 MHz, (CD$_3$)$_2$CO, 20 °C]: δ = 142.9, 136.0 and 126.3, (ABC$_2$, $J_{A,B}$ = 41.4 Hz, $J_{A,C}$ = 70.0 Hz, $J_{B,C}$ = 53.0 Hz) ppm. ^{13}C NMR [75.48 MHz, (CD$_3$)$_2$CO, 20 °C]: δ = 163–122 (m, Ph), 158.6 (dm, C2), 120.2 (m, C1), 109.4 (s, C3), 62.5 (m, CH$_2$ phos), 16.2 (m, CH$_3$ phos) ppm. C$_{63}$H$_{93}$BO$_{13}$P$_4$Ru (1294.19): calcd. C 58.47, H 7.24; found C 58.29, H 7.37. Data for **1b**: Λ_M = 53.8 S cm^2 mol^{-1}. ^1H NMR [300 MHz, (CD$_3$)$_2$CO, 20 °C]: δ = 7.65–6.86 (m, 25 H, Ph), 5.84 and 5.43 (ABCDXY, X = α-H, Y = β-H; $J_{A,X}$ = 10.5 Hz, $J_{A,Y}$ = 20.9 Hz, $J_{B,X}$ = 1.20 Hz, $J_{B,Y}$ = 1.20 Hz, $J_{C,X}$ = 2.70 Hz, $J_{C,Y}$ = 2.84 Hz, $J_{D,X}$ = 2.70 Hz, $J_{D,Y}$ = 2.84 Hz, $J_{X,Y}$ = 0.50 Hz; 2 H; CH$_2$ vinyl), 3.02 (m, 1 H, OH), 4.35–3.64 (m, 24 H, CH$_2$ phos), 1.67 (s, 3 H, CH$_3$-C3), 1.35, 1.28, 1.27, 1.12 (t, J = 7.0 Hz, 36 H, CH$_3$ phos) ppm. $^{31}P\{^1H\}$ NMR [121.52 MHz, (CD$_3$)$_2$CO, 20 °C]: δ = 143.0, 135.3, 128.8 and 128.7 (ABCD, $J_{A,B}$ = 44.5 Hz, $J_{A,C}$ = 67.2 Hz, $J_{A,D}$ = 70.7 Hz, $J_{B,C}$ = 49.9 Hz, $J_{B,D}$ = 53.2 Hz, $J_{C,D}$ = 0.1 Hz) ppm. ^{13}C NMR [75.48 MHz, (CD$_3$)$_2$CO, 20 °C]: δ = 160.3 (dm, C2), 165–122 (m, Ph), 118.1 (m, C1), 109.2 (s, C3), 34.2 (s, CH$_3$-C3), 62.6–61.1 (m, CH$_2$ phos), 16.2 (m, CH$_3$ phos) ppm. C$_{58}$H$_{91}$BO$_{13}$P$_4$Ru (1232.12): calcd. C 56.54, H 7.44; found C 56.44, H 7.29.

[Os{η^2-C(=CH$_2$)CPh(R)OH(Os–O)}{P(OEt)$_3$}$_4$]BPh$_4$ (2) and [Os{η^2-CH=C(H)CPh(R)OH(Os–O)}{P(OEt)$_3$}$_4$]BPh$_4$ (3) [R = Ph (a), Me (b)]: An equimolar amount of CH$_3$OTf (0.23 mmol, 26 μL) was added to a solution of OsH$_2$P$_4$ (0.23 mmol, 197 mg) in toluene (4 mL) allowed to stand under an argon atmosphere and cooled to –196 °C. The reaction mixture was left to reach room temperature, stirred for 30 min and then cooled again to –196 °C. An excess amount of the appropriate propargylic alcohol HC≡CCPh(R)OH (0.69 mmol) in CH$_2$Cl$_2$ (8 mL) was added, and the reaction mixture, brought to room temperature, was stirred for 8 h. The solvent

