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Buta-1,2,3-trienylidene, acylvinylidene and acylalkynyl ruthenium complexes via activation of alkynes with $RuCl_2(dppe)_2$. X-ray structure of *trans*-$[Ru(=C=CHCOCH_2Ph)(Cl)(dppe)_2]O_3SCF_3$[1]

Pierre Haquette [a], Daniel Touchard [a], Loïc Toupet [b], Pierre Dixneuf [a,*]

[a] *UMR 6509 CNRS-Université de Rennes, Laboratoire de Chimie de Coordination et Catalyse, 35042 Rennes, France*
[b] *Groupe Matière Condensée et Matériaux, UMR 6626, Campus de Beaulieu, Université de Rennes, 35042 Rennes, France*

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Abstract

The activation of several functional alkynes HC≡C–C≡C–Ph (**a**), HC≡CCOCHPh$_2$ (**b**) and HC≡C–CHOH–CHPh$_2$ (**c**) with the precursor $[RuCl(dppe)_2]PF_6$ [$RuCl(dppe)_2$ = {Ru}], in situ generated from $RuCl_2(dppe)_2/NaPF_6$, has been performed. It selectively produces the buta-1,2,3-trienylidene $\{Ru\}=C=C=C=CHR]^+PF_6^-$ intermediates (**I**) from **a**, and acylvinylidene complexes $\{Ru\}=C=CH-COR]^+PF_6^-$ [R = CH_2Ph **(3)** and R = $CHPh_2$ **(5)**] from **a** and **b** and $\{Ru\}=C=CH-CH=CPh_2]^+PF_6^-$ **(10)** from **c**. The deprotonation of **3**, **5** and **10**, respectively, affords acylalkynyl derivatives {Ru}–C≡C–CO–R] **4**, **6** and {Ru}–C≡C–CH=CPh$_2$] **11**. The X-ray diffraction study of *trans*-$[(Cl)(dppe)_2Ru=C=CHCOCH_2Ph]O_3SCF_3$ **3**, obtained by reaction of {Ru}–C≡C–C≡CPh] with CF_3SO_3H and water, has been carried out. Crystal data are: *a* 13.362(4), *b* 23.669(4), *c* 42.218(6) Å, orthorhombic space group *Pbca*, *Z* = 8. The structure shows Ru–C(1) (1.77(1) Å) and C(1)–C(2) (1.36(2) Å) bond distances.

Keywords: Butatrienylidene; Acylvinylidene; Alkenylvinylidene; Acylacetylide; Ruthenium complexes

1. Introduction

Among the cumulenylidene–metal complexes of general formula $LnM=(C=)_nCR_2$ only the chemistry of the first members $n = 1$ and 2 is well documented. Since the discovery of the first vinylidene metal complex $LnM=C=CR_2$ in 1972 [1] several routes leading to their formation have been discovered [2,3], including the direct tautomerisation of $M(\eta^2\text{-}HC\equiv CR)$ into $M(\eta^1\text{-}C=CHR)$, observed during the activation of terminal alkynes. Such vinylidene intermediates are now well recognized as key active species in catalytic selective transformations of alkynes, mostly promoted by ruthenium catalysts [4–6]. The next members, the allenylidenes $LnM=C=C=CR_2$, first prepared in 1976 [7] are resulting from a powerful method of preparation since the Selegue's discovery of the activation of a prop-2-yn-1-ol by $RuCl(PMe_3)_2(C_5H_5)$, directly leading to the stable $[(C_5H_5)(PMe_3)_2Ru=C=C=CPh_2]PF_6$ complex [8]. This strategy has been extensively used for the straightforward production of allenylidenes [9–17]. The latter just begin to be used in organic synthesis [18,19].

Following some efforts to generate penta-1,2,3,4-tetraenylidene intermediates by activation of diynes with a leaving group linked to carbon C(5) [17,20], the first C_5 cumulene $[Cl(dppe)_2Ru=C=C=C=C=CPh_2]PF_6$ (dppe, $Ph_2PCH_2CH_2PPh_2$) was isolated in 1994 [21]. Since then four additional $LnM=(C=)_4CR_2$ derivatives of iridium [22], chromium and tungsten [23] have been characterized.

* Corresponding author.

[1] Dedicated to Professor Michael I. Bruce on the occasion of his 60th birthday and in recognition of his contribution to vinylidene and metallacumulene chemistry.

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By contrast no buta-1,2,3-trienylidene–metal complexes [LnM=C=C=C=CR_2] have been isolated till now. However, some pioneering works by Selegue et al. [24] and Bruce et al. [25] have shown that such intermediates can be generated by elimination of a leaving group at carbon C(3), of an alkenynyl complex LnRu–C≡C–C(O_2CCF_3)=CR_2 [24], by protonation of a diynyl–metal derivative or by direct activation of butadiyne [25,26].

The scarcity of such M=(C=)$_3CR_2$ intermediates motivates the study of the activation of functional C_4 alkynes or diynes by metal complexes. This article reports our effort results in this direction. We can now show that (i) the activation of HC≡C–C≡C–Ph**(a)** with $RuCl_2(dppe)_2$ leads either to a diynylruthenium derivative, a powerful acylvinylidene precursor, or to a methoxyallenylidene, both of them arising from the [Cl(dppe)$_2$Ru=C=C=C=CHPh]$^+$ intermediate, (ii) the activation of HC≡C–$COCHPh_2$ **(b)** produces an acylvinylidene derivative whereas that of HC≡C–CHO-$HCHPh_2$ **(c)** affords a new alkenyl vinylidene ruthenium compound and (iii) all these complexes can be deprotonated to afford C_4 functional alkynyl ruthenium derivatives.

2. Results and discussion

Under the conditions allowing the direct access to alkynyl metal complexes from terminal alkynes [27], the activation of PhC≡C–C≡CH with $RuCl_2(dppe)_2$ **1** in THF, but in the presence of an excess of $NaPF_6$ and triethylamine at room temperature (r.t.), led to the formation of the yellow butadiynyl–ruthenium complex **2** isolated in 56% yield. The presence of $NaPF_6$ allows the in situ formation of the 16-electron intermediate [RuCl(dppe)$_2$]PF_6 which is able to activate the alkyne and favour its deprotonation on treatment with NEt_3 [27,28]. As an attempt to produce a vinylidene via protonation at C(2) or the buta-1,2,3-trienylidene complex (**I**) via protonation at C(4), the compound **2** in dichloromethane was reacted with the strong acid CF_3SO_3H. Immediately a bright red colour appeared which turned to green within a few seconds. The green ketonic vinylidene derivative **3** was obtained (82%) [29] (Scheme 1). The structure of **3** was determined by X-ray diffraction study (Fig. 1). The complex **3** shows an IR absorption at ν(CO) = 1525 cm^{-1}. In ^{1}H-NMR the vinylidene proton appears as a quintet (δ = 4.45 ppm, $^4J_{PH}$ = 2 Hz) and in ^{13}C-NMR the low field quintet at δ = 334.5 ppm ($^2J_{PC}$ = 13 Hz) is typical of a Ru=C carbon nucleus resonance for vinylidene–ruthenium(II) complexes [30,31].

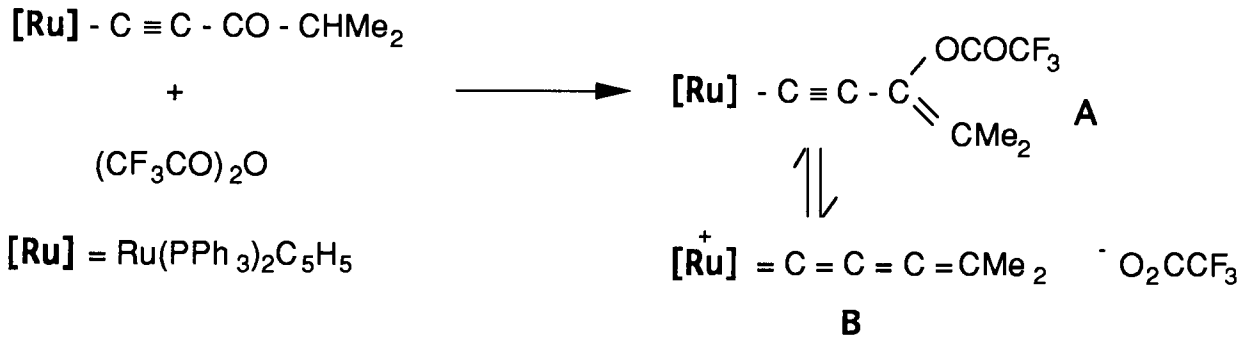
The formation of **3** can be explained via the initial formation of the cumulene intermediate (**I**), which might be responsible for the bright red colour, followed by addition of the hydroxy group of water at carbon C(3), and protonation at carbon C(2) to give the green complex **3**. The formation of an alkynylvinylidene intermediate LnRu=C=CH–C≡C–Ph (**II**) followed by the addition of water at the (C≡C) carbon C(3) is not likely. Indeed the C≡C bond of analogous to (**II**) compounds is not expected to be electrophilic enough to add water [32] and the metallacumulene [LnRu=C=C=C=C=CR_2] contains an especially electrophilic carbon C(3) very reactive toward traces of water [33], alcohol [17] or amine [21,34] to generate metallacycles or 3-alkenylallenylidene derivatives.

