# Vinylacetylene (Butenyne) Derivatives as Precursors of Alkenylcarbene Ruthenium Complexes *via* Allenylidene Metal Intermediates

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Complexes ($\eta^6$-arene)($PR_3$)$RuCl_2$ (**1a—c**) react with $HC{\equiv}C{-}C(R^1){=}CHR^2$ derivatives in methanol to afford in one step the alkenylcarbene–ruthenium cations $[(\eta^6\text{-arene})(PR_3)ClRu{=}C(OMe)CH{=}C(R^1)CH_2R^2]^+$ (**2**)—(**6**) ($R^1$ and $R^2$ = H or Me) which on deprotonation give cyclometallacarbenes (**7**)—(**8**); on the basis of labelling experiments the formation of (**2**)—(**6**) involves an allenylidene intermediate $Ru{=}C{=}C{=}C(R^1)(CH_2R^2)^+$ instead of the expected allylcarbene moiety $Ru{=}C(OMe)CH_2C(R^1)(=CHR^2)^+$.

Unsaturated carbene–metal complexes have been shown to be key intermediates in alkyne polymerization[1] and to provide access to organometallic polymers.[2] Vinylcarbene–metal derivatives have been of particular value in organic synthesis: *via* Diels–Alder reactions involving their activated double bond,[3] in the formation of unsaturated cyclopropanes by transfer to an alkene,[4] or on coupling with alkynes in the formation of functional phenol or furan derivatives.[5] Only a few vinylcarbene–metal complexes do not contain a carbonyl ligand,[6—8] and most have usually been obtained by classical methods starting from metal carbonyls[9] or by transformation of carbene ligands.[10]

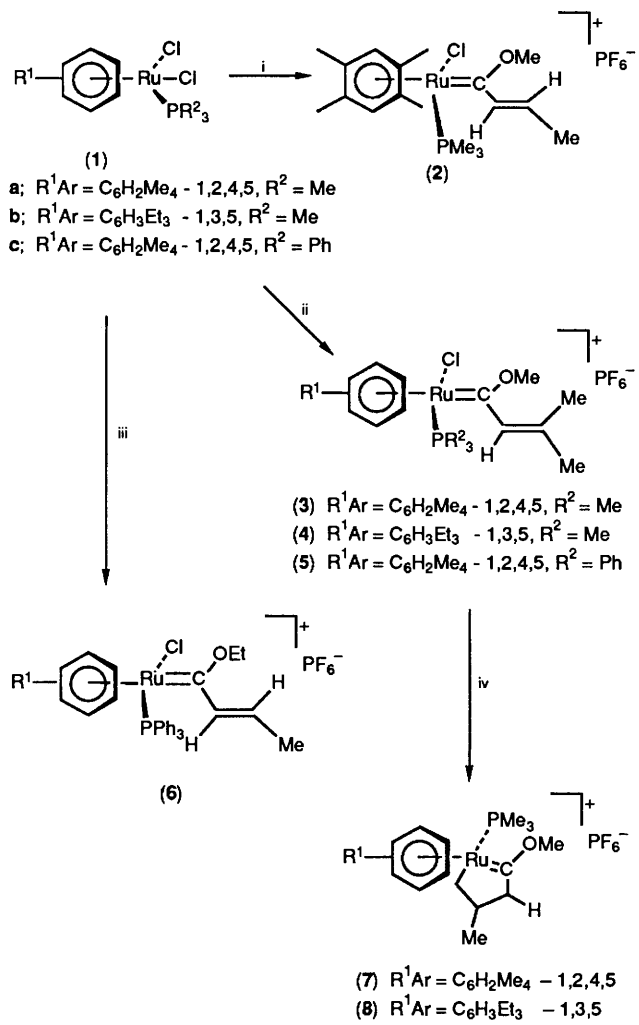
As terminal alkynes have been shown to react with (arene)$RuCl_2PR_3$ complexes to afford alkylcarbene ruthenium complexes *via* a vinylidene–metal intermediate,[11] we have considered the possibility of producing allylcarbene complexes by the use of vinylacetylene derivatives. We now report that vinylacetylenes actually give a direct and new access to alkenylcarbene–ruthenium(arene) complexes and that the reaction does not proceed by isomerization of the expected

allylcarbene–metal but by formation of an allenylidene–metal intermediate.