was removed under reduced pressure to leave an oil, which was triturated with ethanol (2 mL) containing an excess amount of $NaBPh_4$ (0.46 mmol, 157 mg). An orange solid slowly separated out, which was filtered and crystallised from ethanol. Yield: 248 mg for **2a+3a** (78%), 225 mg for **2b+3b** (74%). Data for **2a+3a**: Λ_M = 51.6 $S cm^2 mol^{-1}$. ^1H NMR (300 MHz, CD_2Cl_2, 20 °C): δ = 7.60–6.87 (m, 30 H, Ph), 6.50 and 5.65 (AB_2CXY, X = α-H, Y = β-H; $J_{A,X}$ = 16.2 Hz, $J_{A,Y}$ = 8.9 Hz, $J_{B,X}$ = 3.5 Hz, $J_{B,Y}$ = 3.1 Hz, $J_{C,X}$ = 0.5 Hz, $J_{C,Y}$ = 0.3 Hz, $J_{X,Y}$ = 0.1 Hz; 2 H; CH_2 vinyl; **2a**), 8.28 and 6.75 (AB_2CXY, X = α-H, Y = β-H; $J_{A,X}$ = 5.35 Hz, $J_{A,Y}$ = 10.3 Hz, $J_{B,X}$ = 2.0 Hz, $J_{B,Y}$ = 3.3 Hz, $J_{C,X}$ = 2.0 Hz, $J_{C,Y}$ = 1.0 Hz, $J_{X,Y}$ = 10.5 H; 2 H; CH_2 vinyl; **3a**), 4.51, 4.43 (m, 1 H, OH), 4.01–3.58 (m, 24 H, CH_2 phos), 1.35, 1.32, 1.27, 1.25, 1.16, 1.14 (t, J = 7.0 Hz, 36 H, CH_3 phos) ppm. $^{31}P\{^1H\}$ NMR (121.52 MHz, CD_2Cl_2, 20 °C): δ = 104.5, 93.0 and 76.5 (AB_2C, $J_{A,B}$ = 39.7 Hz, $J_{A,C}$ = 25.0 Hz, $J_{B,C}$ = 46.9 Hz, **2a**), 106.1, 95.3 and 79.4 (AB_2C, $J_{A,B}$ = 40.0 Hz, $J_{A,C}$ = 26.6 Hz, $J_{B,C}$ = 46.9 Hz, **3a**) ppm. ^{13}C NMR (75.48 MHz, CD_2Cl_2, 20 °C): δ = 165–122 (m, Ph); 145.1 (m, C2), 119.7 (m, C1), 114.4 (s, C3), 61.6 (m, CH_2 phos), 16.2 (m, CH_3 phos) (**2a**); 145.8 (m, C2), 133.8 (m, C1), 101.4 (s, C3), 62.6 (m, CH_2 phos), 16.5 (m, CH_3 phos) (**3a**) ppm.$C_{63}H_{93}BO_{13}OsP_4$ (1383.32): calcd. C 54.70, H 6.78; found C 54.58, H 6.90. Data for **2b+3b**: Λ_M = 53.0 $S cm^2 mol^{-1}$. ^1H NMR (300 MHz, CD_2Cl_2, 20 °C): δ = 7.65–6.86 (m, 25 H, Ph), 5.56 and 6.05 (ABCDXY, X = α-H, Y = β-H; $J_{A,X}$ = 8.18 Hz, $J_{A,Y}$ = 16.20 Hz, $J_{B,X}$ = 2.64 Hz, $J_{B,Y}$ = 3.76 Hz, $J_{C,X}$ = 2.64 Hz, $J_{C,Y}$ = 3.76 Hz, $J_{D,X}$ = 2.74 Hz, $J_{D,Y}$ = 1.8 Hz, $J_{X,Y}$ = 0.22 Hz; 2 H; CH_2 vinyl; **2b**), 6.27 and 8.05 (ABCDXY, X = α-H, Y = β-H; $J_{A,X}$ = 10.90 Hz, $J_{A,Y}$ = 2.6 Hz, $J_{B,X}$ = 3.9 Hz, $J_{B,Y}$ = 2.0 Hz, $J_{C,X}$ = 3.9 Hz, $J_{C,Y}$ = 2.0 Hz, $J_{D,X}$ = 0.96 Hz, $J_{D,Y}$ = 0.42 Hz, $J_{X,Y}$ = 11.3 Hz; 2 H; CH_2 vinyl; **3b**), 4.16–3.45 (m, 24 H, CH_2 phos), 4.05, 3.80 (m, 1 H, OH), 1.65, 1.64 (s, 3 H, CH_3-C3), 1.36, 1.34, 1.28, 1.26, 1.08 (t, J = 7.0 Hz, 36 H, CH_3 phos) ppm. $^{31}P\{^1H\}$ NMR (121.52 MHz, CD_2Cl_2, 20 °C): δ = 103.7, 96.2, 95.9 and76.9 (ABCD, $J_{A,B}$ = 38.9 Hz, $J_{A,C}$ = 38.9 Hz, $J_{A,D}$ = 26.6 Hz, $J_{B,C}$ = 1.30 Hz, $J_{B,D}$ = 46.3 Hz, $J_{C,D}$ = 46.3 Hz, **2b**), 105.8, 97.7, 96.6 and 80.1 (ABCD, $J_{A,B}$ = 38.5 Hz, $J_{A,C}$ = 38.5 Hz, $J_{A,D}$ = 27.4 Hz, $J_{B,C}$ = 1.60 Hz, $J_{B,D}$ = 45.8 Hz, $J_{C,D}$ = 45.8 Hz, **3b**) ppm. ^{13}C NMR (75.48 MHz, CD_2Cl_2, 20 °C): δ = 165–122 (m, Ph); 148.1 (dm, C2), 117.7 (m, C1), 114.4 (s, C3), 62.5 (m, CH_2 phos), 34.8 (s, CH_3-C3), 16.2 (m, CH_3 phos) (**2b**); 165–122 (m, Ph), 142.3 (dm, C1), 134.63 (t, C2), 92.65 (d, C3), 61.4 (m, CH_2 phos), 29.9 (s, CH_3-C3), 16.4 (m, CH_3 phos) (**3b**) ppm. $C_{58}H_{91}BO_{13}OsP_4$ (1321.25): calcd. C 52.73, H 6.94; found C 52.87, H 7.05.