Bruce et al. [35] attempted to protonate the complex $C_5H_5(PPh_3)_2$Ru–C≡C–C≡CH and obtained $C_5H_5(PPh_3)_2$Ru–C≡C–CO–CH_3 analogous to **3**. This reaction is also consistent with the addition of water at the carbon C(3) of the suggested [Ru=(C=)$_3CH_2$]$^+$ intermediate. Recent results obtained by Bruce et al. are consistent with the addition of amine and *N*-methylpyrrole [26] or imine [36] at the carbon C(3) of a [Ru=(C=)$_3CH_2$]$^+$ moiety, directly generated by activation of HC≡C–C≡C–H. Winter et al. has also just shown an example of addition of a functional amine to the expected [X(dppm)$_2$Ru=(C=)$_3CH_2$]$^+$]PF_6^- intermediate [37].

The deprotonation of **3** is very easily achieved by treatment with DBU in dichloromethane and the acylethynyl complex **4** is isolated in 91% yield. It shows a typical ν(C≡) = 2030 cm^{-1} IR absorption and in the ^{13}C-NMR spectrum the Ru–C≡ carbon nucleus resonance appears as a quintet at high field δ = 154.22 ppm ($^2J_{PC}$ = 14 Hz).

Another acylvinylidene ruthenium(II) derivative **5**, analogous to **3**, was obtained by direct activation of HC≡C–$COCHPh_2$. The latter was produced by addition of lithium acetylide to the aldehyde Ph_2CH–CHO, followed by oxidation of the alcohol with CrO_3 in acidic medium [39,40]. The activation of the alkyne HC≡C–$COCHPh_2$ with the $RuCl_2(dppe)_2/NaPF_6$ system afforded 81% of the vinylidene complex **5** which showed spectroscopic data closely related to that of **3** [δ = 3.68 ppm, quintet, Ru=C=C*H*, $^4J_{PH}$ = 2 Hz]. Complex **5** on deprotonation with DBU afforded the acylethynyl–ruthenium complex **6** in 78% yield. The compound **6** ressembles that obtained by Bruce et al. $(C_5H_5)(Ph_3P)_2$Ru–C≡C–$COCH_3$ on reaction of Ru-Cl$(PPh_3)_2C_5H_5$ with the 3-butyn-2-one in the presence of NH_4PF_6 followed by the treatment with MeONa [38].

The complex **6** offered the possibility to be deprotonated at the C(4) carbon atom, and then O-acylated, in an attempt to generate a C_4 cumulene of type Ru=(C=)$_3CR_2$. Indeed, Selegue et al. [24] have shown for the first time, that the 3-trifluoroacetato alkynyl derivative **A**, generated by acylation of the complex [Ru–C≡C–CO–$CHMe_2$] was in equilibrium with the C_4 cumulene **B** (Eq. 1).



The O-acylation of complex **6** was attempted by reaction with an excess of trifluoracetic anhydride, but failed. The deprotonation of **6** with LDA followed by the addition of $ClSiMe_3$ led to the C-silylation product but not to the expected O-silylated derivative $Cl(dppe)_2Ru–C\equiv C–C(OSiMe_3)=CPh_2$ which should have given a $[Ru^+=C=C=C=CPh_2$ intermediate on displacement of the leaving group Me_3SiO^-. Complex **7** obtained instead is not stable and in the presence of air or moisture it readily gives back complex **6**.

In order to ascertain the direct activation of Ph–C≡C–C≡CH (**a**) by **1** into the buta-1,2,3-trienylidene ruthenium intermediate (**I**) the activation of (**a**) was performed in the presence of methanol and the red 3-methoxy allenylidene derivative **8** was obtained in 77% yield (Scheme 2). The complex **8** characterization suggests the initial formation of the C_4 cumulene intermediate (**Ia**) followed by addition of methanol to the electrophilic carbon C(3). The deprotonation of **8** is easily performed by triethylamine and the yellow enynyl metal complex **9** was isolated in 97% yield.

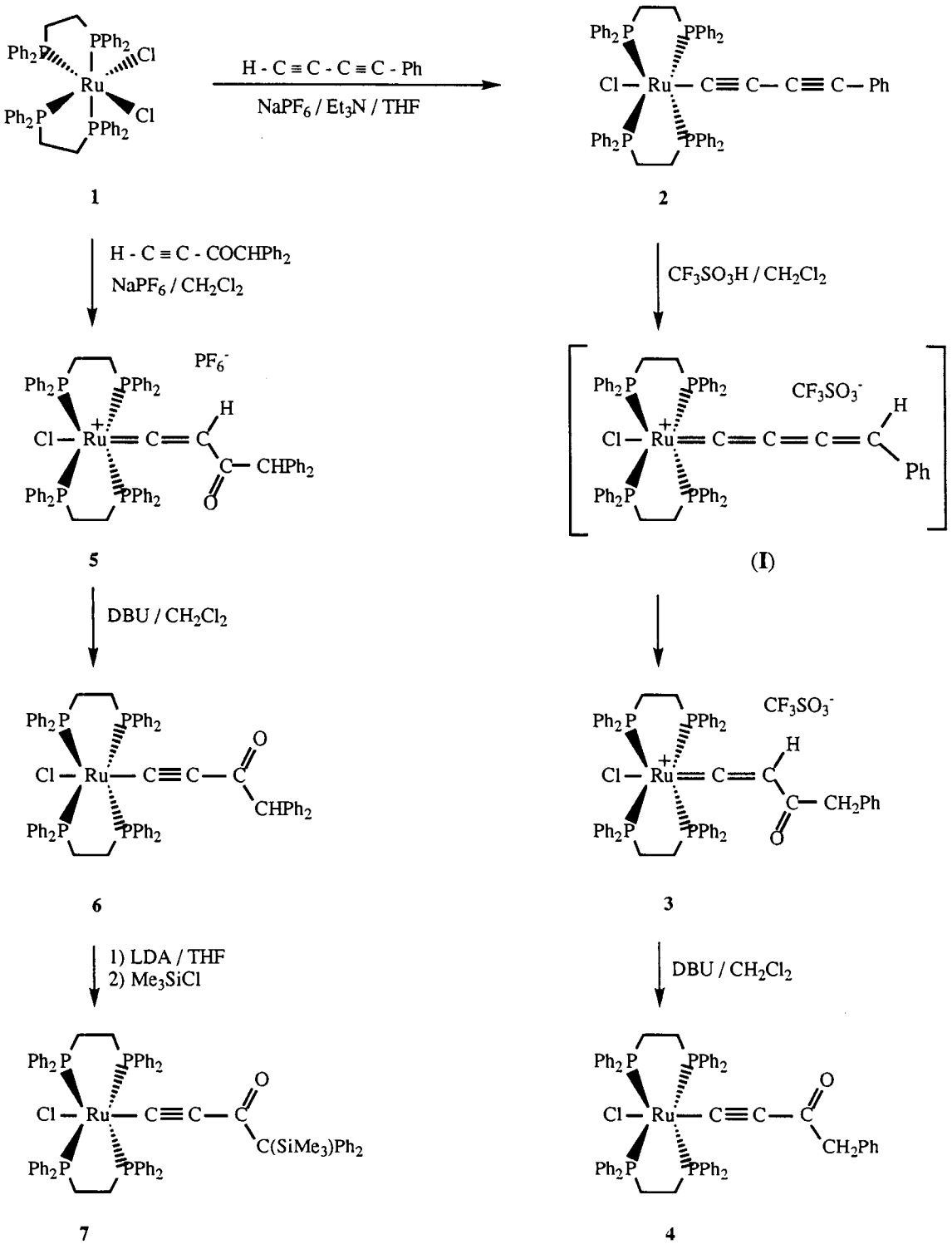
The activation of secondary propargylic alcohols HC≡C–CHOHR by $RuCl_2(dppe)_2$ **1** was found to be a unique route for the access to stable secondary allenylidene ruthenium complexes $[Cl(dppe)_2Ru=C=C=CHR]PF_6$ [29,41]. This route actually demonstrated that, with a relatively electron-releasing $Cl(dppe)_2Ru^+$ moiety, it was not necessary to stabilize the allenylidene–metal linkage by the introduction of a donating heteroatom group at C(3). Thus the activation of HC≡C–CHOH–$CHPh_2$ with complex **1** was performed under the usual conditions and the red 2-alkenyl vinylidene complex **10** (73%) was obtained instead of the 3-monosubstituted allenylidene derivative [16] (Scheme 2). This demonstrates the higher stability of an alkenylvinylidene with respect to a monosubstituted allenylidene $[Ru=C=C=CH–CHPh_2]^+$ with a mobile proton at C(4).