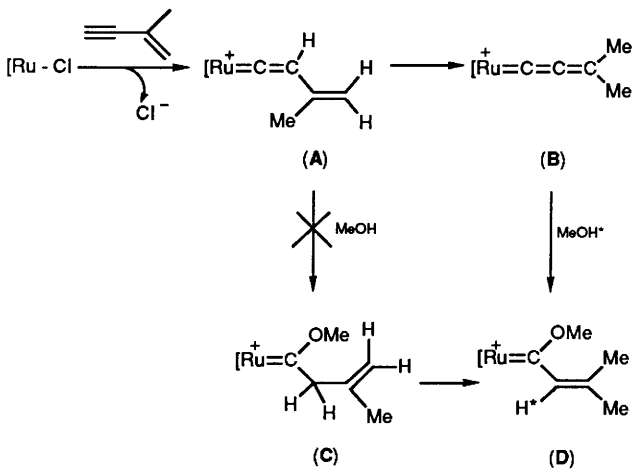
The $RuCl_2(PMe_3)(\eta^6\text{-}C_6H_2Me_4)$ complex (**1a**) in $CH_2Cl_2$–MeOH was treated with a slight excess (1.5 equiv.) of vinylacetylene in the presence of $NaPF_6$ (1 equiv.). After 45 min at room temperature orange–red crystals of (**2**) were isolated in 72% yield† (Scheme 1). Under similar conditions complexes (**1a**) and (**1b**) reacted with isopropenylacetylene and the vinylcarbene derivatives (**3**) (80%) and (**4**) (78%) were obtained respectively.† The red complex (**1c**) containing the bulky $PPh_3$ ligand also reacted with isopropenylacetylene and pent-3-en-1-yne, but slowly; a violet intermediate was rapidly formed and after 2 h at room temperature was transformed into the orange–red complexes (**5**) (65%) and (**6**) (69%) respectively.†

Deprotonation of complexes (**3**) and (**4**) with $Bu^tOK$ (1 equiv.) in $CH_2Cl_2$ did not give the expected dienylruthenium derivative but led to complexes (**7**) (65%) and (**8**) (68%) for which the NMR spectra† establish the metallacyclocarbene arrangement {$^{13}C$ NMR δ(Ru=C), [$^2J_{PC}$/Hz]: (**7**), 287.6 [19.6]; (**8**), 288.4, [18.4]} rather than a dienylmetal moiety with a co-ordinated terminal $CH_2$=C bond. The formation of complexes (**7**) and (**8**) can be explained by an initial deprotonation of one methyl group followed by cyclisation on nucleophilic substitution of the chloride ligand.

The formation of the vinylcarbene derivatives (**2**)—(**6**) can be explained by isomerization[12] of an allylcarbene ruthenium




**Scheme 1.** *Reagents and conditions* [room temp. with $NaPF_6$ in $CH_2Cl_2$/ROH (1:1)]: i, HC≡CCH=$CH_2$, MeOH, 45 min; ii, HC≡CC(Me)=$CH_2$, MeOH, 45 min—2 h; iii, HC≡CCH=CHMe, EtOH, 2 h; iv, $Bu^tOK$ in $CH_2Cl_2$, 12 h.