$[Ru(PhNHNH_2)_2\{P(OEt)_3\}_4](BPh_4)_2$ (4): An excess amount of phenylhydrazine (0.92 mmol, 90 μL) was added to a solution of $[Ru\{\eta^2\text{-}C(=CH_2)CPh_2OH\}\{P(OEt)_3\}_4]BPh_4$ (300 mg, 0.23 mmol) in 1,2-dichloroethane (15 mL), and the reaction mixture was heated at reflux for 1 h. The solvent was removed under reduced pressure to give an oil, which was treated with ethanol (5 cm^3) containing an excess amount of $NaBPh_4$ (0.46 mmol, 157 mg). A yellow solid slowly separated out from the resulting solution, which was filtered and crystallised from CH_2Cl_2 and ethanol. Yield: 168 mg (45%). Λ_M = 122 $S cm^2 mol^{-1}$. IR (KBr): $\tilde{\nu}$ = 3318 (m), 3300 (w), 3240 [w, (ν_{NH})], 1605 [w, (δ_{NH_2})] cm^{-1}. ^1H NMR [300 MHz, $(CD_3)_2CO$, 20 °C]: δ = 7.48–6.67 (m, 50 H, Ph), 6.61 (br. t, 2 H, NH), 5.80 (br., 4 H, NH_2), 4.55–4.30 (m, 24 H, CH_2), 1.42, 1.39 (t, J = 7.0 Hz, 36 H, CH_3) ppm. $^{31}P\{^1H\}$ NMR [121.52 MHz, $(CD_3)_2CO$, 20 °C]: δ = 130.3 and 120.4 (A_2B_2, $J_{A,B}$ = 62.0 Hz) ppm. $C_{84}H_{116}B_2N_4O_{12}P_4Ru$ (1620.45): calcd. C 62.26, H 7.22, N 3.46; found C 62.04, H 7.30, N 3.33.