The complex **10** is characterized by NMR, with a double quintet resonance for the vinylidene proton [$\delta = 5.08$ ppm, Ru=C=*CH*–, $^4J_{PH} = 3$ Hz, $^3J_{HH} = 10$ Hz] and with a low field quintet for the Ru=C carbon nucleus [$\delta = 361.5$ ppm, $^2J_{PC} = 13$ Hz]. The deprotonation of the vinylidene **10** is readily performed with DBU and takes place at C(2) affording 73% of the yellow 2-alkenyl alkynyl ruthenium complex **11**, closely related to derivative **9** (Scheme 2).

It is noteworthy that the 2-alkenylalkynyl complexes **9** and **11** correspond to the hypothetical addition product, respectively of a methoxide and a hydride, at the electrophilic carbon C(3) of the searched C_4 cumulene intermediates Ru=(C=)$_3$C(X)Ph (X = H, Ph).

3. X-ray diffraction study of 3

The molecular structure of complex **3** is shown in Fig. 1. Experimental crystallographic data are given in Tables 1 and 2 and selected bond lengths and angles are contained in Table 3. The structure shows an octahedral coordination of the ruthenium atom, with the apical positions occupied by the chloride and the vinylidene ligands. The Cl–Ru–C–C linkage is orthogonal to the plane of the four phosphorous atoms and almost linear: Cl–Ru–C(1), 174.9(4) and Ru–C(1)–C(2), 177.6(4)°. The Ru–C(1) bond distance (1.77(1) Å) is shorter and the C(1)–C(2) bond distance (1.36(2) Å) is longer than in vinylidene complexes containing an alkyl or aryl group at carbon C(2): 1.882(1) and 1.22(1) Å in *trans*-$[(dppm)_2(Cl)Ru(=C=CH_2)]$ [33]; 1.86(1) and 1.29(2) Å in $[Ru(Cp)(PPh_3)_2(=C=CMePh)]$ [42]; 1.97(9) and 1.30(1)Å in $[Ru(\eta^5\text{-}C_9H_7)(PPh_3)_2(=C=CMe_2)]$ [43]. These bond lengths of **3** are comparable to that of vinylidenes substituted with a withdrawing group $[Ru(C_5Me_5)(Cl)(^iPr_2PCH_2CO_2Me)(=C=CH\ CO_2Me)]$ [44] and $[Ru(Cp)(PPh_3)_2(=C=C[C(OCOCF_3)=CMe_2](COCF_3)]$ [24] in which the Ru–C(1) and C(1)–C(2) bond lengths are: 1.783(3); 1.322(5) and 1.812(9); 1.35(1) Å, respectively. This is likely due to the strong electron withdrawing effect of the COR group. Indeed a vinylidene ligand is known to have stronger electron withdrawing capability than an η^2-alkyne ligand [45]. Thus LnM=C=CHR complexes are stable only when the LnM moiety is able to compensate the electron demand of the vinylidene ligand. In the case of **3** the electron transfer from the $Cl(dppe)_2Ru$ moiety is important and thus the Ru–C bond has a double bond character.



Scheme 1. Reaction of complex **2** in CH_2Cl_2 with the strong acid CF_3SO_3H producing the ketonic vinylidene derivative complex **3**.

4. Conclusion

The above results show that $[M{=}C{=}C{=}C{=}CHR]^+$ intermediates can be produced either via protonation of a diynyl metal complex or direct activation of a diyne $HC{\equiv}C{-}C{\equiv}C{-}R$ with a 16-electron metal species. These intermediates are very reactive and this study of their reactivity suggests that they behave as a $[M{=}C{=}C{-}C^+{=}CHR]$ cation. Indeed, addition of nucleophiles or water always takes place at the electrophilic C(3) carbon. Actually the direct activation of a 1,3-diyne by a metal complex, if it does not afford stable buta-1,2,3-trienyli-

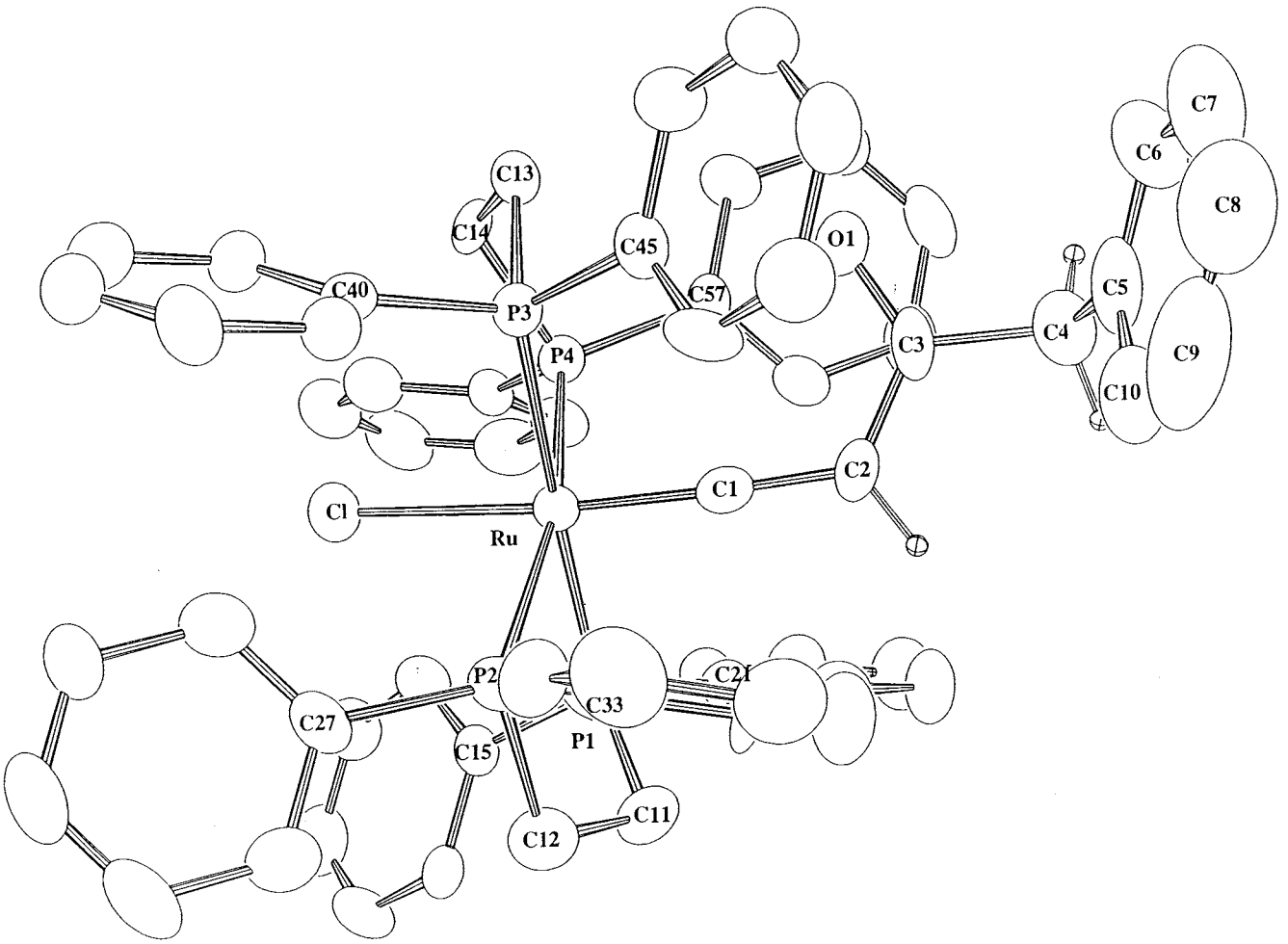


Fig. 1. ORTEP drawing of the cation [*trans*-(dppe)$_2$(Cl)Ru(=C=CHC(O)CH$_2$Ph)]. Hydrogen atoms are omitted for clarity.

