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Nucleophilic additions of anionic Group 6 carbene complexes on cationic indenyl–ruthenium(II) allenylidene derivatives: an easy entry to bimetallic complexes containing σ-alkynyl–carbene and vinylidene–carbene bridges†

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The novel indenyl–ruthenium(II) allenylidene complexes [Ru{=C=C=C(R)Ph}(η^5-C_9H_7)(PPh_3)L][PF_6] (L = $PMePh_2$, R = Ph **4a**, H **4b**; L = PMe_2Ph, R = Ph **5**) have been prepared by reaction of [RuCl(η^5-C_9H_7)(PPh_3)L] (L = $PMePh_2$ **2**, PMe_2Ph **3**) with HC≡CC(OH)(R)Ph and $NaPF_6$ in methanol. These allenylidene derivatives as well as [Ru{=C=C=C(R)-Ph}(η^5-C_9H_7)(PPh_3)$_2$][PF_6] (R = Ph **1a**, H **1b**) undergo regioselective nucleophilic additions of anionic Fischer type carbene complexes [Li][(CO)$_5$M{=C(OMe)CH_2}] (M = Cr, W, Mo) at the C_γ atom of the unsaturated chain to afford the neutral bimetallic σ-alkynyl derivatives [Ru(C≡CC(R)Ph{CH_2C(OMe)=M(CO)$_5$})(η^5-C_9H_7)(PPh_3)L] (L = PPh_3, R = Ph, M = Cr **6a**, W **6b**, Mo **6c**; L = PPh_3, R = H, M = Cr **7a**, W **7b**; L = $PMePh_2$, R = Ph, M = Cr **8a**, W **8b**; L = $PMePh_2$, R = H, M = Cr **9a**, W **9b**; L = PMe_2Ph, R = Ph, M = Cr **10a**, W **10b**). Protonation of these derivatives with HBF_4·Et_2O yields cationic vinylidene complexes [Ru(=C=C(H)C(R)Ph{CH_2C(OMe)=M(CO)$_5$})(η^5-C_9H_7)-(PPh_3)L][BF_4] **11a–c**, **12–15a,b** which represent the first examples of bimetallic species containing a vinylidene–carbene bridge. Heating under reflux solutions of vinylidene complexes **11b** and **12b** in acetonitrile affords the carbene derivatives [(CO)$_5$W{=C(OMe)CH_2C(R)Ph(C≡CH)}] (R = Ph **16a**, H **16b**) and the nitrile complex [Ru(N≡CMe)(η^5-C_9H_7)(PPh_3)$_2$][BF_4] **17**. The diphenylallenylidene complex **1a** regioselectively reacts with NaC≡N to yield the σ-alkynyl derivative [Ru{C≡CCPh_2(C≡N)}(η^5-C_9H_7)(PPh_3)$_2$] **18**. Treatment of **18** with one equivalent of [M(CO)$_5$(THF)] leads to the formation of the bimetallic σ-alkynyl complexes [Ru(C≡CCPh_2{C≡N–M(CO)$_5$})-(η^5-C_9H_7)(PPh_3)$_2$] (M = Cr **20a**, W **20b**, Mo **20c**).

The reactivity of transition metal complexes containing unsaturated carbene ligands (cumulenylidene complexes) [M]=C=(C)$_n$=CR_2 has been the subject of longstanding interest mainly focused on the vinylidene derivatives (n = 0).[1a–d] Despite the large number of allenylidene derivatives (n = 1) reported to date [most of them containing late transition metals such as Cr(0), W(0), Fe(II), Ru(II), Os(II), Rh(I), Ir(I), Re(I)] their reactivity has been only sparsely investigated.[1e–h] However, the last few years have witnessed significant developments showing that these species are involved in a series of transformations with potential utility in organic synthesis. Thus, allenylidene complexes undergo stoichiometric cycloaddition[2] as well as C–C and C–heteroatom coupling[3] reactions. Furthermore they are active species in catalytic reactions such as ring closing metathesis (RCM) of olefins[4a–e] or the coupling of 1-alkyn-3-ols with allylic alcohols.[4f,g] In spite of these reports the synthetic applications of these highly unsaturated species are still scarce, probably due to the absence of systematic studies on their reactivity.