$[Ru\{\eta^3\text{-}PhC_3C(H)Ph\}\{P(OEt)_3\}_4]BPh_4$ (5a): To a solution of $[Ru\{\eta^2\text{-}C=(CH_2)CPh_2OH\}\{P(OEt)_3\}_4]BPh_4$ (**1a**) (200 mg, 0.15 mmol) in 1,2-dichloroethane was added an excess amount of phenylacetylene (0.6 mmol, 67 μL), and the reaction mixture was heated at reflux for 1 h. The solvent was removed under reduced pressure to give an oil, which was triturated with ethanol (3 mL) containing an excess amount of $NaBPh_4$ (0.30 mmol, 103 mg). A yellow solid slowly separated out by cooling the resulting solution to –25 °C, which was filtered and crystallised from ethanol. Yield: 128 mg (66%). Λ_M = 55.1 $S cm^2 mol^{-1}$. ^1H NMR (300 MHz, CD_2Cl_2, 20 °C): δ = 8.05–6.85 (m, 30 H, Ph), 4.30, 3.85 (m, 24 H, CH_2 phos), 1.40, 1.30, 1.03 (t, J = 7.0 Hz, 36 H, CH_3 phos) ppm. $^{31}P\{^1H\}$ NMR (121.52 MHz, CD_2Cl_2, 20 °C): δ = 137.9, 136.3 and 121.5 (ABC_2, $J_{A,B}$ = 49.3 Hz, $J_{A,C}$ = 58.0 Hz, $J_{B,C}$ = 63.8 Hz) ppm. $C_{64}H_{91}BO_{12}P_4Ru$ (1288.18): calcd. C 59.67, H 7.12; found C 59.48, H 7.26.

$[Os\{\eta^3\text{-}p\text{-tolyl-}C_3C(H)\text{-}p\text{-tolyl}\}\{P(OEt)_3\}_4]BPh_4$ (6): To a solution of $[Os\{\eta^2\text{-}C=(CH_2)CPh_2OH\}\{P(OEt)_3\}_4]BPh_4$ (**2a+3a**; 208 mg, 0.15 mmol) in 1,2-dichloroethane (10 mL) was added an excess amount of *p*-tolyl acetylene (0.6 mmol, 78 μL), and the reaction mixture was heated at reflux for 2 h. The solvent was removed under reduced pressure to give an oil, which was triturated with ethanol (3 mL) containing an excess amount of $NaBPh_4$ (0.30 mmol, 103 mg). A yellow solid slowly separated out by cooling the resulting solution to –25 °C, which was filtered and crystallised from ethanol. Yield: 38 mg (18%). Λ_M = 55.0 $S cm^2 mol^{-1}$. ^1H NMR (300 MHz, CD_2Cl_2, 20 °C): δ = 7.85–6.86 (m, 28 H, Ph), 4.20–4.00, 3.80–3.60 (m, 24 H, CH_2 phos), 2.40, 2.35 (s, 6 H, CH_3 *p*-tolyl), 1.39, 1.28, 1.01 (t, J = 7.0 Hz, 36 H, CH_3 phos) ppm. $^{31}P\{^1H\}$ NMR (121.52 MHz, CD_2Cl_2, 20 °C): δ = 93.6, 83.4 and 83.0 (ABC_2, $J_{A,B}$ = 24.3 Hz, $J_{A,C}$ = 38.8 Hz, $J_{B,C}$ = 37.5 Hz) ppm. ^{13}C NMR (75.48 MHz, CD_2Cl_2, 20 °C): δ = 165–122 (m, Ph), 141.3 (dm, $^1J_{C,H}$ = 160 Hz, C-δ], 111.3 (m, C-α or C-β), 62.2 (m, CH_2 phos), 22.0, 21.7 (s, CH_3 *p*-tolyl), 16.1 (m, CH_3 phos) ppm. $C_{66}H_{95}BO_{12}OsP_4$ (1405.37): calcd. C 56.41, H 6.81; found C 56.50, H 6.74.