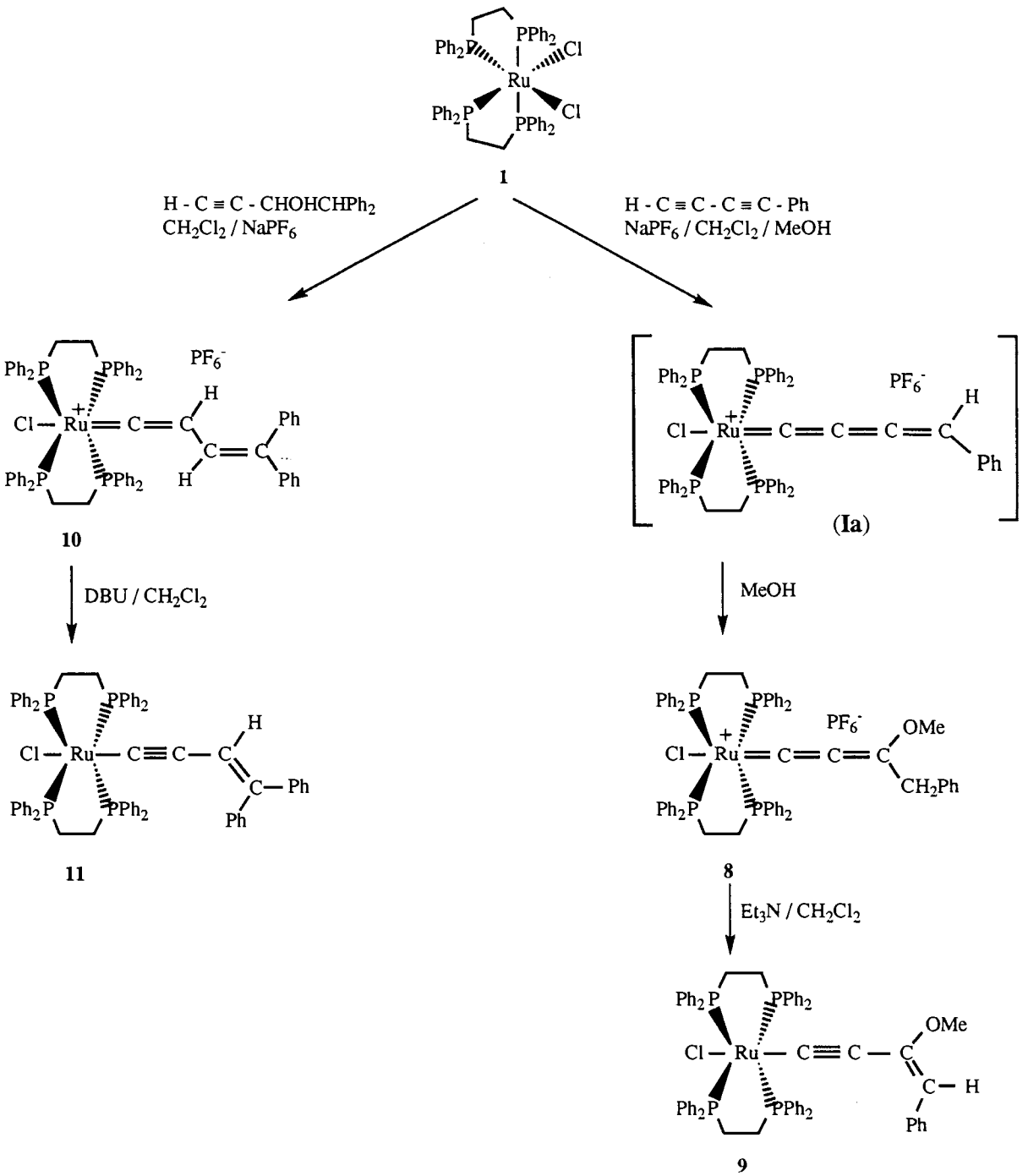
dene complexes, is a process allowing the direct access to either 3-substituted allenylidene or acylvinylidene derivatives.

5. Experimental section

All synthetic operations were performed under a dry dinitrogen or argon atmosphere following conventional Schlenk techniques. Dichloromethane, THF, hexane and diethylether were distilled from the appropriate drying agents. IR spectra were recorded on a Nicolet 205 FT-IR spectrometer. ^{1}H- (300.13 MHz), ^{31}P- (121.50 MHz) and ^{13}C- (75.47 MHz)NMR spectra were recorded on a Bruker AC 300 P spectrometer at 297 K and referenced to TMS for ^{1}H and ^{13}C and to 85% H_3PO_4 for ^{31}P. Elemental analysis were performed by the 'Service Central d'Analyses du CNRS' at Vernaison, France. The complex *cis*-RuCl$_2$(dppe)$_2$ [46] and the alkynes H–C≡C–C≡C–Ph, H–C≡C–CHOH–CHPh$_2$ and H–C≡C–C(O)–CHPh$_2$ [39,40] were prepared by literature methods.

5.1. Preparation of [trans-(dppe)$_2$(Cl)Ru(C≡C–C≡C–Ph)] **2**

A solution of phenylbuta-diyne (0.126 g, 1 mmol), triethylanmine (280 μl, 2 mmol) in 60 ml of THF was added to (0.484 g, 0.5 mmol) of *cis*-RuCl$_2$(dppe)$_2$ **1** and (0.168 g, 1 mmol) of $NaPF_6$. After 16 h of stirring at r.t., the solution was filtered through a filter-paper-tipped cannula and the solvent removed under vacuum. The residue was purified by filtration through a column of neutral alumina using diethylether as eluent. After crystallization in a mixture (CH_2Cl_2–hexane) yellow crystals of **2** (0.295 g, 56%) were obtained. Anal. Calc. for $C_{62}H_{53}ClP_4Ru$: C, 70.35; H, 5.05%. Found C, 70.03; H, 4.98%. IR (KBr): ν(C≡C) 2154, 2018 cm^{-1}. NMR ($CDCl_3$): ^{1}H 7.33–6.42 (m, 45H, Ph); 2.69 (m, 8H, PCH$_2$CH$_2$P). ^{31}P{^{1}H} 48.81 (s, PPh$_2$). ^{13}C{^{1}H} 133.55–125.83 (Ph); 131.67 (quint, Ru–*C*≡, $^2J_{PC}$ = 15 Hz); 95.53 (s, Ru–C≡C–C≡*C*); 81.22 (quint, Ru–C≡*C*, $^3J_{PC}$ = 2Hz); 62.73 (quint, Ru–C≡C–*C*≡, $^4J_{PC}$ = 1 Hz); 30.69 (quint, PCH$_2$CH$_2$ P, $|^1J_{PC} + {}^3J_{PC}|$ = 24 Hz).



Scheme 2. Production of the 3-methoxy allenylidene derivative **8**, the 2-alkenyl vinylidene complex **10** and the 2-alkenyl alkynyl ruthenium complex **11**, which is closely related to derivative **9**.

*5.2. Preparation of [trans-(dppe)$_2$(Cl)Ru(=C=CHC(O)CH$_2$Ph)][CF$_3$SO$_3$] **3***

To 0.53 g (0.5 mmol) of **2** in solution in 50 ml of dichloromethane, 0.5 mmol of trifluorosulfonic acid was added. Immediately the coloration of the solution turn red and then rapidly green. After 30 min of stirring, the solvent was removed and the residue washed with diethylether and dried. After dissolution in a minimum amount of dichloromethane and slow addition of hexane, in order to form a biphasic system, 0.505 g (82%) of green crystals of **3** were obtained. Anal. Calc. for $C_{63}H_{56}Cl\ F_3O_4P_4SRu$: C, 61.69; H, 4.57%. Found C, 62.02; H, 4.48%. IR (KBr): ν(C=C) 1658, ν(C=O) 1525 cm^{-1}. NMR (CD_2Cl_2): ^{1}H 8.26–6.96 (m, 45H, Ph); 4.45 (quint, 1H, =C*H*, $^4J_{PH} = 2$ Hz);

3.54 (s, 2 H, C(O)CH_2); 2.90 (m, 8H, PCH_2CH_2P). $^{31}P\{^1H\}$ 40.23 (s, PPh_2). $^{13}C\{^1H\}$ 334.5 (quint, Ru=*C*, $^2J_{PC} = 13$ Hz); 197.3 (s, CO); 120.2 (q, CF_3, $^1J_{CF} = 319$ Hz); 110.8 (s, Ru=C=*C*); 47.8 (s,*C*H_2Ph); 29.1 (quint, PCH_2CH_2P, $|^1J_{PC} + {}^3J_{PC}| = 22$ Hz).

5.3. Preparation of [trans-(dppe)$_2$(Cl)Ru(C≡C≡C(O)CH$_2$Ph)] **4**

To 0.37 g of **3** (0.5 mmol) in 40 ml of dichloromethane, four equivalents of DBU (1-8-diazabicyclo-[5,4,0]-undec-7-ene) were added. The solution was stirred for 1 h at r.t. and then the solvent was evaporated. The residue was filtered through an alumina column with ether as eluent. After crystallization in a mixture (CH_2Cl_2–hexane), 0.295 g of yellow crystals of **4** were obtained (91%). Anal. Calc. for $C_{62}H_{55}ClOP_4Ru$: C, 69.17; H, 5.15%. Found C, 68.94; H, 5.17%. IR (KBr): ν(C≡C) 2031 cm^{-1}. NMR ($CDCl_3$): ^1H 7.40–6.83 (m, 45H, Ph); 3.00 (s, 2 H, CH_2Ph); 2.57 (m, 8H, PCH_2CH_2P). $^{31}P\{^1H\}$ 49.53 (s, PPh_2). $^{13}C\{^1H\}$ 179.34 (s, Ru–C≡C–*C*(O)); 154.22 (quint, Ru=*C*, $^2J_{PC} = 14$ Hz); 136.22–126.14 (m, Ph); 121.31 (s, Ru–C≡*C*); 50.25 (s, *C*H_2Ph); 30.51 (quint, PCH_2CH_2P, $|^1J_{PC} + {}^3J_{PC}| = 23$ Hz).