Theoretical calculations on the models [Mn(=C=C=CH_2)-(η^5-C_5H_5)(CO)$_2$],[5] [Ru(=C=C=CH_2)(η^5-C_9H_7)(PH_3)$_2$]$^+$,[6] and [Ru(=C=C=CH_2)(η^5-C_5H_5)(CO)(PH_3)]$^+$[7] show that the carbon atoms of the allenylidene ligand are alternatively electron-deficient and electron-rich when moving along the unsaturated chain starting from the metal centre: M=$C_\alpha^{\delta+}$=$C_\beta^{\delta-}$=$C_\gamma^{\delta+}$. In agreement with the nucleophilic character of C_β the neutral allenylidene complexes [Mn(=C=C=CR_2)(η^5-C_5H_5)(CO)$_2$] (R = Ph, Bu^t) and [Os(=C=C=CPh_2)Cl(η^5-C_5H_5)(PPr^i_3)] undergo C_β protonations to generate the cationic alkenyl–carbyne derivatives [Mn{≡CC(H)=CR_2}(η^5-C_5H_5)(CO)$_2$]$^+$,[8] and [Os{≡CC(H)=CPh_2}Cl(η^5-C_5H_5)(PPr^i_3)]$^+$,[9] respectively. Addition of HCl on the neutral allenylidene–ruthenium(II) complex [Ru(=C=C=CPh_2)Cl_2{κ^2-P,O-$PPr^i_2CH_2$C(=O)OMe}{κ^1-P-$PPr^i_2CH_2$C(=O)-OMe}] has been reported to occur at the C_α–C_β to give the alkenyl–carbene derivative [Ru{=C(Cl)C(H)=CPh_2}Cl_2-{κ^2-P,O-$PPr^i_2CH_2$C(=O)OMe}{κ^1-P-$PPr^i_2CH_2$C(=O)OMe}].[10] Although experimental studies on neutral and cationic allenylidene complexes also confirm the electrophilic character of the C_α and C_γ atoms, there are remarkable differences in the regioselectivity of the nucleophilic additions which seem to be dependent on the nature of the metal fragment as well as on the allenylidene substituents.[1e–h] This is nicely illustrated by the behaviour of allenylidene–ruthenium(II) complexes towards alcohols which can be added either at the C_α atom of the cumulenic chain to afford alkenyl–carbene derivatives[11] [Ru]=C(OR)C(H)=CR_2 or at the C_γ atom to yield vinylidene complexes[12] [Ru]=C=C(H)C(OR)R_2. In contrast, allenylidene ligands stabilized by sterically hindered and/or electron-rich metallic fragments, such as *trans*-[RuCl(PP)$_2$]$^+$ (PP = dppm, dppe),[1e] [Ru{N($CH_2CH_2PPh_2$)$_3$}]$^+$,[13] [Ru(η^5-C_9H_7)L_2]$^+$ (L_2 = 2PPh_3, dppe, dppm),[6a] [Ru(η^5-1,2,3-$Me_3C_9H_7$)(dppm)]$^+$,[11e] [Ru(η^5-C_5H_5)L_2]$^+$ [L_2 = 2PPh_3,[14] 1,2-bis(diisopropylphosphino)-ethane (dippe)[15]], [Ru(Tp)(dippe)]$^+$ [Tp = hydrotris(pyrazolyl)-borate][16] or [RuCl(PPh_3)(κ^3-N,N,N-(S,S)-Pr^i-pybox)]$^+$ [(S,S)-Pr^i-pybox = 2,6-bis[4-(S)-isopropyloxazolin-2-yl]pyridine][11f] do not react with alcohols.

As part of our current research work dealing with the synthesis and reactivity of unsaturated carbene complexes, we have investigated[6a,11e,17] the influence of the steric and electronic properties of the metal fragments on the reactivity of the allenylidene group in complexes of general formula [Ru-(=C=C=CR^1R^2)(η^5-$C_9H_{7-n}R_n$)LL′]$^+$ (L, L′ = phosphine or

† Electronic supplementary information (ESI) available: analytical and spectroscopic data. See http://www.rsc.org/suppdata/dt/a9/a908493b/

CO; $n = 3$; R = H, Me). Thus, we have found that the allenylidene derivatives $[Ru\{=C=C=C(R)Ph\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]^+$ (R = Ph **1a**, H **1b**) add a large variety of anionic nucleophiles regioselectively at the C_γ atom of the cumulenic chain to afford functionalized neutral σ-alkynyl species $[Ru\{C\equiv CC(R)Ph(Nu)\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]$.[17c,e,f] The high regioselectivity of these nucleophilic additions arises from the efficient steric protection of the electrophilic C_α atom in **1a,b** due to the preferred *cis* orientation of the benzo ring of the indenyl group with respect to the allenylidene chain and to the presence of the bulky ancillary triphenylphosphine ligands. In contrast, the C_γ atom is more accessible and nucleophiles can be added at this position. Furthermore, we have recently reported that these processes have a potential synthetic utility since the functionalized σ-alkynyl fragments in complexes $[Ru(C\equiv CR)(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ [R = CH=CPh₂, (*E*)-CH=CH(4-MeOC₆H₄), (*E*)-CH=CH(4-NO₂C₆H₄), (*E*)-CH=CH(η⁵-C₅H₄)Fe(η⁵-C₅H₅), C(C≡CH)-C₁₃H₂₀] have been used as efficient precursors of the corresponding terminal alkynes HC≡CR. They are readily generated quantitatively from the corresponding vinylidene species $[Ru\{=C=C(H)(R)\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]^+$ which undergo a demetalation process by treatment with acetonitrile leading to the acetonitrile complex $[Ru(N\equiv CMe)(\eta^5\text{-}C_9H_7)(PPh_3)_2]^+$ and the free alkynes.[17g]

On the basis of the aforementioned regioselective nucleophilic additions we have explored the synthesis of novel highly functionalized σ-alkynyl and vinylidene derivatives while continuing with our studies aimed at showing the synthetic utility of the allenylidene complexes. Thus, in this work we report (see Chart 1): *i*) the synthesis of bimetallic σ-alkynyl–carbene derivatives $[Ru(C\equiv CC(R)Ph\{CH_2C(OMe)=M(CO)_5\})(\eta^5\text{-}C_9H_7)(PPh_3)L]$ (R = Ph, H; L = PPh₃, PMePh₂, PMe₂Ph; M = Cr, Mo, W) (**A**) which are obtained *via* regioselective nucleophilic additions of anionic Group 6 carbene complexes $[Li][(CO)_5M\{=C(OMe)CH_2\}]$ at the C_γ atom of the corresponding allenylidene derivatives (**B**), *ii*) the first examples of bimetallic species containing a vinylidene–carbene bridge $[Ru(=C=C(H)C(R)Ph\{CH_2C(OMe)=M(CO)_5\})(\eta^5\text{-}C_9H_7)(PPh_3)L]^+$ (M = Cr, Mo, W) (**C**) prepared *via* protonation of the σ-alkynyl compounds (**A**), and *iii*) Fischer-type carbene complexes $[(CO)_5W\{=C(OMe)CH_2C(R)Ph(C\equiv CH)\}]$ (R = Ph, H) (**D**) formed through the selective demetalation of vinylidene–carbenes (**C**) with acetonitrile. The synthesis of the bimetallic σ-alkynyl derivatives $[Ru(C\equiv CCPh_2\{C\equiv N\text{–}M(CO)_5\})(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ (M = Cr, Mo, W) (**E**) as well as the allenylidene precursor complexes (**B**) are also described. Part of this work has been preliminarily communicated.[18]