$[Os(C=C=C=Ph_2)\{P(OEt)_3\}_5](BPh_4)_2$ (7a): An equimolar amount of CH_3OTf (0.35 mmol, 39 μL) was added to a solution of the hydride $OsH_2[P(OEt)_3]_4$ (0.35 mmol, 300 mg) in toluene (8 mL) allowed to stand under an argon atmosphere and cooled to –196 °C. The reaction mixture was warmed to room temperature, stirred for 30 min and cooled again to –196 °C. An equimolar amount of triflic acid (TfOH, 0.35 mmol, 31 μL) was added, and the reaction mixture was brought to room temperature and stirred for 1 h. After cooling to –196 °C, an excess amount of 1,1-diphenyl-2-propyn-1-ol (1.05 mmol, 219 mg) in CH_2Cl_2 (8 mL) was added, and the solution, brought to room temperature, was stirred for 8 h. The solvent was removed under reduced pressure to give an oil, which was triturated with ethanol (2 mL) containing an excess amount of $NaBPh_4$ (1 mmol, 0.34 g). A purple solid slowly separated out, which was filtered and crystallised from CH_2Cl_2 and ethanol. Yield: 142 mg (22%). Λ_M = 124 $S cm^2 mol^{-1}$. IR (KBr): $\tilde{\nu}$ = 1955 [m ($\nu_{C=C=C}$)] cm^{-1}. ^1H NMR (300 MHz, CD_2Cl_2, 20 °C): δ = 7.60–6.85 (m, 50 H, Ph), 4.10 (m, 30 H, CH_2 phos), 1.35, 1.32 (t, J = 7.0 Hz, 45 H, CH_3 phos) ppm. $^{31}P\{^1H\}$ NMR (121.52 MHz, CD_2Cl_2, 20 °C): δ = 85.1 and 69.1 (A_4B, $J_{A,B}$ = 40.7 Hz) ppm. ^{13}C NMR (75.48 MHz, CD_2Cl_2, 20 °C): δ = 281.5 (br. m, C-α), 195.5 (br. m, C-β), 165–120 (m, Ph), 162.9 (s, C-γ), 62.9, 62.5 (d, CH_2 phos), 16.2 (m, CH_3 phos) ppm. $C_{93}H_{125}B_2O_{15}OsP_5$ (1849.69): calcd. C 60.39, H 6.81; found C 60.21, H 6.90.

X-ray Crystallography: Mo-K_α radiation (λ = 0.71073 Å), T = 293K with a SMART AXS 1000 CCD diffractometer. Lorentz, polarization and absorption corrections were applied.[27] Structure was solved by direct methods by using SIR97[28] and refined by full-

matrix least-squares on all F^2 by using SHELXL97[29] implemented in the WingX package.[30] Hydrogen atoms partly located on Fourier difference maps and refined isotropically and partly introduced in calculated positions. Anisotropic displacement parameters refined for all non-hydrogen atoms. Molecular geometry was analysed by PARST97,[31] and use was made of the Cambridge Crystallographic Data Centre packages.[32] Table 2 summarises crystal data and structure determination results for **1a**. CCDC-670373 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 2. Crystal data and structure refinement for **1a**.

Empirical formula	$C_{63}H_{93}BO_{13}P_4Ru$
Formula weight	1294.13
Temperature [K]	293(2)
Wavelength [Å]	0.71073
Crystal system	triclinic
Space group	$P\bar{1}$
a [Å]	13.4303(4)
b [Å]	13.7527(4)
c [Å]	18.8951(6)
α [°]	76.962(1)
β [°]	88.241(1)
γ [°]	89.096(1)
Volume [Å^3]	3398.3(2)
Z	2
$D_{calcd.}$ [Mg m^{-3}]	1.265
Absorption coefficient [mm^{-1}]	0.382
$F(000)$	1368
θ range for data collection [°]	1.52–27.50
Reflections collected	37192
Independent reflections	14856 (R_{int} = 0.0194)
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	14856/0/755
Goodness-of-fit on F^2	1.071
Final R indices [$I>2\sigma(I)$]	R_1 = 0.0456, wR_2 = 0.1294
R indices (all data)	R_1 = 0.0597, wR_2 = 0.1366
Largest ΔF maximum/minimum [e Å^{-3}]	0.838/–0.704

Acknowledgments

The "Laboratorio di Strutturistica Mario Nardelli" of the University of Parma and Daniela Baldan of the University Ca' Foscari Venezia are gratefully acknowledged.

