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Neutral carbene and vinylidene cyclopentadienyl ruthenium complexes with $PPh_2(2\text{-}MeC_6H_4)$

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Abstract

The complex $[RuCl(\eta^5\text{-}C_5H_5)\{PPh_2(2\text{-}MeC_6H_4)\}_2]$ (**1**), unlike the triphenylphosphine analog $[RuCl(\eta^5\text{-}C_5H_5)(PPh_3)_2]$, reacts under mild conditions with CO, N_2CPh_2 and HC≡CPh to give the neutral carbonyl, carbene and vinylidene derivatives $[RuCl(\eta^5\text{-}C_5H_5)(L)\{PPh_2(2\text{-}MeC_6H_4)\}]$ (L = CO **2**, CPh_2 **5**, C=CHPh **6**), respectively, via displacement of one phosphine ligand. The vinylidene complex **6** promptly reacts with benzylamine affording the aminocarbene $[RuCl(\eta^5\text{-}C_5H_5)\{=C(NHCH_2Ph)CH_2Ph\}\{PPh_2(2\text{-}MeC_6H_4)\}]$ (**7**). Moreover, the cyclometalated derivative $[\overline{Ru(\eta^5\text{-}C_5H_5)\{PPh_2(2\text{-}C\overline{H}_2C_6H_4)\}}\{PPh_2(2\text{-}MeC_6H_4)\}]$ (**4**) has been obtained from the methyl complex $[RuMe(\eta^5\text{-}C_5H_5)\{PPh_2(2\text{-}MeC_6H_4)\}_2]$ (**3**) by intramolecular C–H bond cleavage and methane elimination. Complex **1**, whose X-ray structure analysis is also reported, has been found to catalyze alkyne coupling reactions.

Keywords: Ruthenium; Carbenes; Vinylidenes; Cyclometalation

1. Introduction

The easily accessible half-sandwich ruthenium complex $[RuCl(\eta^5\text{-}C_5H_5)(PPh_3)_2]$ exhibits a rich chemistry, which is an area of current active interest [1]. Its high reactivity appears to be related to the facile displacement of one of the coordinate ligands, affording neutral or cationic 16-electron unsaturated species. In polar solvents the chloride is readily exchanged with neutral ligands (L), providing a convenient entry for a variety of cationic complexes of the type $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2(L)]^+$ (L = CO, RCN, PR_3, etc.) [1c]. In non-polar solvents, dissociation of one PPh_3 leads to the transient $[RuCl(\eta^5\text{-}C_5H_5)(PPh_3)]$ complex, which can add π-acceptor ligands such as CO [2] and monodentate phosphines [3]. However, the extrusion of PPh_3 to create coordinative unsaturation requires severe conditions [2], and this limits the synthetic and catalytic applications of $[RuCl(\eta^5\text{-}C_5H_5)(PPh_3)_2]$. Thus, displacement of one PPh_3 and formation of neutral vinylidene complexes has not been observed in the reaction with 1-alkynes, whereas this process readily occurs in the case of $[RuCl(\eta^5\text{-}C_5Me_5)(PPh_3)_2]$ [4]. Werner successfully synthesized the first neutral cyclopentadienyl vinylidene complex $[RuCl(\eta^5\text{-}C_5H_5)(=C=CHCO_2Me)(PPh_3)]$, but in a stepwise process starting from the allyl derivative $[Ru(\eta^3\text{-}C_3H_5)(\eta^5\text{-}C_5H_5)(PPh_3)]$ [5]. By contrast, cationic complexes of general formula $[Ru(\eta^5\text{-}C_5H_5)(=C=CHR)(PPh_3)_2]^+$ have been obtained by ready dissociation of the halide, especially in polar solvents [6].

Recently, we have reported that the complexes $[RuCl(\eta^5\text{-}C_5H_5)(PR_3)_2]$ can act as effective catalysts in a variety of reactions involving diazocompounds, such as stereoselective carbene–carbene coupling [7], cyclopropanation [8], carbene insertion into N–H and S–H bonds [9], and nitrogen ylide generation [10]. The key step of these catalytic processes is the formation of the carbene intermediate $[RuCl(\eta^5\text{-}C_5H_5)(=CHR)(PR_3)]$ from the 16-electron species $[RuCl(\eta^5\text{-}C_5H_5)(PR_3)]$.

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Bulky phosphines favor the reaction as shown by the fact that [RuCl(η^5-C_5H_5){PPh_2(2-MeC_6H_4)}$_2$] (**1**) is catalytically active below 20°C, whereas the PPh_3 analog needs heating at 60°C [7b]. The facile displacement of one phosphine in complex **1** is also apparent in the reaction with diethyl maleate (DEM) which leads to the formation of complex [RuCl(η^5-C_5H_5)(η^2-DEM){PPh_2-(2-MeC_6H_4)}] [7b]. The easy cleavage of one Ru–P bond in **1** prompted us to carry out a specific investigation on its properties and its ability to form isolable neutral carbene and vinylidene derivatives. Ruthenium organometallic compounds of this type continue to attract interest, because of their potential use in stoichiometric and catalytic C–C bond forming reactions [11] and alkyne dimerization [12].