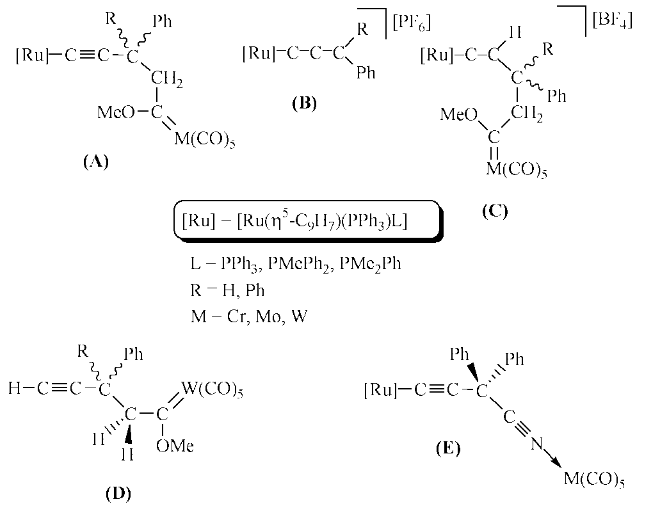
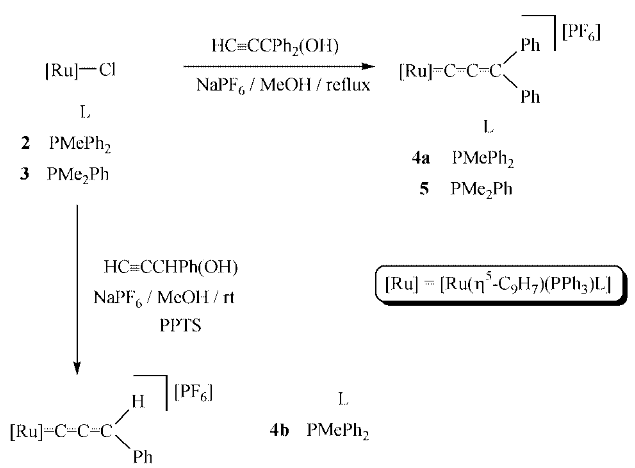


Chart 1 Complexes reported in this paper.

Results and discussion

Synthesis of allenylidene complexes [Ru{=C=C=C(R)Ph}(η⁵-C₉H₇)(PPh₃)L][PF₆] (L = PMePh₂, R = Ph 4a, H 4b; L = PMe₂Ph, R = Ph 5)

Following the standard synthetic procedure used for the preparation of the analogous allenylidene complex $[Ru(=C=C=CPh_2)(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ **1a**[6a] complexes **4a** and **5** have been obtained (79% and 85% yield, respectively) by the treatment of the chloride derivatives $[RuCl(\eta^5\text{-}C_9H_7)(PPh_3)L]$ (L = PMePh₂ **2**, PMe₂Ph **3**)[19] with a two-fold excess of 1,1-diphenyl-2-propyn-1-ol and NaPF₆ in refluxing methanol (Scheme 1).



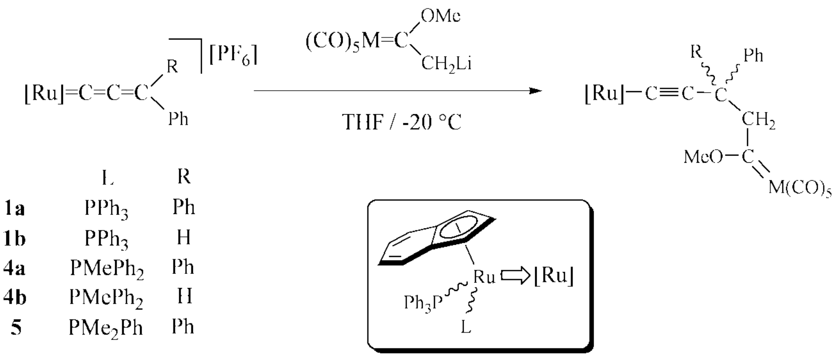
Scheme 1 Synthesis of novel indenyl–ruthenium(II) allenylidene complexes **4a**,**b** and **5**.

The monosubstituted allenylidene derivative **4b** was obtained similarly (76% yield) but, in order to avoid the nucleophilic addition of MeOH, milder reaction conditions (room temperature) have been used. Moreover, the addition of a catalytic amount of pyridinium *p*-toluenesulfonate (PPTS) acting as dehydrating agent is required (Scheme 1).

The unequivocal characterization of these metallacumulenic species was achieved by means of standard spectroscopic techniques (IR and $^{31}P\text{-}\{^1H\}$, ^1H, and $^{13}C\text{-}\{^1H\}$ NMR) as well as elemental analyses, all data being consistent with the proposed formulations (see the Supplementary Information). Indicative of the presence of an allenylidene chain the IR spectra (KBr) exhibit a broad and strong ν(C=C=C) absorption band (asymmetric stretching vibration) in the range 1927–1938 cm^{-1} and the $^{13}C\text{-}\{^1H\}$ NMR spectra display the characteristic low-field resonance for the carbenic Ru=C_α atom [δ_C 290.15–302.00; ^2J(CP) = 18.0–19.6 Hz]. The spectra also show two singlet signals in the ranges δ_C 208.02–210.70 and 145.60–155.53 corresponding to the β- and γ-carbon nuclei, respectively, as expected for their sp and sp² character. We note also for complex **4b** the presence in the ^1H NMR spectrum of a low-field singlet resonance at δ_H 8.98 assigned to the allenic proton Ru=C=C=CH.