Table 1
Summary of data for the crystal structure analysis of 3

Formula	$RuP_4ClOC_{62}H_{56}\cdot SO_3CF_3$
Molecular weight	1210.63
Crystal system	Orthorhombic
Space group	*Pbca*
a	12.362(4)
b	23.669(4)
c	42.218(6)
V	12353(5)
Z	8
$D_{calc.}$ (g cm^{-3})	1.302
F(000)	4976
μ(Mo–K_α) (cm^{-1})	4.76
T (K)	294
Crystal size (mm)	$0.40 \times 0.45 \times 0.45$
Radiation	Mo–Kα
Max 2θ (°)	50
Scan	$\omega/2\theta = 1$
t_{max} (for one measure) (s)	60
Variance of standards (%)	1.2
Index ranges (*hkl*)	0.14, 0.28, 0.50
Reflections measured	11 854
Reflections observed ($I > \sigma(I)$)	4845 (4σ)
$R_{(isotropic)}$	0.125
$R_{(anisotropic)}$	0.090
N(obs)/*N*(var)	4845/668
Final *R*	0.073
Rw	0.062
Sw	5.27
Max/min residual e $Å^{-3}$ (Δ/σ)	0.32, 0.06

Table 2
Position parameters and their estimated standard deviations for **3**

Atom	*x*	*y*	*z*	*B*(A2)
Ru	0.73888(7)	0.16121(4)	0.85220(2)	2.02(1)
Cl1	0.7767(2)	0.1576(1)	0.79585(6)	2.97(6)
S1	0.3144(4)	0.1294(2)	0.3331(1)	3.2(1)*
S2	0.350	0.117	0.494	2.3*
P1	0.9324(2)	0.1637(1)	0.86438(7)	2.46(6)
P2	0.7725(3)	0.0583(1)	0.85277(8)	2.65(6)
P3	0.5438(2)	0.1591(1)	0.84149(7)	2.31(6)
P4	0.7176(2)	0.2610(1)	0.83977(7)	2.28(6)
F1	0.202(1)	0.0499(8)	0.3594(4)	8.7(4)*
F2	0.373(1)	0.0409(7)	0.3667(4)	8.1(4)*
F3	0.301(1)	0.0224(8)	0.3232(5)	9.5(5)*
F4	0.224	0.044	0.480	7.7*
F5	0.372	0.020	0.485	10.7*
F6	0.383	0.046	0.448	11.0*
O1	0.5305(7)	0.2374(4)	0.9103(2)	3.2(2)
O2	0.416(1)	0.1298(7)	0.3169(4)	5.1(3)*
O3	0.318(1)	0.1605(7)	0.3613(4)	5.8(4)*
O4	0.231(1)	0.1384(7)	0.3111(4)	6.2(4)*
O5	0.325	0.112	0.523	3.5*
O6	0.471	0.136	0.490	4.1*
O7	0.306	0.156	0.472	2.3*
O8	0.3774(9)	0.3002(5)	0.9186(3)	5.5(2)*
C1	0.7031(9)	0.1689(5)	0.8925(3)	2.4(2)
C2	0.672(1)	0.1763(5)	0.9232(3)	2.9(3)
C3	0.587(1)	0.2131(6)	0.9312(3)	3.2(3)
C4	0.562(1)	0.2215(6)	0.9659(3)	4.3(3)
C5	0.469(1)	0.1821(6)	0.9763(3)	4.5(3)
C6	0.363(1)	0.2001(7)	0.9781(4)	4.9(4)
C7	0.286(1)	0.1610(9)	0.9881(4)	6.9(5)
C8	0.308(2)	0.1081(8)	0.9952(4)	7.0(5)
C9	0.411(2)	0.0910(8)	0.9930(4)	8.6(6)
C10	0.496(1)	0.1258(6)	0.9838(4)	5.5(4)
C11	0.955(1)	0.0976(6)	0.8859(3)	3.4(3)
C12	0.913(1)	0.0482(6)	0.8661(3)	3.5(3)
C13	0.505(1)	0.2312(5)	0.8304(3)	2.7(3)
C14	0.597(1)	0.2638(5)	0.8148(3)	2.5(2)
C15	1.0330(9)	0.1641(5)	0.8325(3)	2.7(2)
C16	1.112(1)	0.1219(6)	0.8301(3)	3.3(3)
C17	1.191(1)	0.1263(7)	0.8074(3)	4.6(3)
C18	1.197(1)	0.1719(7)	0.7872(3)	5.0(4)
C19	1.118(1)	0.2116(7)	0.7897(3)	4.3(3)
C20	1.035(1)	0.2081(6)	0.8108(3)	3.2(3)
C21	0.9863(9)	0.2156(5)	0.8925(3)	2.6(3)
C22	1.050(1)	0.2606(6)	0.8834(3)	3.1(3)
C23	1.088(1)	0.2994(7)	0.9059(3)	4.6(3)
C24	1.063(1)	0.2928(7)	0.9362(4)	5.5(4)
C25	1.002(1)	0.2482(7)	0.9457(3)	5.1(4)
C26	0.963(1)	0.2098(6)	0.9238(3)	3.9(3)
C27	0.770(1)	0.0139(5)	0.8178(3)	2.7(2)
C28	0.831(1)	−0.0350(5)	0.8174(3)	4.0(3)
C29	0.830(1)	−0.0707(5)	0.7917(3)	4.5(3)
C30	0.766(1)	−0.0599(5)	0.7662(3)	4.0(3)
C31	0.705(1)	−0.0125(6)	0.7657(3)	3.6(3)
C32	0.707(1)	0.0253(6)	0.7916(3)	3.6(3)
C33	0.696(1)	0.0163(5)	0.8820(3)	3.2(3)
C34	0.623(1)	−0.0248(6)	0.8719(3)	3.6(3)
C35	0.561(1)	−0.0537(6)	0.8929(4)	4.6(3)
C36	0.574(1)	−0.0441(6)	0.9249(4)	4.6(4)
C37	0.647(1)	−0.0030(6)	0.9357(3)	4.8(4)
C38	0.707(1)	0.0257(5)	0.9139(3)	3.4(3)
C39	0.508(1)	0.1357(5)	0.7775(3)	3.0(3)
C40	0.4998(9)	0.1149(5)	0.8083(3)	2.6(2)

Table 2 (Continued)

Atom	x	y	z	B(A2)
C41	0.460(1)	0.0602(5)	0.8140(3)	2.8(3)
C42	0.431(1)	0.0269(5)	0.7888(3)	3.2(3)
C43	0.440(1)	0.0464(6)	0.7584(3)	3.8(3)
C44	0.478(1)	0.1008(5)	0.7522(3)	3.7(3)
C45	0.4446(9)	0.1400(5)	0.8721(3)	2.6(2)
C46	0.461(1)	0.0954(6)	0.8914(3)	3.7(3)
C47	0.381(1)	0.0773(6)	0.9114(3)	4.3(3)
C48	0.286(1)	0.1056(7)	0.9132(3)	4.4(3)
C49	0.269(1)	0.1510(7)	0.8944(3)	4.3(3)
C50	0.347(1)	0.1695(6)	0.8736(3)	3.6(3)
C51	0.817(1)	0.2990(5)	0.8155(3)	2.5(3)
C52	0.889(1)	0.3356(6)	0.8305(3)	3.5(3)
C53	0.966(1)	0.3632(7)	0.8123(4)	4.7(4)
C54	0.970(1)	0.3563(6)	0.7799(4)	4.8(4)
C55	0.897(1)	0.3221(6)	0.7652(3)	4.4(3)
C56	0.820(1)	0.2929(6)	0.7832(3)	3.7(3)
C57	0.693(1)	0.3083(5)	0.8727(3)	2.5(2)
C58	0.611(1)	0.3482(5)	0.8725(3)	3.1(3)
C59	0.594(1)	0.3821(6)	0.8985(3)	4.0(3)
C60	0.657(1)	0.3785(6)	0.9246(3)	4.4(3)
C61	0.742(1)	0.3401(6)	0.9249(3)	4.5(3)
C62	0.759(1)	0.3044(5)	0.8992(3)	3.2(3)
C63	0.297(2)	0.055(1)	0.3471(6)	5.7(6)*
C64	0.302	0.046	0.470	7.4*
H2	0.717(9)	0.160(5)	0.940(3)	5.0*
H4A	0.54(1)	0.264(5)	0.965(3)	5.0*
H4B	0.63(1)	0.206(5)	0.978(3)	5.0*
H6	0.344	0.239	0.971	5.0*
H7	0.210	0.175	0.990	5.0*
H8	0.251	0.082	1.002	5.0*
H9	0.428	0.051	0.998	5.0*
H10	0.572	0.112	0.982	5.0*
H11A	0.917	0.098	0.906	5.0*
H11B	1.031	0.093	0.890	5.0*
H12A	0.959	0.044	0.848	5.0*
H12B	0.918	0.013	0.878	5.0*
H13A	0.481	0.251	0.849	5.0*
H13B	0.445	0.229	0.816	5.0*
H14A	0.613	0.248	0.795	5.0*
H14B	0.577	0.303	0.812	5.0*
H16	1.110	0.090	0.845	5.0*
H17	1.246	0.096	0.806	5.0*
H18	1.255	0.177	0.772	5.0*
H19	1.120	0.244	0.776	5.0*
H20	0.978	0.236	0.811	5.0*
H22	1.068	0.266	0.861	5.0*
H23	1.135	0.330	0.900	5.0*
H24	1.089	0.320	0.952	5.0*
H25	0.985	0.244	0.968	5.0*
H26	0.918	0.177	0.931	5.0*
H28	0.875	−0.045	0.836	5.0*
H29	0.876	−0.104	0.791	5.0*
H30	0.763	−0.086	0.748	5.0*
H31	0.660	−0.004	0.747	5.0*
H32	0.664	0.060	0.791	5.0*
H34	0.616	−0.032	0.849	5.0*
H35	0.509	−0.081	0.885	5.0*
H36	0.532	−0.065	0.940	5.0*
H37	0.654	0.005	0.958	5.0*
H38	0.759	0.054	0.921	5.0*
H40	0.523	0.138	0.826	5.0*
H41	0.451	0.047	0.836	5.0*
H42	0.404	−0.011	0.793	5.0*