We report herein the preparation in high yield of the new carbene and vinylidene derivatives [RuCl(η^5-C_5H_5)(=CPh_2){PPh_2(2-MeC_6H_4)}] (**5**) and [RuCl-(η^5-C_5H_5)(=C=CHPh){PPh_2(2-MeC_6H_4)}] (**6**) from the easily available precursor **1**. Complex **6** reacts with benzylamine affording the aminocarbene [RuCl(η^5 - C_5H_5){=C(NHCH$_2$Ph)CH$_2$Ph}{PPh_2(2 - MeC_6-H_4)}] (**7**). Furthermore, complex **1**, whose X-ray structure is also reported, was found to catalyze the cyclotrimerization of dimethyl acetylenedicarboxylate. The cyclometalated derivative [Ru(η^5-C_5H_5){PPh_2(2-$CH_2C_6H_4$)}{PPh_2(2-MeC_6H_4)}] (**4**) is easily formed from [RuMe(η^5-C_5H_5){PPh_2(2-MeC_6H_4)}$_2$] (**3**) through methane elimination.

Table 1
Crystallographic data for **1**·C_2H_6O

Empirical formula	$C_{45}H_{45}ClOP_2Ru$
Formula weight	800.27
Crystal system	Monoclinic
Space group	$P2_1/c$ (no. 14)
Unit cell parameters	
a (Å)	11.446(1)
b (Å)	11.797(1)
c (Å)	28.238(2)
β (°)	98.01(1)
V (Å^3)	3775.7(5)
Z	4
D_{calc} (g cm^{-3})	1.408
$F(000)$	1656
μ (mm^{-1})	0.606
θ range for data collection (°)	2.26–25.67
Limiting hkl indices	± 13, ± 14, ± 34
Reflections collected	52576
Independent reflections (all data)	6847
Observed reflections ($I_o > 2\sigma(I_o)$)	5118
Data/restraints/parameters	6847/0/469
R_1 [a] ($I_o > 2\sigma(I_o)$/all data)	0.0327/0.0453
wR_2 [b]	0.0943
GOF [c]	0.936
Weights a/b [d]	0.0686/0
Largest difference peak and hole (e Å^{-3})	0.60, −0.26

[a] $R_1 = \Sigma(||F_o|-|F_c||)/\Sigma|F_o|$.
[b] $wR_2 = [\Sigma w (F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.
[c] GOF $= [\Sigma w(F_o^2-F_c^2)^2/(N_O-N_V)]^{1/2}$.
[d] $w = 1/[\sigma^2(F_o^2)+(aP)^2+bP]$ with P: [max (0 or F_o^2)+$2F_c^2$]/3.

2. Results and discussion

2.1. Structural characterization and reactivity of [RuCl(η^5-C_5H_5){PPh_2(2-MeC_6H_4)}$_2$] (1)

During studies directed towards the synthesis of cyclopentadienylruthenium complexes containing bulky phosphines, we have recently isolated the complex [RuCl(η^5-C_5H_5){PPh_2(2-MeC_6H_4)}$_2$] (**1**) in high yield in a one-pot reaction from ruthenium trichloride, cyclopentadiene and PPh_2(2-MeC_6H_4) [7b]. Among the few cyclopentadienylruthenium compounds bearing phosphines with a cone angle larger than that of PPh_3 (145°), **1** has been found to be the most reactive in several catalytic reactions [7b,8]. With the aim of comparing structurally the PPh_3 and the PPh_2(2-MeC_6H_4) systems, complex **1** was investigated by X-ray single-crystal analysis. The crystallographic parameters are collected in Table 1, whereas an ORTEP view of **1** is shown in Fig. 1 with selected bond distances and angles.

The geometry of **1** is distorted octahedral about the ruthenium center due to the severe steric interactions between the phosphines. The two phosphorus ligands are not equivalent and one methyl group of the tolyl substituent is directed towards the chloride ligand. The Ru–P and Ru–Cl distances are very similar to those reported for the PPh_3 analog but with a slightly smaller P–Ru–P angle (101.12° versus 103.99° [13]).

Complex **1** is thermally stable in toluene solution under inert atmosphere even at 100°C, but decomposes in air within a few minutes at room temperature with the formation of phosphine oxide and brown insoluble products. The ^{31}P-NMR spectra of **1** show that the compound has a fluxional behavior in solution on the NMR time-scale. Thus, at 20°C the ^{31}P{^{1}H}-NMR spectrum shows a sharp singlet at $\delta = 37.9$ and no phosphine dissociation is observed even at 100°C. On cooling, the signal broadens and at -80°C the spectrum displays an AX pattern with two doublets at $\delta = 43.2$ and 35.6, and ^2J(P,P) = 35.4 Hz. The observed behavior is reversible and may be explained by the low temperature restricted rotation of the phenyl and tolyl rings that leads to the magnetic inequivalence of the two phosphorus atoms.

Although there is no significant structural difference between the PPh_3 and the PPh_2(2-MeC_6H_4) derivatives, their behavior in phosphine-substitution reactions is markedly different. It has been reported that one PPh_3 ligand in [RuCl(η^5-C_5H_5)(PPh_3)$_2$] can be replaced by CO under forcing carbonylation conditions (150 atm carbon monoxide, 70°C, 48 h) [2], whereas at lower CO