[1] a) A. F. Hill, *Comprehensive Organometallic Chemistry II* (Eds.: E. W. Abel, F. G. A. Stone, G. Wikinson), Pergamon, Oxford, **1995**, vol. 7; b) J. P. Collman, L. S. Hegedus, J. R. Norton, R. G. Finke, *Principles and Applications of Organotransition Metal Chemistry*, University Science Books, Mill Valley, **1987**.

[2] a) J. D. E. T. Wilton-Ely, S. J. Honarkhah, M. Wang, D. A. Tocher, A. M. Z. Slawin, *Dalton Trans.* **2005**, 1930–1939; b) A. F. Hill, J. D. E. T. Wilton-Ely, *J. Chem. Soc., Dalton Trans.* **1998**, 3501–3510; c) A. F. Hill, A. J. P. White, D. J. Williams, J. D. E. T. Wilton-Ely, *Organometallics* **1998**, *17*, 4249–4258; d) A. F. Hill, C. T. Ho, J. D. E. T. Wilton-Ely, *Chem. Commun.* **1997**, 2207–2208.

[3] a) R. Castarlenas, M. A. Esteruelas, E. Oñate, *Organometallics* **2001**, *20*, 2294–2302; b) M. A. Esteruelas, C. García-Yebra, M. Oliván, E. Oñate, M. A. Tajada, *Organometallics* **2000**, *19*, 5098–5106; c) R. Castarlenas, M. A. Esteruelas, E. Oñate, *Organometallics* **2000**, *19*, 5454–5463; d) M. L. Buil, M. A. Esteruelas, C. García-Yebra, E. Guttiérez-Puebla, M. Oliván, *Organometallics* **2000**, *19*, 2184–2193; e) C. Bohanna, M. L. Buil, M. A. Esteruelas, E. Oñate, C. Valero, *Organometallics* **1999**, *18*, 5176–5179; f) C. Bohanna, B. Callejas, A. J. Edwards, M. A. Esteruelas, F. J. Lahoz, L. A. Oro, N. Ruiz, C. Valero, *Organometallics* **1998**, *17*, 373–381; g) M. A. Esteruelas, A. V. Gómez, A. M. López, E. Oñate, *Organometallics* **1998**, *17*, 3567–3573; h) M. A. Esteruelas, F. Liu, E. Oñate, E. Sola, B. Zeier, *Organometallics* **1997**, *16*, 2919–2928; i) M. L. Buil, S. Elipe, M. A. Esteruelas, E. Oñate, E. Peinado, N. Ruiz, *Organometallics* **1997**, *16*, 5748–5755; j) M. A. Esteruelas, F. J. Lahoz, E. Oñate, L. A. Oro, E. Sola, *J. Am. Chem. Soc.* **1996**, *118*, 89–99; k) C. Bohanna, M. A. Esteruelas, J. Herrero, A. M. López, L. A. Oro, *J. Organomet. Chem.* **1995**, *498*, 199–206; l) C. Bohanna, M. A. Esteruelas, F. J. Lahoz, E. Oñate, L. A. Oro, E. Sola, *Organometallics* **1995**, *14*, 4825–4831; m) M. A. Esteruelas, F. J. Lahoz, E. Oñate, L. A. Oro, B. Zeier, *Organometallics* **1994**, *13*, 1662–1668.

[4] a) S. Jung, K. Ilg, C. D. Brandt, J. Wolf, H. Werner, *Eur. J. Inorg. Chem.* **2004**, 469–480; b) S. Jung, C. D. Brandt, J. Wolf, H. Werner, *Dalton Trans.* **2004**, 375–383; c) S. Jung, K. Ilg, J. Wolf, H. Werner, *Organometallics* **2001**, *20*, 2121–2123.