5.4. Preparation of [trans-(dppe)$_2$(Cl)Ru(=C=CHC(O)CHPh$_2$)][PF$_6$] **5**

To 0.485 g of **1** (0.5 mmol) and 0.168 g of $NaPF_6$ (1 mmol), a solution of 0.22 g of the alkyne H–C≡C–C(O)$CHPh_2$ in 50 ml of dichloromethane was added. After 4 h of stirring at r.t., the solution was filtered and the solvent pumped off. The crude product was washed with ether and dried. After dissolution in a minimum amount of dichloromethane and slow addition of hexane, in order to form a biphasic system, 0.525 g of red crystals (81%) of **5** were obtained. Anal. Calc. for $C_{68}H_{60}ClF_6OP_5Ru$: C, 62.89; H, 4.66%. Found C, 63.09; H, 4.82%. IR (KBr): ν(C=C) 1657, ν(C=O) 1540 cm^{-1}. NMR ($CDCl_3$): ^1H 7.36–6.98 (m, 50H, Ph); 4,05 (s, 1H, C*H*Ph_2); 3.68 (quint, 1H, =C*H*, $^4J_{PH} = 2$ Hz); 2.87 (m, 8H, PCH_2CH_2P). $^{31}P\{^1H\}$ 41.84 (s, PPh_2).

5.5. Preparation of [trans-(dppe)$_2$(Cl)Ru(C≡C–C(O)CHPh$_2$)] **6**

To 0.52 g (0.4 mmol) of **5** in 50 ml of dichloromethane, four equivalents of DBU were added. The mixture was stirred during 1 h at r.t. After evaporation of the solvent, the residue was filtered through an alumina column. After recrystallization in a mixture CH_2Cl_2–hexane 0.36 g of yellow crystals of **6** (78%) were obtained. Anal. Calc. for $C_{68}H_{59}ClOP_4Ru \cdot CH_2Cl_2$: C, 66.97; H, 4.97%. Found C, 66.58; H, 4.96%. IR (KBr): ν(C≡C) 2011 cm^{-1}. NMR ($CDCl_3$): ^1H 7.62–6.91 (m, 50H, Ph); 4.57 (s,1H, C*H*Ph_2); 2.62 (m, 4H, PCH_2CH_2P); 2.41 (m, 4H, PCH_2CH_2P). $^{31}P\{^1H\}$ 50.63 (s, PPh_2). $^{13}C\{^1H\}$ 178.22 (s, CO); 154.88 (quint, Ru–*C*, $^2J_{PC} = 15$ Hz); 140.90–126.69 (m, Ph); 123.47 (s, Ru–C≡*C*); 63.88 (s, *C*HPh_2); 30.78 (quint, PCH_2CH_2P, $|^1J_{PC} + {}^3J_{PC}| = 23$ Hz).

5.6. Preparation of [trans-(dppe)$_2$(Cl)Ru(C≡C–C(O)–CPh$_2$Si Me$_3$)] **7**

To 0.29 g (0.25 mmol) of **6** in solution in THF, 0.67 ml of lithiumdiisopropylamide (1.5 M solution in THF) (1 mmol) was added at −40°C. After 1 h of stirring at r.t. 0.13 ml of chlorotrimethylsilane (1 mmol) was added. After 1 h of contact, the solvent was evaporated and the residue washed with hexane. A yield of 0.12 g of complex **7** was obtained (40%). IR (KBr): ν(C≡C) 2011 cm^{-1}. NMR ($CDCl_3$): ^1H 7.90–6.70 (m, 50H, Ph); 2.53 (m, 4H, PCH_2CH_2P); 2.09 (m, 4H, PCH_2CH_2P); −0.19 (s, 9H, $SiMe_3$). $^{31}P\{^1H\}$ 49.77 (s, PPh_2). $^{13}C\{^1H\}$ 179.2 (s, CO), 154.9 (quint, Ru–*C*, $^2J_{PC} = 14.6$ Hz), 140.4 (m, Ph) 126.3 (m, Ph), 123.6 (s, Ru–C≡*C*), 63.8 (s, *C*Ph_2 $SiMe_3$), 30.6 (quint, PCH_2CH_2P, $|^1J_{PC} + {}^3J_{PC}| = 22$ Hz), 2.0 (s, Si(*C*H_3)$_3$).

Table 2 (Continued)

Atom	x	y	z	B(A2)
H43	0.420	0.021	0.741	5.0*
H44	0.484	0.115	0.730	5.0*
H46	0.531	0.077	0.891	5.0*
H47	0.392	0.043	0.924	5.0*
H48	0.229	0.093	0.928	5.0*
H49	0.201	0.172	0.896	5.0*
H50	0.335	0.202	0.860	5.0*
H52	0.884	0.342	0.853	5.0*
H53	1.019	0.388	0.823	5.0*
H54	1.024	0.376	0.768	5.0*
H55	0.898	0.318	0.742	5.0*
H56	0.769	0.268	0.773	5.0*
H58	0.565	0.352	0.854	5.0*
H59	0.535	0.409	0.898	5.0*
H60	0.645	0.402	0.943	5.0*
H61	0.791	0.338	0.943	5.0*
H62	0.816	0.277	0.900	5.0*

5.7. Preparation of [trans-(dppe)$_2$(Cl)Ru(=C=C=(OMe)–CH_2Ph)][PF_6] **8**

In a Schlenk tube containing 0.968 g of **1** (1 mmol) and 0.336 g of $NaPF_6$ (2 mmol), 0.252 g of phenylbutadiyne (2 mmol) in solution in a mixture of 70 ml of dichloromethane and 15 ml of methanol was added. The solution was stirred for 16 h at r.t. and was then filtered and evaporated. The crude product was washed with diethylether and recrystallized by biphasic system (CH_2Cl_2–hexane). A total of 0.95 g of red crystals (77%) of **8** were obtained. Anal. Calc. for $C_{63}H_{58}ClF_6OP_5Ru$: C, 61.19; H, 4.73%. Found C, 60.92; H, 4.65%. IR (KBr): ν(C=C=C) 1932 cm^{-1}. NMR ($CDCl_3$): ^1H 7.37–6.95 (m, 45H, Ph); 3.25 (s, 2H, CH_2Ph); 3.00 (m, 4H, PCH_2CH_2P); 2.74 (s, 3H, OMe); 2.71 (m, 4H, PCH_2CH_2P). $^{31}P\{^1H\}$ 44.63 (s, PPh_2); − 143.64 (sept, PF_6, $^1J_{PF} = 713$ Hz). ^{13}C 259.01 (quint, Ru=*C*, $^2J_{PC} = 13$ Hz); 160,04 (quint, Ru=C=C=*C*, $^4J_{PC} = 1$ Hz); 145.35 (quint, Ru=C=*C*, $^3J_{PC} = 2$ Hz); 134.7–126.6 (m, Ph); 60.15 (q, OCH_3, $^1J_{CH} = 150$ Hz); 46.82 (t, *C*H_2Ph, $^1J_{CH} = 131$ Hz); 29.88 (t m, PCH_2CH_2P, $^1J_{CH} = 132$ Hz). $^{13}C\{^1H\}$ 259.01 (quint, Ru=*C*, $^2J_{PC} = 13$ Hz); 160.06 (quint, Ru=C=C=*C*, $^4J_{PC} = 1$ Hz); 145.35 (quint, Ru=C=*C*, $^3J_{PC} = 2$ Hz); 133.7–127.7 (m, Ph); 60.16 (s, OCH_3); 46.82 (s, *C*H_2Ph); 29.85 (quint, PCH_2CH_2P, $|^1J_{PC} + {}^3J_{PC}| = 23$ Hz).