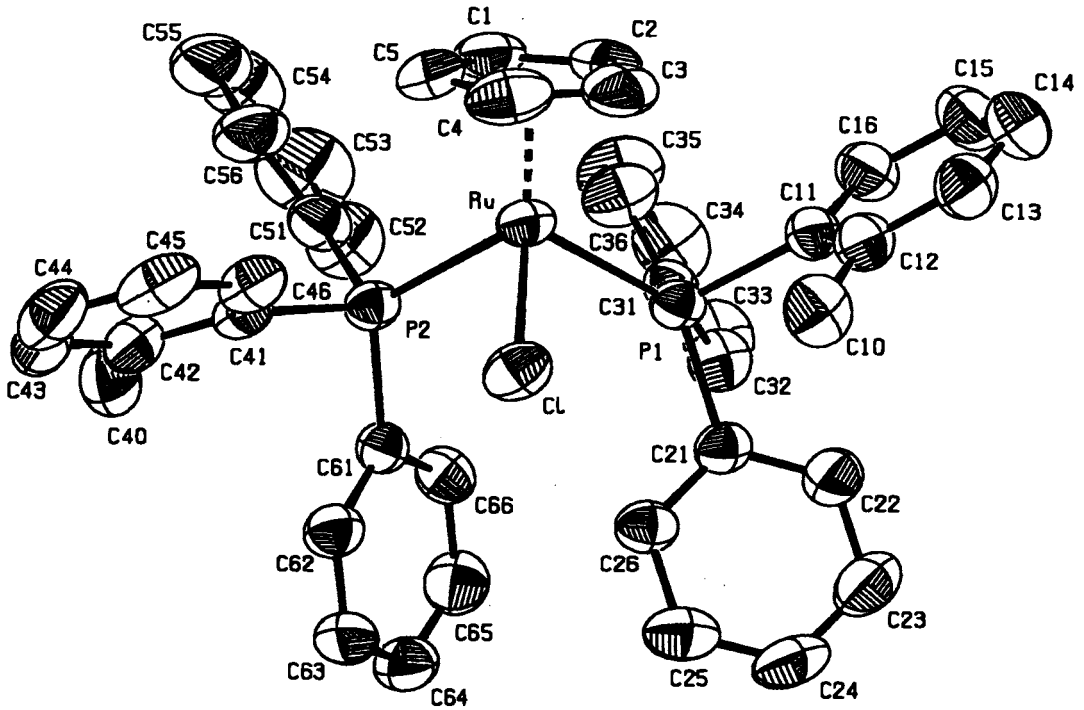
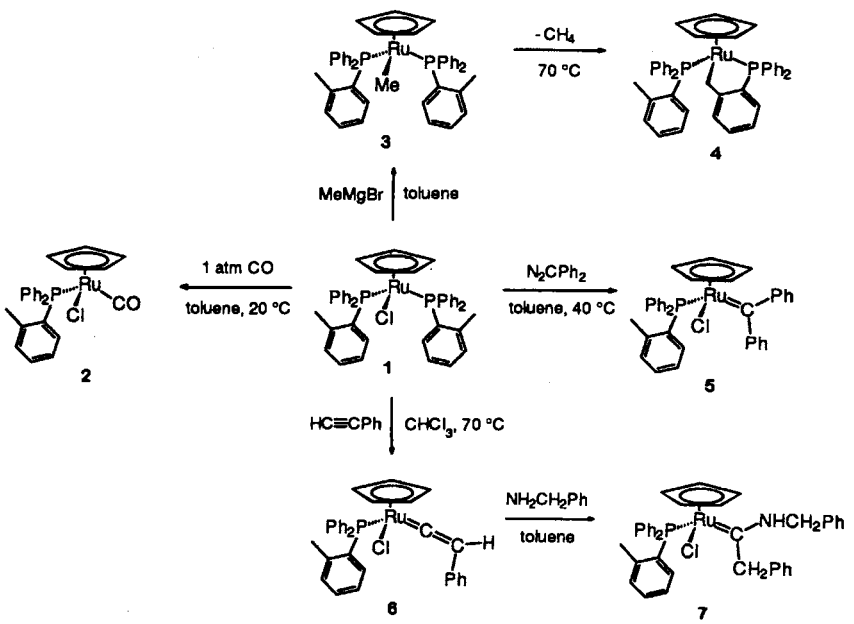


Fig. 1. ORTEP representation of the molecular structure of **1** in the solid state. Thermal ellipsoids are at the 50% probability level. Hydrogens omitted for clarity. Selected bond lengths [Å] and angles [°]: Ru–Cl 2.4372(8), Ru–P1 2.3271(7), Ru–P2 2.3390(8), Ru–C1 2.167(3), Ru–C2 2.167(3), Ru–C3 2.198(3), Ru–C4 2.204(3), Ru–C5 2.203(3); C1–Ru–P1 92.92(3), C1–Ru–P2 87.85(3), P1–Ru–P2 101.12(2), Ru–P1–C11 111.34(9), Ru–P1–C21 125.20(11), Ru–P1–C31 114.18(9), Ru–P2–C41 114.67(9), Ru–P2–C51 112.45(9), Ru–P2–C61 119.71(8), P1–Ru–Cen 120.9, P2–Ru–Cen 122.8, Cl–Ru–Cen 123.2. Cen: centroid of the C_5H_5–ligand.



Scheme 1.

pressure (2 atm) sulfur is needed to remove the phosphine as $S{=}PPh_3$ [14]. By contrast, the monocarbonyl derivative $[RuCl(\eta^5\text{-}C_5H_5)(CO)\{PPh_2(2\text{-}MeC_6H_4)\}]$ (**2**) was obtained quantitatively by stirring **1** under 1 atm CO at room temperature within a few minutes (Scheme 1).

The $^{13}C\{^1H\}$-NMR spectrum of **2** in $CDCl_3$ shows a doublet at $\delta = 203.8$ ($^2J(C,P) = 20.0$ Hz), whereas the ν_{CO} appears at 1946 cm^{-1}, and is shifted 12 cm^{-1} to lower wavenumbers compared to $[RuCl(\eta^5\text{-}C_5H_5)(CO)(PPh_3)]$ [14], in agreement with the more basic character of the *ortho*-methylated phosphine.