Synthesis of bimetallic alkynyl–carbene bridged complexes [Ru(C≡CC(R)Ph{CH₂C(OMe)=M(CO)₅})(η⁵-C₉H₇)(PPh₃)L] (L = PPh₃, R = Ph, M = Cr 6a, W 6b, Mo 6c; L = PPh₃, R = H, M = Cr 7a, W 7b; L = PMePh₂, R = Ph, M = Cr 8a, W 8b; L = PMePh₂, R = H, M = Cr 9a, W 9b; L = PMe₂Ph, R = Ph, M = Cr 10a, W 10b)

Dinuclear transition-metal complexes containing hydrocarbon bridges linking the metal fragments and without metal–metal bonds are of particular current interest due to their unique chemical and physical properties.[20] One of the most efficient synthetic approaches to generate the hydrocarbon chain is based on C–C coupling reactions between two organometallic substrates each of them bearing either an electrophilic or



	L	R
1a	PPh$_3$	Ph
1b	PPh$_3$	H
4a	PMePh$_2$	Ph
4b	PMePh$_2$	H
5	PMe$_2$Ph	Ph

	L	R	M
6a	PPh$_3$	Ph	Cr
6b	PPh$_3$	Ph	W
6c	PPh$_3$	Ph	Mo
7a	PPh$_3$	H	Cr
7b	PPh$_3$	H	W
8a	PMePh$_2$	Ph	Cr
8b	PMePh$_2$	Ph	W
9a	PMePh$_2$	H	Cr
9b	PMePh$_2$	H	W
10a	PMe$_2$Ph	Ph	Cr
10b	PMe$_2$Ph	Ph	W

Scheme 2 Synthesis of bimetallic σ-alkynyl derivatives **6a–c** and **7–10a**,**b**.

nucleophilic carbon site. With this idea in mind we explored the reactivity of the electrophilic cationic allenylidenes [Ru{=C=C=C(R)Ph}(η^5-C$_9$H$_7$)(PPh$_3$)L][PF$_6$] (R = Ph, L = PPh$_3$ **1a**, PMePh$_2$ **4a**, PMe$_2$Ph **5**; R = H, L = PPh$_3$ **1b**, PMePh$_2$ **4b**) with nucleophilic anionic metallic complexes such as the readily available anionic Fischer type methoxy–carbene derivatives [(CO)$_5$M{=C(OMe)CH$_2$}]$^-$ (M = Cr, Mo, W).[21]

Thus, complexes **1a**,**b**, **4a**,**b** and **5** were treated in THF at −20 °C with one equivalent of the corresponding lithium salt [Li][(CO)$_5$M{=C(OMe)CH$_2$}] (M = Cr, Mo, W) (prepared *in situ* from [(CO)$_5$M{=C(OMe)CH$_3$}] and LiBu^n at −20 °C). The mixture was allowed to reach room temperature affording the σ-alkynyl complexes **6a–c**, **7a**,**b**, **8a**,**b**, **9a**,**b** and **10a**,**b** (51–88% yield) which are formed *via* the expected regioselective nucleophilic addition of the anionic carbene complexes at the C$_\gamma$ atom of the allenylidene chain (Scheme 2).[17]

Spectroscopic data of **6a–c** and **7–10a**,**b** (IR and ^{31}P-{^{1}H}, ^{1}H, and ^{13}C-{^{1}H} NMR) clearly reveal the presence of the η^5-indenyl ring and the [Ru]–C≡C moiety, being comparable with those reported for related indenylruthenium(II) σ-alkynyl complexes (see Tables 1 and 2 provided as Supplementary Information).[6a,17,22] Remarkable features are: (*i*) (IR) the ν(C≡C) absorption at 2078–2098 cm^{-1}, and (*ii*) (^{13}C-{^{1}H} NMR) the typical chemical shifts of the Ru–C$_\alpha$, C$_\beta$ and C$_\gamma$ carbon nuclei [δ_C: 94.80–101.87 (C$_\alpha$), 106.97–115.83 (C$_\beta$) and 39.58–52.39 (C$_\gamma$)]. In accordance with the proposed formulations, ^{1}H and ^{13}C-{^{1}H} NMR spectra exhibit the expected resonances for the methoxy–carbene units [(CO)$_5$M=C(OMe)CH$_2$] (see Tables 1 and 2). We note in particular the presence in the ^{13}C-{^{1}H} NMR spectra of the characteristic low-field singlet resonance for the carbenic carbon M=C (δ_C: 306.81–362.44). The structure of complex **6b** has been confirmed by a single-crystal X-ray study.[18] It should be mentioned that the NMR spectra of complexes **9a**,**b** (see Tables 1 and 2 in the Supplementary Information) reveal the presence of two diastereoisomers in *ca.* 1:1 ratio in agreement with the presence of two stereogenic centers at the C$_\gamma$ and ruthenium atoms indicating that the nuceophilic attack is not stereoselective. All attempts aiming to separate these diastereoisomers have been unsuccessful.