[5] a) B. Gómez-Lor, A. Santos, M. Ruiz, A. M. Echavarren, *Eur. J. Inorg. Chem.* **2001**, 2305–2310; b) J. Montoya, A. Santos, J. López, A. M. Echavarren, J. Ros, A. Romero, *J. Organomet. Chem.* **1992**, *426*, 383–398; c) A. Pedersen, M. Tilset, K. Folting, K. G. Caulton, *Organometallics* **1995**, *14*, 875–888; d) A. V. Marchenko, H. Gérard, O. Eisenstein, K. G. Caulton, *New J. Chem.* **2001**, *25*, 1244–1255.

[6] a) L. She, X. Li, H. Sun, J. Ding, M. Frey, H.-F. Klein, *Organometallics* **2007**, *26*, 566–570; b) M. R. Chaulagain, G. M. Mahandru, J. Montgomery, *Tetrahedron* **2006**, *62*, 7560–7566.

[7] a) H. Werner, U. Meyer, M. A. Esteruelas, E. Sola, L. A. Oro, *J. Organomet. Chem.* **1989**, *366*, 187–196; b) J. Espuelas, M. A. Esteruelas, F. J. Lahoz, L. A. Oro, C. Valero, *Organometallics* **1993**, *12*, 663–670; c) T. G. Appleton, H. C. Clark, R. J. Puddephatt, *Inorg. Chem.* **1972**, *11*, 2074–2081; d) A. Hills, D. L. Hughes, N. Kashef, R. L. Richards, M. A. N. D. A. Lemos, A. J. L. Pombeiro, *J. Organomet. Chem.* **1988**, *350*, C4–C7.

[8] a) J. Espuelas, M. A. Esteruelas, F. J. Lahoz, L. A. Oro, N. Ruiz, *J. Am. Chem. Soc.* **1993**, *115*, 4683–4689; b) M. A. Esteruelas, L. A. Oro, N. Ruiz, *Organometallics* **1994**, *13*, 1507–1509; c) M. Olivan, E. Clot, O. Eisenstein, K. G. Caulton, *Organometallics* **1998**, *17*, 3091–3100.

[9] a) G. Albertin, P. Amendola, S. Antoniutti, S. Iannelli, G. Pelizzi, E. Bordignon, *Organometallics* **1991**, *10*, 2876–2883; b) G. Albertin, S. Antoniutti, E. Bordignon, *J. Chem. Soc., Dalton Trans.* **1995**, 719–725.

[10] a) G. Albertin, S. Antoniutti, J. Castro, S. García-Fontán, G. Schipilliti, *Eur. J. Inorg. Chem.* **2007**, 1713–1722; b) G. Albertin, S. Antoniutti, J. Castro, S. García-Fontán, E. Gurabardhi, *J. Organomet. Chem.* **2006**, *691*, 1012–1024; c) G. Albertin, S. Antoniutti, M. Bortoluzzi, G. Zanardo, *J. Organomet. Chem.* **2005**, *690*, 1726–1738; d) G. Albertin, S. Antoniutti, A. Bacchi, C. D'Este, G. Pelizzi, F. Piasente, *Dalton Trans.* **2003**, 2881–2888; e) G. Albertin, S. Antoniutti, E. Bordignon, M. Pegoraro, *J. Chem. Soc., Dalton Trans.* **2000**, 3575–3584; f) G. Albertin, S. Antoniutti, E. Bordignon, D. Bresolin, *J. Organomet. Chem.* **2000**, *609*, 10–20.

[11] P. Amendola, S. Antoniutti, G. Albertin, E. Bordignon, *Inorg. Chem.* **1990**, *29*, 318–324.

[12] X. Li, T. Vogel, C. D. Incarvito, R. H. Crabtree, *Organometallics* **2005**, *24*, 62–76 and references cited therein.

[13] D. H. Gerlach, W. G. Peet, E. L. Muetterties, *J. Am. Chem. Soc.* **1972**, *94*, 4545–4549.