Moreover, treatment at 25°C of **1** in C_6D_6 with an equimolar amount of PPh_3 promptly affords the mixed phosphine complex [RuCl(η^5-C_5H_5)(PPh_3){PPh_2(2-MeC_6H_4)}], whose $^{31}P\{^1H\}$-NMR spectrum exhibits two doublets at $\delta = 40.8$ and 38.8 with $^2J(P,P) = 41.7$ Hz. Addition of a twofold molar amount of PPh_3 to **1** at 50°C gives [RuCl(η^5-C_5H_5)(PPh_3)$_2$] quantitatively, as result of complete displacement of PPh_2(2-MeC_6H_4).

Aryl phosphines with methyl groups in ortho position have been extensively employed to synthesize cyclometalated complexes [15], which result from intramolecular C–H activation of methyl groups, and more recently to prepare a 14-electron complex [$RuCl_2${PPh_2(2,6-$Me_2C_6H_3$}$_2$] stabilized by two agostic interactions [16]. In the case of **1**, cyclometalation was not observed even when it was refluxed in toluene and in the presence of base. However, starting from the methyl derivative [RuMe(η^5-C_5H_5){PPh_2(2-MeC_6H_4)}$_2$] (**3**), the cyclometalated complex [Ru(η^5-C_5H_5){PPh_2(2-$CH_2C_6H_4$)}{PPh_2(2-MeC_6H_4)}] (**4**) can be easily obtained according to the procedure adopted by Lehmkuhl for the synthesis of the orthometalated product [Ru(η^5-C_5H_5){PPh_2(2-C_6H_4)}(PPh_3)] [17]. Treatment of **1** in toluene at -40°C with a slight excess of methylmagnesium bromide in diethyl ether gave complex **3**, which was isolated as yellow powder in 78% yield (Scheme 1). The most characteristic feature in the ^{1}H-NMR spectrum of **3** is the presence of a triplet at $\delta = 0.82$ with a $^3J(H,P) = 6.1$ Hz, whereas the ^{13}C-NMR DEPT spectrum shows a singlet at $\delta = 1.5$, attributed to the Ru–CH_3 methyl. This product slowly decomposes in solution at room temperature with methane evolution and the reaction can be readily monitored by $^{31}P\{^1H\}$-NMR. When heated in toluene at 70°C, **3** is quantitatively converted into complex **4** within 30 min (Scheme 1). The yellow complex **4** was isolated and fully characterized. Consistent with the cyclometalated structure, the $^{31}P\{^1H\}$-NMR spectrum shows two doublets at δ 75.2 and 59.4 with a $^2J(P,P) =$ 34.2 Hz. The strongly downfield-shifted resonance is attributed to the P atom of the cyclometalated phosphine that is part of a five-membered chelate ring [18]. In the ^{1}H-NMR spectrum the two signals due to the Ru–CH_2 methylene appear as a doublet at 4.44 ppm with a $J(H,H) = 15.5$ Hz and a doublet of doublets at 4.26 ppm with a $J(H,P) = 7.0$ Hz as inferred by $^1H\{^{31}P\}$-NMR experiments. Furthermore, the $^{13}C\{^1H\}$-NMR signal at $\delta = 13.1$ (part of an AXY spin system, $^2J(C,P) = 12.3$ Hz, $^2J(C,P') = 8.4$ Hz) was attributed to the $RuCH_2$ carbon through a ^{13}C-NMR DEPT experiment. Complex **4** is relatively stable in solution and no phosphine displacement was observed by reaction with CO or CN^{t}Bu ligand.

It should be noted that cyclometalation in **3** proceeds more easily than in the PPh_3 analog [RuMe(η^5-C_5H_5)(PPh_3)$_2$] for which heating at 100°C for 6 h is necessary. In both cases cyclometalation probably occurs by intramolecular C–H bond cleavage, induced by the generation of a vacant coordination site at the metal center. Therefore, formation of **4** is favored by the more facile dissociation of one phosphine to give the coordinatively unsaturated 16-electron species [RuMe(η^5-C_5H_5)(PR_3)]. We can observe that a related cyclometalated complex [RuCl{PPh_2(2-$CH_2C_6H_4$)}(η^6-C_6Me_6)] was obtained by the reaction of [$RuCl_2${PPh_2(2-MeC_6H_4)}(η^6-C_6Me_6)] with Na_2CO_3 in 2-propanol [19]. However, attempts to obtain **4** by treatment of **1** with Na_2CO_3 in 2-propanol or CaH_2 in toluene resulted in the formation of only trace amounts of the cyclometalated product.

2.2. Preparation of carbene and vinylidene complexes

The synthesis of electrophilic carbene complexes of ruthenium still remains an area of great interest because of the manifold applications in organic synthesis for C–C carbon bond forming reactions. We have now found that compound **1** reacts with diphenydiazomethane in toluene at 40°C affording the green carbene complex [RuCl(η^5-C_5H_5)(=CPh_2){PPh_2(2MeC_6H_4)}] (**5**), which was isolated in 81% yield and characterized by elemental analysis and NMR spectroscopy (Scheme 1). The presence of a carbene ligand in **5** was unambiguously established by the $^{13}C\{^1H\}$-NMR spectrum which contains a typical doublet at $\delta = 319.3$ with a $^2J(C,P) = 15.3$ Hz, attributed to the Ru=C carbon; these values are similar to those reported for [RuCl(η^5-C_5H_5)(=CPh_2)(PPh_3)] [11b]. It should be mentioned that we have recently reported that complex **1** and the PPh_3 analog efficiently catalyze the cyclopropanation of styrene and other electron-rich alkenes in the presence of ethyl diazoacetate. Moreover, when diphenyldiazomethane is employed as carbene source, the reaction with styrene affords mainly 1,1,3-triphenylpropene, as result of a formal :CPh_2–:$CHCH_2$Ph coupling. For these catalytic reactions there is strong evidence that complexes of type **5** are key intermediates in the C–C coupling processes [8].