These dinuclear complexes containing C$_5$ hydrocarbon bridges are unprecedented and belong to the unusual series of heterobimetallic alkynyl–carbene bridged derivatives. Some related bi-, tri- and penta-nuclear derivatives are known (see Chart 2).[23]

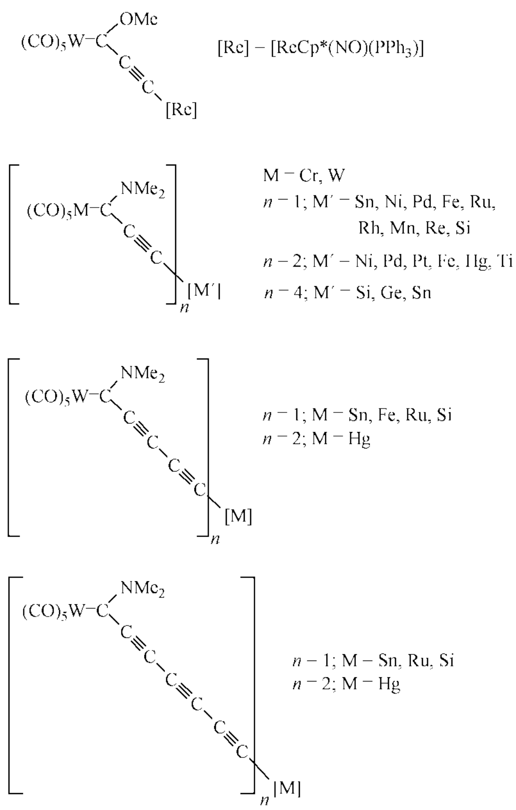
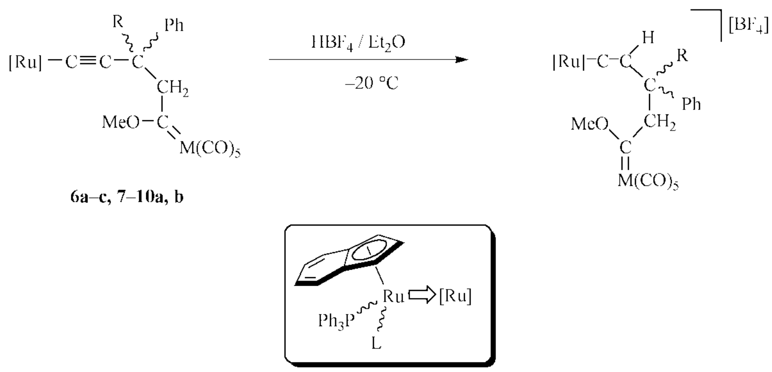


Chart 2 Related bi-, tri- and penta-nuclear complexes containing σ-alkynyl–carbene bridges.

Synthesis of bimetallic vinylidene–carbene bridged complexes [Ru(=C=C(H)C(R)Ph{CH$_2$C(OMe)=M(CO)$_5$})(η^5-C$_9$H$_7$)(PPh$_3$)-L][BF$_4$] (L = PPh$_3$, R = Ph, M = Cr 11a, W 11b, Mo 11c; L = PPh$_3$, R = H, M = Cr 12a, W 12b; L = PMePh$_2$, R = Ph, M = Cr 13a, W 13b; L = PMePh$_2$, R = H, M = Cr 14a, W 14b; L = PMe$_2$Ph, R = Ph, M = Cr 15a, W 15b)

Addition of electrophiles at the C$_\beta$ of neutral σ-alkynyl ruthenium(II) complexes is a well-known route to the corresponding cationic vinylidene derivatives.[1b] Taking into account that no examples of dinuclear species containing vinylidene–carbene type hydrocarbon bridges have been reported to date,[20] we became interested in the study of the protonation processes of σ-alkynyl derivatives **6a–c**, **7–10a**,**b** (the monuclear complex [Ru{=C=C(H)Ph}{=C(NHPh)(CH$_2$Ph)}Cl(PNP)]$^+$ (PNP = ^{n}PrN(CH$_2$CH$_2$PPh$_2$)$_2$) bearing both vinylidene and carbene ligands on the same metal atom has been reported).[20h] Furthermore, we have recently discovered that primary vinylidene moieties can be detached from the metal to give quantitatively the corresponding free terminal alkyne.[17g] This synthetic approach would provide a route for the synthesis of unprecedented alkyne functionalized Fischer type carbene complexes. Thus, the addition of HBF$_4$·Et$_2$O to solutions of **6a–c**, **7–10a**,**b** in diethyl ether at −20 °C, affords the cationic heterobimetallic vinylidene–carbene complexes [Ru(=C=C(H)-C(R)Ph{CH$_2$C(OMe)=M(CO)$_5$})(η^5-C$_9$H$_7$)(PPh$_3$)L][BF$_4$] (L = PPh$_3$, R = Ph, M = Cr **11a**, W **11b**, Mo **11c**; L = PPh$_3$, R = H, M = Cr **12a**, W **12b**; L = PMePh$_2$, R = Ph, M = Cr **13a**, W **13b**; L = PMePh$_2$, R = H, M = Cr **14a**, W **14b**; L = PMe$_2$Ph, R = Ph, M = Cr **15a**, W **15b**), isolated as air-sensitive brown solids in



	L	R	M
11a	PPh_3	Ph	Cr
11b	PPh_3	Ph	W
11c	PPh_3	Ph	Mo
12a	PPh_3	H	Cr
12b	PPh_3	H	W
13a	$PMePh_2$	Ph	Cr
13b	$PMePh_2$	Ph	W
14a	$PMePh_2$	H	Cr
14b	$PMePh_2$	H	W
15a	PMe_2Ph	Ph	Cr
15b	PMe_2Ph	Ph	W

Scheme 3 Synthesis of bimetallic vinylidene derivatives **11a–c** and **12–15a**,**b**.