Table 3
Selected bond distances (Å) and angles (°) for **3**

Intramolecular distances (Å)			
Ru–Cl	2.426(3)	Ru–C_1	1.77(1)
Ru–P_1	2.448(3)	C_1–C_2	1.36(2)
Ru–P_2	2.471(3)	C_2–C_3	1.41(2)
Ru–P_3	2.454(3)	C_3–O	1.26(2)
Ru–P_4	2.433(3)	C_3–C_4	1.51(2)
Intramolecular bond angles (°)			
Cl–Ru–P_1	91.1(1)	P_2–Ru–C_1	97.7(4)
Cl–Ru–P_2	86.7(1)	P_3–Ru–C_1	86.2(4)
Cl–Ru–P_3	90.5(1)	P_4–Ru–C_1	94.7(4)
Cl–Ru–P_4	81.0(1)	Cl–Ru–C_1	174.9(4)
P_1–Ru–P_2	81.8(1)	Ru–C_1–C_2	177.6(4)
P_2–Ru–P_3	98.5(1)	C_1–C_2–C_3	121(1)
P_3–Ru–P_4	82.8(1)	O_1–C_3–C_2	122(1)
P_1–Ru–P_4	97.3(1)	O_1–C_3–C_4	120(1)
P_1–Ru–C_1	92.3(4)	C_2–C_3–C_4	118(1)

5.8. Preparation of [trans-(dppe)$_2$(Cl)Ru(C≡C–C(OMe)=CHPh)] **9**

To a solution of 0.412 g of **8** (0.33 mmol) in solution in 50 ml of dichloromethane, 840 μl of triethylamine (6 mmol) were added. The solution was stirred for 30 min at r.t. and pumped off. The residue was filtered through an alumina column with ether as eluent. After recrystallization in CH_2Cl_2–hexane mixture 0.205 g of yellow crystals of **9** (57%) were obtained. Anal. Calc. for $C_{63}H_{57}ClOP_4Ru$: C, 69.39; H, 5.27%. Found C, 68.98; H, 5.44%. IR (KBr): ν(C≡C) 2033 cm^{-1}. NMR ($CDCl_3$): ^1H 7.83–6.90 (m, 45H, Ph); 4.94 (s, 1H, C*H*Ph); 3,06 (s, 3H, OMe); 2.82 (m, 4H, PCH_2CH_2P); 2.57 (m, 4H, PCH_2CH_2P). $^{31}P\{^1H\}$ 51.07 (s, PPh_2). $^{13}C\{^1H\}$ 142.94 (s, Ru–C≡C–*C*); 138.70–123.67 (m, Ph); 132.59 (quint, Ru–*C*≡, $^2J_{PC} = 15$ Hz); 110.49 (s, Ru–C≡*C*); 108.23 (s, *C*HPh); 55.23 (s, O Me); 30.81 (quint, PCH_2CH_2P, $|^1J_{PC} + {}^3J_{PC}| = 24$ Hz). ^{13}C 142.95 (m, Ru–C≡C–*C*); 138.70–122.60 (m, Ph); 132.59 (quint, Ru–*C*≡C, $^2J_{PC} = 15$ Hz); 110.49 (m, Ru–C≡*C*); 108.23 (d m, =*C*HPh, $^1J_{CH} = 155$ Hz); 55.32 (q, OCH_3, $^1J_{CH} = 143$ Hz); 30.81 (t m, PCH_2CH_2P, $^1J_{CH} = 131$ Hz).

5.9. Preparation of [trans-(dppe)$_2$(Cl)Ru(=C=CH–C(H)=CPh_2)][PF_6] **10**

To 0.485 g of **1** (0.5 mmol) and 0.168 g of $NaPF_6$ (1 mmol), a solution of 0.222g of propargyl alcohol H–C≡C–CH(OH)($CHPh_2$) in 50 ml of dichloromethane was added. After 4 h of stirring at r.t., the solution was filtered and the solvent evaporated. The crude product was washed with diethylether and dried. After recrystallization in a mixture (CH_2Cl_2–hexane), 0.47 g of red crystals of **10** (73%) were obtained. Anal. Calc. for $C_{68}H_{60}ClF_6P_5Ru$: C, 63.68; H, 4.72%. Found C, 63.52; H, 4.73%. IR (KBr): ν(C=C) 1618, 1585 cm^{-1}. NMR ($CDCl_3$): ^1H 7.45–6.59 (m, 50H, Ph); 5.08 (d, 1H, Ru=C=C(H)=C*H*, $^3J_{HH} = 10$Hz); 3.84 (d quint, 1H, Ru=C=C*H*, $^3J_{HH} = 10$ Hz, $^4J_{PH} = 3$ Hz); 2.95 (m, 4H, PCH_2CH_2P); 2.72 (m, 4H, PCH_2CH_2P). $^{31}P\{^1H\}$ 41,24 (s, PPh_2), − 143.66 (sept, PF_6, $^1J_{PF} = 713$ Hz). $^{13}C\{^1H\}$ 361.50 (quint, Ru=*C*, $^2J_{PC} = 13$ Hz); 140.28–127.17 (m, Ph); 108.71 and 108.40 (s, Ru=C=*C*H and Ru=C=CH–

*C*H); 28.87 (quint, PCH_2CH_2P, $|^1J_{PC} + {}^3J_{PC}| = 23$ Hz). ^{13}C 361.50 (quint, Ru=*C*, $^2J_{PC} = 13$ Hz); 140.32–126.79 (m, Ph); 108.72 and 108.34 (d, Ru=C=*C*H and Ru=C=CH–*C*H, $^1J_{CH} = 157$ Hz); 28.87 (t m, PCH_2CH_2P, $^1J_{CH} = 136$ Hz).

*5.10. Preparation of [trans-(dppe)$_2$(Cl)Ru(C≡C–C(H)=CPh$_2$)] **11***

To 0.64 g of **10** (0.5 mmol) in 50 ml of dichloromethane, four equivalents of DBU were added. After stirring for 1 h at r.t., the solvent was evaporated and the residue filtered through an alumina column using diethylether as eluent. After crystallization in a mixture CH_2Cl_2–hexane, 0.364 g of yellow crystals of **11** (73%) were obtained. Anal. Calc. for $C_{68}H_{59}ClP_4Ru \cdot 2CH_2Cl_2$: C, 64.35; H, 4.86%. Found C, 64.84; H, 4.80%. IR (Kbr): ν(C≡C) 2035 cm^{-1}. NMR ($CDCl_3$): ^1H 7.33–6.78 (m, 50H, Ph); 5.98 (s, 1 H, Ru–C≡C–C*H*); 2.45 (m, 4H, PCH_2CH_2P); 2.26 (m, 4H, PCH_2CH_2P). $^{31}P\{^1H\}$ 50.29 (s, PPh_2). $^{13}C\{^1H\}$ 143.78–126 (m, Ph); 139.12 (s, Ru–C≡C–CH=*C*Ph_2); 135.09 (quint, Ru–C≡, $^2J_{PC} =$ 15 Hz); 115.71 (s, Ru–C≡C–*C*H); 115.36 (s, Ru–C≡*C*); 30.49 (quint, PCH_2CH_2P, $|^1J_{PC} + {}^3J_{PC}| = 24$ Hz). ^{13}C 143.79–125.77 (m, Ph); 139.09 (m, Ru–C≡C–CH=*C*Ph_2); 135.10 (quint, Ru–*C*≡, $^2J_{PC} = 15$ Hz); 115.71 (d, Ru–C≡C–CH, $^1J_{CH} = 154$ Hz); 115.34 (s, Ru–C≡*C*); 30.48 (t m, PCH_2CH_2P, $^1J_{CH} = 138$ Hz).

5.11. Experimental data for the X-ray crystal structure determination

The sample ($0.40 \times 0.45 \times 0.45$ mm) is studied on an automatic diffractometer CAD4 ENRAF-NONIUS with graphite monochromatized Mo–K_α radiation. The all parameters are obtained by fitting a set of 25 high-θ reflections. The data collection was as follows: $2\theta_{max} = 54°$, scan $\omega/2\theta = 1$, $t_{max} = 60$ s, range *hkl*: *h*, 0.14; *k*, 0.28; *l*, 0.50, intensity controls without appreciable decay (1.2%) gives 11854 reflections from which 4845 with $I > 4\sigma(I)$. After Lorenz and polarization corrections the structure was solved with direct methods which reveal the Ru, Cl, P and some C atoms. The remaining non-H atoms of the structure are found after successive scale factor refinements and Fourier differences. The triflate anion is found in two different sites. After isotropic ($R = 0.125$), then anisotropic refinement ($R = 0.09$), some H atoms are found with a Fourier difference (in particular H2, H4A and H4B), the remaining ones are set in geometrical position. The whole structure was refined by the full-matrix least-square technique i.e. use of F magnitude; x, y, z, β_{ij} for Ru, P, Cl, O and C atoms, x, y, z, for triflate anion and x, y, z, fixed for H atoms; 819 variales and 5134 observations; $w = 1/\sigma(F_o)^2 = [\sigma^2(I) + (0.04F_o^2)^2]^{1/2}$ with the resulting $R = 0.073$, $Rw = 0.062$ and $Sw = 5.27$ (residual $\Delta\rho \leq 0.32$ e $Å^{-3}$). Atomic scattering factors from International Tables for X-ray Crystallography [47]. The calculations were performed on a Hewlett Packard 9000-710 for structure determination and on a Digital Micro Vax 3100 computer with the MOLEN package [48] for refinement and ORTEP calculations.

6. Supplementary material available

Tables of bond lengths and angles, torsions angles, positional parameters, displacement parameters and ORTEP diagram for **3** are available from the authors.