Complex **1** is also an excellent starting material to give neutral alkyne or vinylidene ruthenium complexes. Indeed, selective dimerization of alkynes [12] is thought to occur via ruthenium vinylidene intermediates which are also involved in various other ruthenium catalyzed reaction of acetylenes [20].

Treatment of **1** in $CDCl_3$ with an equimolar amount of internal alkynes RC≡CR containing electron-withdrawing groups such as R = CO_2Me leads to the alkyne complex [RuCl(η^5-C_5H_5)(η^2-$MeO_2CC{\equiv}CCO_2Me$)-{PPh_2(2-MeC_6H_4)}] which was found in equilibrium with the starting product. The $^{31}P\{^1H\}$-NMR spectrum

exhibits a signal at $\delta = 45.5$, whereas the ^{1}H-NMR spectrum shows a resonance at $\delta = 5.08$ for the cyclopentadienyl ligand and a broad signal at 3.52 ppm for the methyl protons of the coordinated alkyne. It should be noted that a similar π-alkyne complex $[OsCl(\eta^5\text{-}C_5H_5)(\eta^2\text{-}MeCO_2C{\equiv}CCO_2Me)(P^iPr_3)]$ has been obtained by reaction of the alkyne with $[OsCl(\eta^5\text{-}C_5H_5)(P^iPr_3)_2]$ [21], which also shows a high tendency to release a phosphine ligand in solution. When complex **1** (3 mol%) is added to a $CDCl_3$ solution of dimethyl acetylenedicarboxylate, a catalytic cyclotrimerization occurs at room temperature with 90% conversion of the alkyne into hexamethyl benzenehexacarboxylate after 1 day [22].

By contrast, the reaction of **1** with terminal alkynes leads to formation of neutral vinylidene derivatives. Thus, treatment of a $CHCl_3$ solution of **1** with phenylacetylene in excess at reflux affords the neutral vinylidene complex $[RuCl(\eta^5\text{-}C_5H_5)(=C{=}CHPh)\{PPh_2(2\text{-}MeC_6H_4)\}]$ (**6**), isolated as a pale brown powder in 63% yield (Scheme 1). The most characteristic feature in the $^{13}C\{^1H\}$-NMR spectrum of **6** is the presence of a doublet at $\delta = 345.6$ with a $J(P,C) = 20.4$ Hz for the carbon bound to ruthenium, whereas the ^{1}H-NMR spectrum shows a singlet at 4.74 ppm for the vinylidene proton, and these values are close to those given by $[RuCl(\eta^5\text{-}C_5Me_5)(=C{=}CHPh)(PPh_3)]$ [4a]. It should be noted that the reaction of the above-mentioned $[OsCl(\eta^5\text{-}C_5H_5)(P^iPr_3)_2]$ with phenylacetylene initially gives $[OsCl(\eta^5\text{-}C_5H_5)(\eta^2\text{-}HC{\equiv}CPh)(P^iPr_3)]$ which subsequently isomerizes to $[OsCl(\eta^5\text{-}C_5H_5)(=C{=}CHPh)(P^iPr_3)]$ [21]. By contrast, in the formation of **6** from **1**, the π-alkyne intermediate was not detected. The nature of the solvent seems to play a delicate role for the isolation of the vinylidene complexes. In fact, if toluene is used instead of $CHCl_3$, complex **6** is formed in low amounts along with catalytic conversion of phenylacetylene into the dimers arising from head-to-head and head-to-tail alkyne coupling. Also the type of alkyne seems to be important for the isolation of the vinylidene derivative. Although the reaction of **1** with a series of terminal alkynes HC≡CR (R = CH_2Ph, $SiMe_3$, CO_2Me) in $CHCl_3$ leads to mixtures of products, with HC≡C^{t}Bu we were able to detect the corresponding vinylidene complex. Reaction of a $CDCl_3$ solution of **1** with HC≡C^{t}Bu in the presence of CuCl, which has been used as phosphine scavenger for ruthenium complexes [23], in 1:10:2 molar ratio at 70° C for 5 min, afforded almost quantitatively the complex $[RuCl(\eta^5\text{-}C_5H_5)(=C{=}CH^tBu)\{PPh_2(2\text{-}MeC_6H_4)\}]$ as inferred by ^{1}H and ^{31}P-NMR data. The $^{31}P\{^1H\}$-NMR spectrum shows a signal at $\delta = 51.1$, whereas the ^{1}H-NMR spectrum shows singlets at $\delta = 5.02$ for the cyclopentadienyl ring and $\delta = 3.74$ for the C=CH vinylidene proton, which can be compared with those of **6**. In the reaction performed without CuCl we observed a lower conversion into the vinylidene complex (30%) and prolonged heating of the reaction mixture led to catalytic alkyne dimerization. The results here obtained for **1** can be compared with those previously reported for the 16-electron derivatives $[RuCl(\eta^5\text{-}C_5Me_5)(L)]$ (L = *N*-heterocyclic carbene). With the latter, we observed highly efficient catalytic dimerization of terminal alkynes, with no detection of the corresponding vinylidene complexes [24]. The systems $[RuCl(\eta^5\text{-}C_5H_5)(PR_3)_2]$ with bulky phosphines are currently under investigation to establish their potential in catalytic alkyne coupling reactions. On the other hand, stoichiometric C–C coupling reactions of terminal alkynes in cyclopentadienyl ruthenium complexes have been extensively described [25].