45–75% yield (Scheme 3). Compounds **14a,b** have been obtained as non-separable mixtures of diastereoisomers (*ca.* 1 : 1 ratio) in accordance with the diasteromeric mixtures of the precursor derivatives **9a**,**b**.

Spectroscopic data are in agreement with the proposed formulations (see Tables 3 and 4 provided as Supplementary Information). In particular, the presence of the vinylidene moiety was identified, as usual, on the basis of: (*i*) (^{1}H NMR) the singlet (**11a–c**, **15a**,**b**), doublet (**12a**,**b**, **14a**,**b**) or doublet of doublets (**14a,b**) signal of the Ru=C=CH proton at δ_H 4.32–6.39, and (*ii*) (^{13}C-{^{1}H} NMR) the typical low-field resonance of the carbenic Ru=C_α which appears as a triplet (**11a–c**; **12a**,**b**, **13a**,**b**, **15a**,**b**) or multiplet (**14a**,**b**) at δ_C 341.40–348.44 [^2J(CP) = 15.3–18.8 Hz], as well as the C_β singlet resonance (δ_C: 114.96–121.43). IR, ^{1}H and ^{13}C-{^{1}H} NMR spectra also show the expected signals for the methoxy–carbene units [$(CO)_5M$=C(OMe)CH_2] (see the Supporting Information).

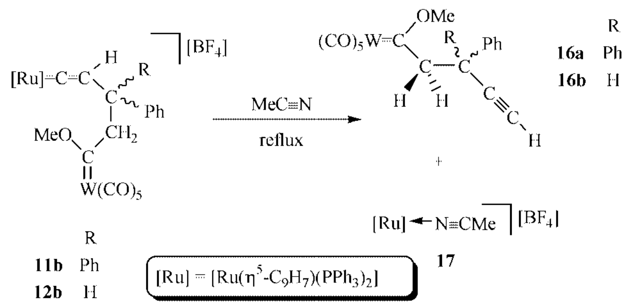
Synthesis of Fischer-type carbene complexes [$(CO)_5$W{=C(OMe)-CH_2C(R)Ph(C≡CH)}] (R = Ph 16a, H 16b)

We have recently shown that monosubstituted indenyl-ruthenium(II) vinylidene complexes [Ru{=C=C(H)R}(η^5-C_9H_7)-$(PPh_3)_2$]$^+$ are able to undergo demetalation reactions by heating in acetonitrile to afford the corresponding terminal alkyne HC≡CR and the nitrile complex [Ru(N≡CMe)(η^5-C_9H_7)-$(PPh_3)_2$]$^+$ in excellent yields.[17g] This process, which discloses a new entry for the synthesis of functionalized terminal alkynes, proceeds through the initial tautomerization at the ruthenium center of the η^1-vinylidene group to the η^2-terminal alkyne and subsequent elimination of the organic fragment from the metal by exchange with acetonitrile.

The methodology has proven to be useful also for the detaching of the ruthenium fragment in the heterobimetallic vinylidene–carbene complexes **11b** and **12b**. Thus, the reaction of **11b** and **12b** with refluxing acetonitrile proceeds smoothly and gives, besides the nitrile derivative **17**,[17g] the novel Fischer type methoxy–carbene complexes [$(CO)_5$W{=C(OMe)CH_2C(R)Ph-(C≡CH)}] (R = Ph **16a**, H **16b**) which were isolated after work-up as red-orange oils in 71 and 76% yield, respectively (Scheme 4). Spectroscopic data support the proposed formulations (see the Supporting Information). Significant spectroscopic features are: (*i*) (^{1}H NMR) the ≡CH proton resonance at δ_H 2.16 (**16a**) and 1.91 [d, J(HH) = 2.6 Hz, **16b**], and (*ii*) (^{13}C-{^{1}H} NMR) the characteristic acetylenic and carbenic carbon resonances [*ca.* δ_C: 69 (≡CH), 85 (≡C) and 332 (W=C)].

Synthesis and reactivity of bimetallic alkynyl–cyanide bridged complexes [Ru(C≡CCPh_2{C≡N–M$(CO)_5$})(η^5-C_9H_7)$(PPh_3)_2$] (M = Cr 20a, W 20b, Mo 20c)

Starting from the allenylidene complex **1a**, we have also developed an alternative two-step entry to bridged hetero-bimetallic ruthenium(II)–Group 6 complexes. This method is based on the nucleophilic addition of a cyanide group at the



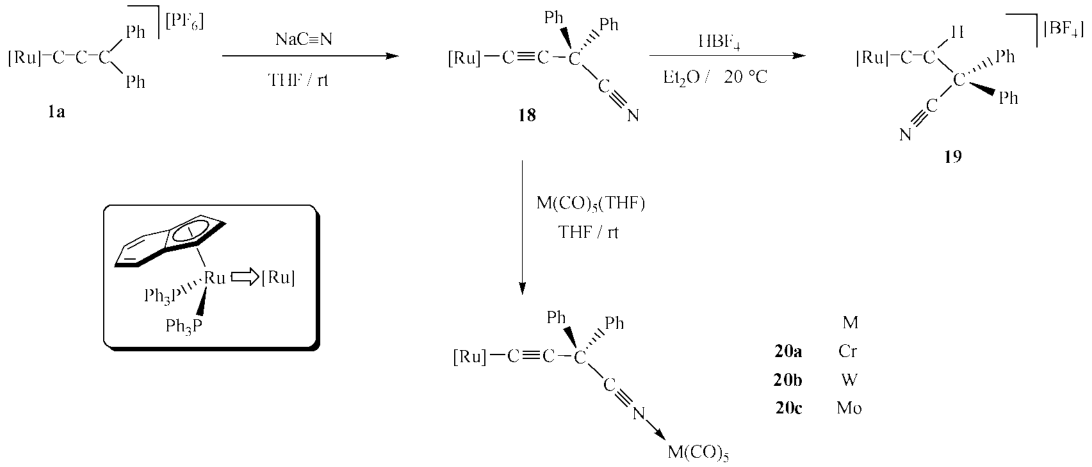
Scheme 4 Synthesis of carbene complexes **16a**,**b**.