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References

[1] (a) R.B. King, M.S. Saron, J. Chem. Soc. Chem. Commun. (1972) 1052. (b) R.B. King, M.S. Saron, J. Am. Chem. Soc. 95 (1972) 1817.
[2] M.I. Bruce, A.G. Swincer, Adv. Organomet. Chem. 22 (1983) 60.
[3] N.E. Kobobova, L. Ivanov, O.S. Zhoanho, V.V. Derunov, I.N. Chechulina, Izv. Akad. Nauk. SSSR Ser. Khim. 11 (1982) 2632.
[4] (a) C. Bruneau, P.H. Dixneuf, J. Chem. Soc. Chem. Commun. (1997) 507. (b) B.M. Trost, Chem. Ber. 129 (1996) 1313.
[5] (a) R. Mahé, P.H. Dixneuf, S. Lécolier, Tetrahedron Lett. 27 (1986) 6333. (b) R. Mahé, Y. Sasaki, C. Bruneau, P.H. Dixneuf, J. Org. Chem. 54 (7) (1989) 1518. (c) H. Doucet, J. Höfer, N. Derrien, C. Bruneau, P.H. Dixneuf, Bull. Soc. Chim. Fr. 133 (1996) 939.
[6] (a) Y. Wakatsuki, H. Yamazaki, N. Kumegawa, T. Satoh, J.Y. Satoh, J. Am. Chem. Soc. 113 (1991) 9604. (b) C. Bianchini, M. Peruzzini, P. Frediani, J. Am. Chem. Soc. 113 (1991) 5453. (c) C.A. Merlic, M.E. Pauly, J. Am. Chem. Soc. 118 (1996) 11319. (d) C. Slugovc, K. Mereiter, E. Zobetz, R. Schmid, K. Kirchner, Organometallics 15 (1996) 5275. (e) C.S. Yi, N. Liu, Organometallics 15 (1996) 3968.
[7] (a) E.O. Fischer, H.J. Kalder, A. Franck, F.H. Köhler, G. Huttner, Angew. Chem. Int. Ed. Engl. 15 (1976) 623. (b) H. Berke, Angew. Chem. Int. Ed. Engl. 15 (1976) 624.
[8] J.P. Selegue, Organometallics 1 (1982) 217.
[9] For reviews see: (a) M.I. Bruce, Chem. Rev. 91 (1991) 197. (b) H. Le Bozec, P.H. Dixneuf, Russ. Chem. Rev. 44 (1995) 801. (c) P.H. Dixneuf, C. Bruneau, in: C. Helmchen (Ed.), Organic Synthesis via Organometallics, OSM5, Vieweg, Wiesbaden, 1997. (d) S.G. Davies, J.P. McWally, A.J. Smallbridge, Adv. Organomet. Chem. 30 (1990) 1.
[10] M. Tamm, Organometallics 16 (1997) 1418.
[11] (a) V. Cadierno, M.P. Gamasa, J. Gimeno, E. Lastra, J. Borge, S. Garcia-Granda, Organometallics 13 (1994) 745. (b) V. Cadierno, M.P. Gamasa, J. Gimeno, M.C. Lopez-Gonzales, J. Borge, S. Garcia-Granda, Organometallics 16 (1997) 4453 and references therein.

[12] G. Roth, H. Fischer, J. Organomet. Chem. 507 (1996) 125 and references therein.
[13] M.I. Bruce, R.C. Wallis, Aust. J. Chem. 32 (1979) 1471.
[14] M.A. Esteruelas, L.A. Oro, J. Schrickel, Organometallics 16 (1997) 796.
[15] (a) H. Werner, T. Rappert, R. Wiedemann, J. Wolf, N. Mahr, Organometallics 13 (1994) 2721. (b) T. Braun, P. Steinert, H. Werner, J. Organomet. Chem. 488 (1995) 169 and references therein.
[16] D. Touchard, N. Pirio, P.H. Dixneuf, Organometallics 14 (1995) 4920 and references therein.
[17] (a) D. Péron, A. Romero, P.H. Dixneuf, Organometallics, 14 (1995) 3319. (b) N. Ruiz, D. Péron, S. Sinbandhit, P.H. Dixneuf, C. Badioli, S. Maiorana, J. Organomet. Chem. 533 (1997) 213 and references therein.
[18] B.M. Trost, J.A. Flygare, J. Am. Chem. Soc. 14 (1992) 5477.
[19] H. Werner, J. Chem. Soc. Chem. Commun. (1977) 903.
[20] D. Péron, A. Romeno, P.H. Dixneuf, Gazz. Chim. Ital. 124 (1994) 497.
[21] D. Touchard, P. Haquette, A. Daridor, L. Toupet, P.H. Dixneuf, J. Am. Chem. Soc. 116 (1994) 11157.
[22] R.W. Lass, P. Steinert, J. Wolf, H. Werner, Chem. Eur. J. 2 (1996) 19.
[23] (a) G. Roth, H. Fischer, Organometallics 15 (1996) 1139. (b) G. Roth, H. Fischer, Organometallics 15 (1996) 5766.
[24] J.R. Lomprey, J.P. Selegue, Organometallics 12 (1993) 616.
[25] M.I. Bruce, P. Hinterning, E.R.T. Tiekink, B.W. Skelton, A.H. White, J. Organomet. Chem. 450 (1993) 209.
[26] M.I. Bruce, P. Hinterning, P.J. Low, B.W. Skelton, A.H. White, J. Chem. Soc. Chem. Commun. (1996) 1009.
[27] D. Touchard, C. Morice, V. Cadierno, P. Haquette, L. Toupet, P.H. Dixneuf, J. Chem. Soc. Chem. Commun. (1994) 859.
[28] S. Guesmi, D. Touchard, P.H. Dixneuf, J. Chem. Soc. Chem. Commun. (1996) 2773.
[29] P. Haquette, Thèse de Doctorat de l'Université de Rennes, 1996.
[30] D. Touchard, P. Haquette, N. Pirio, L. Toupet, P.H. Dixneuf, Organometallics 12 (1993) 3132.
[31] D. Touchard, P. Haquette, S. Guesmi, L. Le Pichon, A. Daridor, L. Toupet, P.H. Dixneuf, Organometallics 16 (1997) 3640.
[32] (a) C. Cosset, I. del Rio, V. Peron, B. Windmüller, H. Le Bozec, Synlett 5 (1996) 435. (b) V. Peron, E. Porhiel, V. Ferrand, H. Le Bozec, J. Organomet. Chem. 539 (1997) 201. (c) M. Duetsch, F. Stein, R. Lackman, E. Pohl, R. Herbst-Irmer, A. de Meyere, Chem. Ber. 125 (1992) 2051
[33] (a) A. Romero, A. Vegas, P.H. Dixneuf, Angew. Chem. Int. Ed. Engl. 29 (1990) 215. (b) A. Romero, A. Vegas, P.H. Dixneuf, Anal. Quim. Int. Ed. 92 (1996) 299.
[34] D. Touchard, N. Pirio, L. Toupet, M. Fettouhi, L. Ouahab, P.H. Dixneuf, Organometallics 14 (1995) 5263.
[35] M.I. Bruce, P. Hinterning, E.R.T. Tiekink, B.W. Skelton, A.H. White, J. Organomet. Chem. 450 (1993) 209.
[36] M.I. Bruce, P. Hinterning, M. Ke, P.J. Low, B.W. Skelton, A.H. White, J. Chem. Soc. Chem. Commun. (1997) 715.
[37] R.F. Winter, F.M. Hoznung, Organometallics 16 (1997) 4248.
[38] M.I. Bruce, D.N. Duffy, M.G. Humphrey, A.G. Swincer, J. Organomet. Chem. 282 (1985) 383.
[39] M.M. Midland, J. Org. Chem. 40 (1975) 2250.
[40] L. Brandsma, Preparative Acetylenic Chemistry, Elsevier, New York, 1988.
[41] D. Touchard, P. Haquette, A. Daridor, A. Romero, P.H. Dixneuf, Organometallics, submitted.
[42] M.I. Bruce, M.G. Humphrey, M.R. Snow, E.R.T. Tiekink, J. Organomet. Chem. 314 (1986) 213.
[43] M.P. Gamasa, J. Gimeno, B.M. Martin-Vaca, J. Borge, S. Garcia-Granda, E. Perez-Carreno, Organometallics 13 (1994) 4045.
[44] T. Braun, P. Sternert, H. Werner, J. Organomet. Chem. 488 (1995) 369.
[45] N.G. Connelly, A.G. Orpen, A.L. Rieger, P.H. Rieger, C.J. Scott, G.M. Rosair, J. Chem. Soc. Chem. Commun. (1992) 1293.
[46] B. Chaudret, G. Commenges, R. Poilblanc, J. Chem. Soc. Dalton Trans. (1984) 1635.
[47] International Tables for X-Ray Crystallography, vol. IV, Kynoch Press, Birmingham, 1974 (present distributor D. Reidel, Derdrecht).
[48] ENRAF-NONIUS Molecular Structure Determination Package, Mol EN Version, Enraf-Nonius, Delft, The Netherlands, 1990.