Finally, we tested the reactivity of the ruthenium-vinylidene **6** towards nucleophiles such as amines. Due to the electrophilic character of the α-carbon atom in vinylidene complexes, it is well known that these species promptly react with primary amines to give aminocarbene complexes via intermolecular nucleophilic attack of the nitrogen atom [26]. Thus, treatment of **6** with an equimolar amount of benzylamine at room temperature in toluene led to complex $[RuCl(\eta^5\text{-}C_5H_5)\{=C(NHCH_2Ph)CH_2Ph\}\{PPh_2(2\text{-}MeC_6H_4)\}]$ (**7**), which was isolated in 55% yield after appropriate work-up (Scheme 1). The formation of the aminocarbene ligand was unequivocally established by ^{1}H and ^{13}C-NMR spectroscopy. The ^{1}H-NMR spectrum of **7** exhibits a signal at $\delta =$ 10.39 for the NH proton with two doublets at $\delta = 4.83$ and 3.89 for the diasterotopic $=CCH_2$ protons, whereas the $^{13}C\{^1H\}$-NMR spectrum shows a doublet at 255.0 ppm with $J(C,P) = 16.3$ Hz for the Ru=C carbon, which agree well with the literature data [27].

3. Concluding remarks

This study has revealed that the use of $PPh_2(2\text{-}MeC_6H_4)$ as auxiliary ligand in cyclopentadienylruthenium complexes gives rise to a derivative related to $[RuCl(\eta^5\text{-}C_5H_5)(PPh_3)_2]$, but with a remarkably higher reactivity. The easily accessible complex **1** is a convenient starting material for the preparation of neutral cyclopentadienylruthenium carbene and vinylidene derivatives. This results from the high tendency of **1** to release one phosphine ligand to give the coordinatively unsaturated $[RuCl(\eta^5\text{-}C_5H_5)\{PPh_2(2\text{-}MeC_6H_5)\}]$ species which can add a variety of π-acceptor ligands. Probably, as suggested by Nolan et al. on the basis of thermochemical studies on $[RuCl(\eta^5\text{-ligand})(PR_3)_2]$ complexes [28], the high steric requirements of the $PPh_2(2\text{-}MeC_6H_4)$ ligand are responsible for the weakening of the Ru–P bond in **1**, allowing easier formation of the 16-electron complex intermediate. The new ruthenium complexes **5** and **6**, which have been isolated, are thought to be key intermediates in C–C bond

forming reactions. Thus, the carbene derivative **5** has been found to be involved in the catalytic synthesis of the trisubstituted olefin 1,1,3-triphenylpropene from diphenyldiazomethane and styrene [8], whereas complex **6** is formed in the catalytic phenylacethylene dimerization. It is noteworthy that in the reactions of alkynes with $[RuCl(\eta^5\text{-}C_5H_5)(PR_3)_2]$ systems, displacement of one PR_3 ligand and formation of a neutral complex have not been observed prior to this work. In conclusion, complex **1** provides a useful alternative to the widely employed PPh_3 analog in catalytic processes which occur through phosphine displacement.

4. Experimental

All reactions were carried out under an argon atmosphere using standard Schlenck techniques. Solvents were carefully dried by conventional methods and distilled under argon before use. Phenylacetylene, benzylamine and methylmagnesium bromide 3.0 M solution in diethyl ether were purchased from Aldrich Chemical Co. The compounds **1** [7b] and N_2CPh_2 [29] were prepared according to the literature. NMR measurements were carried out using a Bruker AC 200 spectrometer. Chemical shifts, in ppm, are relative to TMS for ^1H and ^{13}C, and to external 85% H_3PO_4 for ^{31}P. IR spectra were recorded with a Nicolet Magna 550 FT spectrometer. Elemental analyses (C, H, N) were performed by the Microanalytical Laboratory of our department.

4.1. Synthesis of $[RuCl(\eta^5\text{-}C_5H_5)(CO)\{PPh_2(2\text{-}MeC_6H_4)\}]$ (2)

The complex **1** (260 mg, 0.345 mmol) was dissolved in 5 ml of toluene and the solution was stirred under CO (1 atm) at room temperature for 1 h. The volume was reduced to 2 ml and heptane was added affording a yellow precipitate. After filtration the product was washed with heptane and dried under reduced pressure. Yield: 151 mg (86%). Anal. Calc. for $C_{25}H_{22}ClOPRu$: C, 59.35; H, 4.38. Found: C, 58.90; H, 4.41%.

Spectroscopic data: ^1H-NMR ($CDCl_3$, 25°C): $\delta =$ 7.42–6.63 (m, 14H; aromatic protons), 4.65 (s, 5H; C_5H_5), 2.08 (s, 3H; CH_3). $^{13}C\{^1H\}$-NMR ($CDCl_3$, 25°C): $\delta = 203.8$ (d, $J(C,P) = 20.0$ Hz; *C*O), 141.5 (d, $J(C,P) = 9.6$ Hz; *C*Me), 134.8 (d, $J(C,P) = 11.2$ Hz; *o*-C_6H_5), 134.0 (d, $J(C,P) = 46.1$ Hz; *ipso*-C_6H_5), 133.4 (d, $J(C,P) = 10.4$ Hz; *o*-C_6H_5), 132.9 (d, $J(C,P) = 10.4$ Hz; *o*-C_6H_4), 132.0 (d, $J(C,P) = 7.8$ Hz; *m*-C_6H_4), 131.5 (d, $J(C,P) = 45.0$ Hz; *ipso*-C_6H_4), 130.5–130.2 (*p*-C_6H_4 and *p*-C_6H_5), 128.4 (d, $J(C,P) = 10.4$ Hz; *m*-C_6H_5), 128.2 (d, $J(C,P) = 10.4$ Hz; *m*-C_6H_5), 125.7 (d, $J(C,P) = 9.7$ Hz; *m*-C_6H_4), 85.6 (d, $J(C,P) = 1.9$ Hz; C_5H_5), 23.2 (d, $J(C,P) = 5.9$ Hz; CH_3). $^{31}P\{^1H\}$-NMR ($CDCl_3$, 25°C): $\delta = 46.9$. IR (nujol): $\nu(CO) = 1946$ cm^{-1}.