**Scheme 2.** [Ru–Cl = $RuCl_2PR_3$(arene).

† Satisfactory elemental analyses were obtained for (**2**)—(**8**). *Selected spectroscopic data*: (**2**): IR (KBr) 1620 (m, ν C=C), 1290 (m, ν C–O), and 860 (s, ν P–F) $cm^{-1}$; $^1H$ NMR (300.134 MHz; $CD_2Cl_2$) δ 7.93 (=C*H*Me), 6.86 [d, C(OMe)C*H*=, $^3J_{HH}$ 14.5 Hz], 4.41 (OMe), and 2.23 (dd, =CHMe, $^3J_{HH}$ 6.9, $^4J_{HH}$ 1.2 Hz); $^{13}C\{^1H\}$ NMR (75.469 MHz; $CD_2Cl_2$) δ 303.98 (d, Ru=C, $^2J_{PC}$ 20.3 Hz), 172.4 (d, CH=, $^3J_{PC}$ 14.6 Hz), 136.4 (s, =CHMe), 65.6 (s, OMe), and 21.9 (s, =CH*Me*); $^{31}P$ NMR (32.80 MHz; $CD_2Cl_2$) δ 12.51 ppm (s, $PMe_3$) with respect to 85% $H_3PO_4$.

(**3**): IR (KBr) 1610 (m, ν C=C), 1285 (m, ν C–O), and 850 (s, ν P–F) $cm^{-1}$; $^1H$ NMR (300.134 MHz; $CD_2Cl_2$) δ 6.56 (s, CH=), 4.85 (s, OMe), and 1.93 (s) and 1.90 (s) (=$CMe_2$); $^{13}C\{^1H\}$ NMR (75.469 MHz; $CD_2Cl_2$) δ 308.1 (d, Ru=C, $^2J_{PC}$ 19.8 Hz), 134.5 (s, *C*$Me_2$), 131.8 (s, CH=), 64.8 (s, OMe), and 25.6 and 21.7 (s, =C*Me*$_2$); $^{31}P$ NMR (32.80 MHz; $CD_2Cl_2$) δ 7.08 ppm (s, $PMe_3$).

(**4**): IR (KBr) 1610 (m, ν C–C), 1295 (m, ν C–O), and 860 (s, ν P–F) $cm^{-1}$; $^{13}C\{^1H\}$ NMR (75.469 MHz; $CD_2Cl_2$) δ 303.8 (d, Ru=C, $^2J_{PC}$ 19.5 Hz), 150.0 (s, =*C*$Me_2$), 140.2 (d, CH=, $^3J_{PC}$ 7.0 Hz), 68.5 (s, OMe), and 23.2 (s, =C*Me*$_2$).

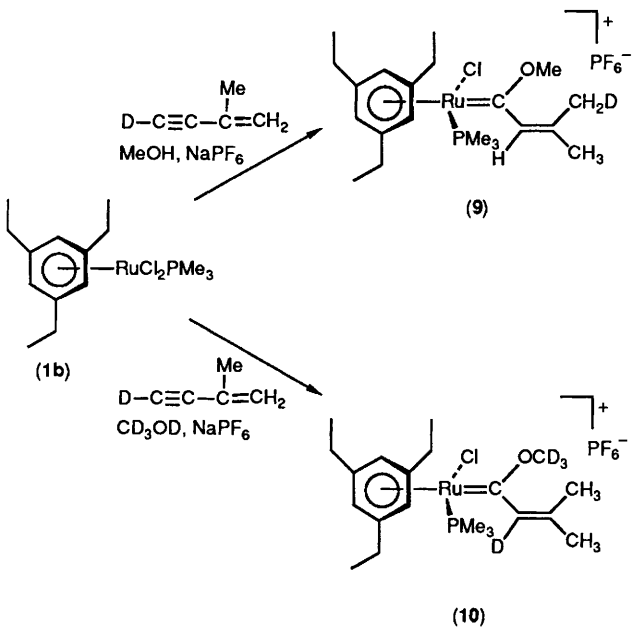
(**5**): IR (KBr) 1620 (ν C–C), 1285 (ν C–O), and 860 (ν P–F) $cm^{-1}$; $^{13}C\{^1H\}$ NMR (75.469 MHz; $CD_2Cl_2$) δ 313.2 (d, Ru=C, $^2J_{PC}$ 18.9 Hz), 137.9 (s, CH=), 69.6 (s, OMe), and 26.7 and 24.5 (s, =$CMe_2$); $^{31}P$ NMR (32.80 Hz; $CD_2Cl_2$) 35.9 ppm (s, $PPh_3$).