[14] G. Albertin, S. Antoniutti, E. Bordignon, M. Pegoraro, *J. Chem. Soc., Dalton Trans.* **2000**, 3575–3584.

[15] A. Andriollo, M. A. Esteruelas, U. Meyer, L. A. Oro, R. A. Sanchez-Delgado, E. Sola, C. Valero, H. Werner, *J. Am. Chem. Soc.* **1989**, *111*, 7431–7437.

[16] W. J. Geary, *Coord. Chem. Rev.* **1971**, *7*, 81–122.

[17] I. Ara, J. R. Berenguer, E. Eguizábal, J. Forniès, J. Gómez, E. Lalinde, J. M. Sáez-Rocher, *Organometallics* **2000**, *19*, 4385–4397.
[18] J. J. Carbó, P. Crochet, M. A. Esteruelas, Y. Jean, A. Lledós, A. M. López, E. Oñate, *Organometallics* **2002**, *21*, 305–314.
[19] J. G. Garcia, B. Ramos, A. Rodriguez, F. R. Fronczek, *Acta Crystallogr., Sect. C Cryst. Struct. Commun.* **1995**, *51*, 2674–2676.
[20] S. Jung, C. D. Brandt, H. Werner, *New J. Chem. (Nouv. J. Chim.)* **2001**, *25*, 1101.
[21] J. M. Bray, R. J. Mawby, *J. Chem. Soc., Dalton Trans.* **1989**, 589–594.
[22] G. Albertin, S. Antoniutti, A. Bacchi, E. Bordignon, P. M. Dolcetti, G. Pelizzi, *J. Chem. Soc., Dalton Trans.* **1997**, 4435–4444.
[23] G. Albertin, S. Antoniutti, E. Bordignon, F. Cazzaro, S. Ianelli, G. Pelizzi, *Organometallics* **1995**, *14*, 4114–4125.
[24] a) M. I. Bruce, *Chem. Rev.* **1998**, *98*, 2797–2858; b) V. Cadierno, M. P. Gamasa, J. Gimeno, *Coord. Chem. Rev.* **2004**, *248*, 1627–1657; c) S. Rigaut, D. Touchard, P. H. Dixneuf, *Coord. Chem. Rev.* **2004**, *248*, 1585–1601; d) J. P. Selegue, *Coord. Chem. Rev.* **2004**, *248*, 1543–1563.
[25] G. Balacco, http://www.inmr.net/.
[26] a) W. G. Peet, D. H. Gerlach, *Inorg. Synth.* **1974**, *15*, 38; b) G. Albertin, S. Antoniutti, E. Bordignon, *J. Chem. Soc., Dalton Trans.* **1989**, 2353–2358.
[27] a) SAINT: *SAX – Area Detector Integration*, Siemens Analytical Instruments Inc., Madison; b) G. Sheldrick, *SADABS: Siemens Area Detector Absorption Correction Software*, University of Goettingen, Germany, **1996**.
[28] A. Altomare, M. C. Burla, M. Cavalli, G. Cascarano, C. Giacovazzo, A. Gagliardi, A. G. Moliterni, G. Polidori, R. Spagna, *Sir97: A New Program For Solving and Refining Crystal Structures*, Istituto di Ricerca per lo Sviluppo di Metodologie Cristallografiche CNR, Bari, **1997**.
[29] G. Sheldrick, *SHELXL97: Program for Structure Refinement*, University of Goettingen, Germany, **1997**.
[30] L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837–838.
[31] M. Nardelli, *J. Appl. Crystallogr.* **1995**, *28*, 659.
[32] a) F. H. Allen, O. Kennard, R. Taylor, *Acc. Chem. Res.* **1983**, *16*, 146; b) I. J. Bruno, J. C. Cole, P. R. Edgington, M. Kessler, C. F. Macrae, P. McCabe, J. Pearson, R. Taylor, *Acta Crystallogr., Sect. B* **2002**, *58*, 389.

Received: December 7, 2007
Published Online: March 3, 2008