4.2. Synthesis of $[RuMe(\eta^5\text{-}C_5H_5)\{PPh_2(2\text{-}MeC_6H_4)\}_2]$ (3)

Methylmagnesium bromide (0.21 ml of a 3.0 M solution in diethyl ether, 0.630 mmol) was added dropwise to **1** (0.400 g, 0.530 mmol) dissolved in toluene (20 ml) at −40°C. The yellow mixture was allowed to attain room temperature and stirred for 15 min. After filtration on alumina, the solvent was removed and pentane (5 ml) was added affording a yellow product, which was filtered, recrystallized from toluene–heptane and dried under reduced pressure. Yield: 0.304 g (78%). Anal. Calc. for $C_{44}H_{42}P_2Ru$: C, 72.02; H, 5.77. Found: C, 71.35; H, 5.65%.

Spectroscopic data: ^1H-NMR (C_6D_6, 25°C): $\delta = 8.0$–6.7 (m, 28H; aromatic protons), 4.23 (s, 5H; C_5H_5), 1.77 (s, 6H; CH_3), 0.82 (t, $J(H,P) = 6.1$ Hz, 3H; RuCH_3). $^{13}C\{^1H\}$-NMR (C_6D_6, 5°C): $\delta = 138.0$–124.9 (aromatic carbons), 84.5 (t, $J(C,P) = 2.0$ Hz; C_5H_5), 23.5 (s; CCH_3), 1.5 (s; RuCH_3). $^{31}P\{^1H\}$-NMR (C_6D_6, 25°C): $\delta = 53.9$.

4.3. Synthesis of $[\overline{Ru(\eta^5\text{-}C_5H_5)\{PPh_2(2\text{-}CH_2C_6H_4)\}}\text{-}\{PPh_2(2\text{-}MeC_6H_4)\}]$ (4)

The complex **3** (0.300 g, 0.409 mmol) was dissolved in toluene (5 ml) and the solution was heated at 70°C for 30 min. The solvent was eliminated and the oily product was treated with pentane (5 ml) affording a yellow precipitate. The product was filtered, recrystallized from toluene–heptane and dried under reduced pressure. Yield: 0.220 g (75%). Anal. Calc. for $C_{43}H_{38}P_2Ru$: C, 71.95; H, 5.34. Found: C, 71.61; H, 5.29%.

Spectroscopic data: ^1H-NMR (C_6D_6, 25°C): $\delta = 8.0$–6.6 (m, 28H; aromatic protons), 4.44 (d, $J(H,H) = 15.5$ Hz, 1H; RuCH_2), 4.26 (s, 5H; C_5H_5), 3.08 (dd, $J(H,H) = 15.5$ Hz, $J(H,P) = 7.0$ Hz, 1H; RuCH_2), 1.77 (s, 3H; CH_3). $^{13}C\{^1H\}$-NMR (C_6D_6, 25°C): $\delta = 146.0$–124.5 (aromatic carbons), 83.5 (t, $J(C,P) = 2.0$ Hz; C_5H_5), 23.4 (d, $J(C,P) = 4.5$ Hz; CH_3), 13.1 (dd, $J(C,P) = 12.3$ Hz, $J(C,P) = 8.4$ Hz; RuCH_2). $^{31}P\{^1H\}$-NMR (C_6D_6, 25°C): $\delta = 75.2$ (d, $J(P,P) = 34.2$ Hz), 59.4 (d, $J(P,P) = 34.2$ Hz).

4.4. Synthesis of $[RuCl(\eta^5\text{-}C_5H_5)(=CPh_2)\text{-}\{PPh_2(2\text{-}MeC_6H_4)\}]$ (5)

The complex **1** (260 mg, 0.345 mmol) and diphenyldiazomethane (150 mg, 0.772 mmol) were dissolved in 10 ml of toluene and the red solution was stirred at 45°C overnight. Diphenyldiazomethane (75 mg, 0.386 mmol)

was added to the resulting green solution, which was stirred at 55°C for 2 h and concentrated to 1 ml. Addition of heptane (10 ml) afforded a green precipitate which was recrystallized from toluene–heptane and dried under reduced pressure. Yield: 180 mg (81%). Anal. Calc. for $C_{37}H_{32}ClPRu$: C, 69.00; H, 5.01. Found: C, 69.30; H, 5.16%.

Spectroscopic data: ^{1}H-NMR (C_6D_6, 25°C): $\delta =$ 7.75–6.75 (m, 24H; aromatic protons), 4.69 (s, 5H; C_5H_5), 1.73 (s, 3H; CH_3). $^{13}C\{^1H\}$-NMR (C_6D_6, 25°C): $\delta = 319.3$ (d, $J(C,P) = 15.3$ Hz; Ru=*C*), 165.2 (d, $J(C,P) = 4.3$ Hz; *ipso*-C_6H_5), 144.2–125.3 (aromatic carbons), 90.7 (d, $J(C,P) = 3.0$ Hz; C_5H_5), 23.4 (d, $J(C,P) = 4.3$ Hz; CH_3). $^{31}P\{^1H\}$-NMR (C_6D_6, 25°C): $\delta = 44.9$.