C_γ atom of the allenylidene chain to give the corresponding σ-alkynyl derivative bearing a terminal cyanide group. This complex can be used as ligand through the co-ordination of the cyanide group to the coordinatively unsaturated moiety [M$(CO)_5$] (M = Cr, Mo, W).

Thus, complex [Ru{C≡CCPh_2(C≡N)}(η^5-C_9H_7)$(PPh_3)_2$] **18** was prepared (85% yield) by reaction of allenylidene **1a** with NaCN in THF at room temperature (Scheme 5). The IR spectrum shows the expected ν(C≡C) and ν(C≡N) absorption bands at 2075 and 2229 cm^{-1}, respectively, and the ^{13}C-{^{1}H} NMR spectrum exhibits typical Ru–C_α, C_β, C_γ and C≡N resonances at δ_C 109.50 [t, ^2J(CP) = 23.4 Hz, C_α], 104.17 (C_β), 49.29 (C_γ) and 121.92 (C≡N). The characterization of **18** was also ascertained by its protonation with HBF_4·Et_2O, in diethyl ether at −20 °C, which takes place selectively on the C_β of the alkynyl chain affording the cationic vinylidene derivative [Ru{=C=C(H)CPh_2-(C≡N)}(η^5-C_9H_7)$(PPh_3)_2$][BF_4] (**19**) (81% yield) (Scheme 5). Analytical and spectroscopic data (IR and ^{31}P-{^{1}H}, ^{1}H, and ^{13}C-{^{1}H} NMR) (see the Supporting Information) support this formulation. The related cyclopentadienyl complex [Ru{C≡CCPh_2(C≡N)}(η^5-C_5H_5)$(PPh_3)_2$] has been recently reported.[14]

As expected, the cyano group acts in complex **18** as a good bridging ligand which allows the synthesis of novel dinuclear metal complexes. Thus, the reaction of **18** with an equimolar amount of [M$(CO)_5$(THF)] (M = Cr, W, Mo) in THF, at room temperature, yields the neutral bimetallic derivatives [Ru(C≡CCPh_2{C≡N–M$(CO)_5$})(η^5-C_9H_7)$(PPh_3)_2$] (M = Cr **20a**, W **20b**, Mo **20c**) in 59–83% yield (Scheme 5). IR and NMR data support the proposed formulations (see the Supporting Information). Thus, the IR spectra show typical ν(C≡C), ν(C≡N) and ν(C≡O) absorptions in the range 1904–2280 cm^{-1}, and the ^{13}C-{^{1}H} NMR spectra display the expected Ru–C_α, C_β and C_γ resonances at *ca.* δ_C 115 [t, ^2J(CP) = 23 Hz, C_α], 101 (C_β) and 51 (C_γ), the C≡N signal being overlapped by the aromatic carbon resonances. Downfield M–CO singlet resonances were also observed in the range δ 197.03–219.54.

All attempts aimed at promoting the removal of the ruthenium fragment *via* protonation of **20a–c** and subsequent treatment with acetonitrile failed, since the addition of HBF_4·



Scheme 5 Synthesis of bimetallic σ-alkynyl complexes **20a–c**.

Et_2O does not proceed selectively, leading instead to mixtures containing the desired bimetallic vinylidene derivatives [Ru(=C=C(H)CPh$_2${C≡N–M(CO)$_5$})(η^5-C_9H_7)(PPh$_3$)$_2$][BF$_4$] along with the mononuclear vinylidene complex **19**.

Conclusions

In this work we report general synthetic routes for the preparation of heterobimetallic ruthenium(II)–Group 6 complexes starting from the readily available indenylruthenium(II) allenylidene derivatives [Ru{=C=C=C(R)Ph}(η^5-C_9H_7)(PPh$_3$)L][PF$_6$] **1a,b**, **4a,b** and **5**. Unprecedented neutral bimetallic σ-alkynyl–carbene complexes [Ru(C≡CC(R)Ph{CH$_2$C(OMe)=M(CO)$_5$})(η^5-C_9H_7)(PPh$_3$)L] **6a–c**, **7–10a,b** have been prepared in high yields through the regioselective nucleophilic addition of anionic Fischer type methoxy–carbene derivatives [(CO)$_5$M{=C(OMe)CH$_2$}]$^-$ at Cγ of the allenylidene chain in complexes **1a,b**, **4a,b** and **5**. Protonation of these σ-alkynyl derivatives with HBF$_4$·Et$_2$O leads to the formation of compounds [Ru(=C=C(H)C(R)Ph{CH$_2$C(OMe)=M(CO)$_5$})(η^5-C_9H_7)(PPh$_3$)L][BF$_4$] **11a–c**, **12–15a,b**, which represent the first examples of bimetallic species containing a vinylidene–carbene type hydrocarbon bridge.[20] Furthermore, it is also shown that the reaction of complexes **11b** and **12b** in refluxing acetonitrile proceeds through a selective demetalation of the ruthenium fragment affording the novel Fischer type methoxy–carbene derivatives [(CO)$_5$W{=C(OMe)CH$_2$C(R)Ph(C≡CH)}] **16a,b** containing a terminal alkyne functionality. Analogous carbene complexes such as [(CO)$_5$M{=C(X)C≡CR′}] (X = OR, NR$_2$; M = Cr, W, Mo) and [(CO)$_5$M{=C(X)CH$_2$(CH$_2$)$_n$CH$_2$C≡CR′}] (X = OR, NR$_2$; M = Cr, W, Mo; n = 0, 1, 2...) are known and their usefulness in organic transformations has been amply demonstrated over the past decades.[24] In addition, the easy preparation of a new family of bimetallic ruthenium(II)–Group 6 complexes namely [Ru(C≡CCPh$_2${C≡N–M(CO)$_5$})(η^5-C_9H_7)(PPh$_3$)$_2$] **20a–c** has also been achieved. All these results extend the scope of our previous results directed at the application of ruthenium–allenylidenes in stoichiometric organometallic and organic synthesis.[17,22c,d]