(**6**): IR (KBr) 1630 (ν C–C) and 865 (ν P–F) $cm^{-1}$; $^{13}C\{^1H\}$ NMR (75.469 MHz; $CD_2Cl_2$) δ 303.4 (d, Ru=C, $^2J_{PC}$ 18.6 Hz), 176.8 (=C*H*Et), 133.9 (CH=), 28.7 (=CHC$H_2$Me), and 14.3 and 12.5 (O–$CH_2$*Me*, $CHCH_2$*Me*); $^{31}P$ NMR δ 38.9 ppm ($PPh_3$).

(**7**): IR (KBr) 1590 (ν C=C) and 865 (ν P–F); $^1H$ NMR (300.134 MHz; $CD_2Cl_2$) δ 6.50 (m, CH=), 4.12 (OMe), 2.56 and 1.92 (AB, $CH_2$Ru, $^2J_{HH}$ 17.9 Hz, $^3J_{PH_a}$ 7.4 Hz), and 2.26 (t, *Me*$CCH_2$Ru, $^4J_{HH}$ 1.2 Hz); $^{13}C\{^1H\}$ NMR (75.469 MHz; $CD_2Cl_2$) δ 287.6 (d, Ru=C, $^2J_{PC}$ 19.6 Hz), 208.3 (Me*C*=), 134.4 (CH=), 33.1 (d, $CH_2$Ru, $^2J_{PC}$ 21.5 Hz), and 25.7 (*Me*C=); $^{31}P$ NMR (100.56 MHz) δ 8.79 ppm ($PMe_3$).

(**8**): $^1H$ NMR (400 MHz; $CD_2Cl_2$) δ 6.47 (CH=), 4.19 (OMe), 2.88 and 1.89 (AB, $CH_2$–Ru, $^2J_{HH}$ 18.4, $^3J_{PH_a}$ 7.6 Hz), and 2.26 (MeC=); $^{13}C\{^1H\}$ (100.56 MHz; $CD_2Cl_2$) δ 288.4 (d, Ru=C, $^2J_{PC}$ 18.4 Hz), 207.6 (=*C*Me), 135.3 (=CH), 30.3 (d, $CH_2$Ru, $^2J_{PC}$ 19.0 Hz), and 25.6 (*Me*C=).

(**9**): $^1H$ NMR (300.134 MHz; $CD_2Cl_2$) δ 6.91 (s, 1H, Ru=CCH) and 1.80—2.10 (m, 5H, $CH_2$D/Me); $^{13}C\{^1H\}$ NMR (75.469 MHz; $CD_2Cl_2$) δ 140.2 (d, CH=), 23.2 (s, C*Me*), and 23.3 (t, $CH_2$D, $^1J_{CD}$ 128 Hz).




Scheme 3

intermediate (**C**) or *via* the allenylidene–ruthenium complex (**B**) (Scheme 2). To identify the nature of the process we have investigated the reaction of labelled compounds with complex (**1b**) which gave rapid reactions and no observable violet intermediate. The reaction of (**1b**) with a 3:2 mixture of D–C≡C–C(Me)=$CH_2$ and H–C≡C–C(Me)=$CH_2$ in MeOH–$CH_2Cl_2$ led to a mixture of complexes (**9**) and (**4**) isolated in 64% yield and in the ratio *ca.* 3:2 (Scheme 3). The formation of (**9**) shows that the deuterium of the alkyne migrates from the terminal carbon to the double bond. The reaction of (**1b**) with H–C≡C–C(Me)=$CH_2$ in $CD_3OD$–$CH_2Cl_2$ led to the complex (**10**) exclusively, isolated in 68% yield. The ethylenic position was 100% deuteriated and D/H exchange involving the methyl groups was not observed. Thus, the formation of (**10**) involves the intramolecular migration of the alkyne proton leading to an allenylidene intermediate (**B**) followed by addition of $CD_3OD$ to give (**D**) (Scheme 3).

It is noteworthy that, even if the formation of (**B**) is likely to proceed *via* the vinylidene (**A**), the overall reaction corresponds to an unexpected 1,4-migration of the alkyne proton.

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