4.5. Synthesis of [RuCl(η^5-C_5H_5)(=C=CHPh)-{PPh_2(2-MeC_6H_4)}] (6)

Phenylacetylene (1.5 ml, $d = 0.93$ g ml^{-1}, 13.7 mmol) was added to **1** (1.00 g, 1.33 mmol) dissolved in chloroform (20 ml). The solution was heated at the reflux point for 1 h and the solvent was completely removed under reduced pressure. The resulting oily product was treated with 50 ml of heptane and the suspension was stirred overnight. After filtration, the product was dissolved in chloroform (20 ml) and phenylacetylene (1.5 ml, 13.7 mmol) was added. The solution was refluxed for 1 h and the solvent was removed under reduced pressure. The product was suspended in heptane (50 ml) and stirred overnight. After filtration the pale brown product was recrystallized from CH_2Cl_2–heptane and dried under reduced pressure. Yield: 0.487 g (63%). Anal. Calc. for $C_{32}H_{28}ClPRu$: C, 66.26; H, 4.87. Found: C, 66.10; H, 4.84%.

Spectroscopic data: ^{1}H-NMR ($CDCl_3$, 25°C): $\delta =$ 7.8–6.8 (m, 19H; aromatic protons), 5.17 (s, 5H; C_5H_5), 4.74 (s, 1H; C=C*H*), 2.19 (s, 3H; CH_3). $^{13}C\{^1H\}$-NMR ($CDCl_3$, 25°C): 345.6 (d, $J(C,P) = 20.4$ Hz; Ru=*C*), 142.2–124.8 (aromatic carbons), 118.2 (s; =*C*HPh), 92.5 (d, $J(C,P) = 2.5$ Hz; C_5H_5), 23.3 (d, $J(C,P) = 5.1$ Hz; CH_3). $^{31}P\{^1H\}$-NMR ($CDCl_3$, 25°C): $\delta = 50.5$.

4.6. Synthesis of [RuCl(η^5-C_5H_5){=C(NHCH$_2$Ph)-CH$_2$Ph}{PPh_2(2-MeC_6H_4)}] (7)

Benzylamine 45 μl ($d = 0.98$ g ml^{-1}, 0.412 mmol) was added to **6** (0.200 g, 0.345 mmol) dissolved in toluene (6 ml) and the solution was stirred for 30 min. After filtration the solution was concentrated to 1 ml and heptane (4 ml) was added affording a yellow precipitate. The product was recrystallized from toluene–heptane and dried under reduced pressure. Yield: 0.13 g (55%). Anal. Calc. for $C_{39}H_{37}ClNPRu$: C, 68.16; H, 5.43; N, 2.04. Found: C, 67.94; H, 5.28; N, 1.93%.

Spectroscopic data: ^{1}H-NMR (C_6D_6, 25°C): $\delta =$ 10.38 (s broad, 1H; N*H*), 8.7–6.8 (m, 24H, aromatic protons), 4.83 (d, $J(H,H) = 15.2$ Hz, 1H; CH_2C=), 4.37 (s, 5H, C_5H_5), 4.01 (dd, $J(H,H) = 14.5$ Hz, $J(H,H) =$ 6.1 Hz, 1H; CH_2NH), 3.89 (d, $J(H,H) = 15.2$ Hz, 1H; CH_2C=), 3.30 (dt, $J(H,H) = 15.0$ Hz, $J(H,H) = 3.0$ Hz, 1H; CH_2NH), 1.85 (s, 3H; CH_3). $^{13}C\{^1H\}$-NMR (C_6D_6, 25°C): $\delta = 255.0$ (d, $J(C,P) = 16.3$ Hz; Ru=*C*); 142.3–125.6 (aromatic carbons), 81.6 (d, $J(C,P) = 2.0$ Hz; C_5H_5), 51.2 (s; NCH_2), 32.2 (s; CH_2Ph), 23.6 (d, $J(C,P) = 5$ Hz; CH_3). $^{31}P\{^1H\}$-NMR (C_6D_6, 25°C): $\delta = 54.1$.

4.7. X-ray structure determination for the complex 1·C_2H_6O

Crystal data and details of the structure determination are presented in Table 1. Suitable single crystals for the X-ray diffraction study were grown by cooling a concentrated solution of **1** in dichloromethane–ethanol. A clear red–brown fragment ($0.34 \times 0.42 \times 0.57$ mm) was stored under perfluorinated ether, transferred in a Lindemann capillary, fixed and sealed. Preliminary examination and data collection were carried out on an imaging plate diffraction system (Ipds; Stoe&Chi) equipped with a rotating anode (Nonius; Fr951) and graphite monochromated Mo–K_α radiation ($\lambda =$ 0.71073 Å). The unit cell parameters were obtained by full-matrix least-squares refinement of 4705 reflections. Data collection were performed at 293 K (θ range $2.26° < \theta < 25.67°$; exposure time 300 s per image; oscillation scan modus $\varphi = 0°$ to 360° with $\Delta\varphi = 1.0°$). A total number of 52576 reflections were collected. Raw data were corrected for Lorentz, polarization, decay and absorption effects. After merging ($R_{int} = 0.042$) a sum of 6847 independent reflections remained and were used for all calculations. The structure was solved by a combination of direct methods and difference Fourier syntheses. All non-hydrogen atoms of the compound **1**·C_2H_6O were refined anisotropically. All hydrogen atoms were calculated in ideal positions (riding model). Full-matrix least-squares refinements with 469 parameters were carried out by minimizing $\Sigma w(F_o^2 - F_c^2)^2$ with the SHELXL-97 weighting scheme and stopped at shift/err < 0.001. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from International Tables for Crystallography. All calculations were performed on a DEC 3000 AXP workstation and an Intel Pentium II PC, with the STRUX-V system, including the programs PLATON, SIR92, and SHELXL-97 [30].

5. Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this paper have been

deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC no. 149912 (**1**). Copies of the data can be obtained, free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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