Experimental

General comments

The manipulations were performed in an atmosphere of dry nitrogen using vacuum-line and standard Schlenk techniques. All reagents were obtained from commercial suppliers and used without further purification. Solvents were dried by standard methods and distilled under nitrogen before use. The compounds [Ru{=C=C=C(R)Ph}(η^5-C_9H_7)(PPh$_3$)$_2$][PF$_6$] (R = Ph **1a**, H **1b**),[6a] [RuCl(η^5-C_9H_7)(PPh$_3$)L] (L = PMePh$_2$ **2**, PMe$_2$Ph **3**)[19] and [(CO)$_5$M{=C(OMe)CH$_3$}] (M = Cr, Mo, W)[21] were prepared by following the methods reported in the literature. Analytical and spectroscopic data for all the complexes reported in this paper have been provided as Supplementary Information.

Preparations

[Ru(=C=C=CPh$_2$)(η^5-C_9H_7)(PPh$_3$)L][PF$_6$] (L = PMePh$_2$ 4a, PMe$_2$Ph 5). *General procedure.* A mixture of the corresponding chloride complex [RuCl(η^5-C_9H_7)(PPh$_3$)L] **2**,**3** (1 mmol), 1,1-diphenyl-2-propyn-1-ol (0.416 g, 2 mmol) and NaPF$_6$ (0.336 g, 2 mmol) in 50 cm^3 of MeOH was heated under reflux for 30 min. The color progressively changed from red to violet. The solvent was then removed under vacuum and the solid residue extracted with CH$_2$Cl$_2$ (*ca.* 20 cm^3) and filtered. Concentration of the resulting solution to *ca.* 5 cm^3 followed by the addition of 50 cm^3 of diethyl ether precipitated a violet solid, which was washed with diethyl ether and dried *in vacuo*. **4a:** Yield: 1.014 g (79%). **5:** Yield: 0.809 g (85%).

[Ru{=C=C=C(H)Ph}(η^5-C_9H_7)(PPh$_3$)(PMePh$_2$)][PF$_6$] 4b. A solution of [RuCl(η^5-C_9H_7)(PPh$_3$)(PMePh$_2$)] **2** (0.174 g, 1 mmol), 1-phenyl-2-propyn-1-ol (0.132 g, 1 mmol), NaPF$_6$ (0.168 g, 1 mmol) and pyridinium *p*-toluenesulfonate (0.025 g, 0.1 mmol) in 50 cm^3 of MeOH was stirred at room temperature for 24 h. The solvent was then removed under vacuum and the solid residue extracted with CH$_2$Cl$_2$ (*ca.* 20 cm^3) and filtered. The resulting solution was stirred at room temperature for 12 h. Concentration to *ca.* 5 cm^3 followed by the addition of 50 cm^3 of diethyl ether precipitated a red solid which was washed with diethyl ether and dried *in vacuo*.Yield: 0.712 g (76%).

[Ru(C≡CC(R)Ph{CH$_2$C(OMe)=M(CO)$_5$})(η^5-C_9H_7)(PPh$_3$)L] (L = PPh$_3$, R = Ph, M = Cr 6a, W 6b, Mo 6c; L = PPh$_3$, R = H, M = Cr 7a, W 7b; L = PMePh$_2$, R = Ph, M = Cr 8a, W 8b; L = PMePh$_2$, R = H, M = Cr 9a, W 9b; L = PMe$_2$Ph, R = Ph, M = Cr 10a, W 10b). *General procedure.* A solution of [Li][(CO)$_5$M=C(OMe)CH$_2$] (1 mmol) in 20 cm^3 of THF (prepared *in situ* by treatment of [(CO)$_5$M=C(OMe)CH$_3$] with one equivalent of LiBu^n at −20 °C for 30 min) was added, at −20 °C,to a solution of the corresponding allenylidene complex [Ru{=C=C=C(R)Ph}(η^5-C_9H_7)(PPh$_3$)L][PF$_6$] **1a**,**b**, **4**, **5a**,**b** (1 mmol) in 30 cm^3 of THF. The mixture was allowed to reach room temperature and the solvent was then removed *in vacuo*. The resulting solid residue was extracted with diethyl ether (*ca.* 40 cm^3) and filtered over silica gel. Evaporation of the solvent gave the σ-alkynyl complexes **6a–c**, **7–10a**,**b**, as yellow-orange solids. **6a:** Yield: 0.849 g (72%). **6b:** Yield: 0.997 g (76%). **6c:**

Yield: 0.624 g (51%). **7a:** Yield: 0.938 g (85%). **7b:** Yield: 1.075 g (87%). **8a:** Yield: 0.984 g (88%). **8b:** Yield: 1.037 g (83%). **9a:** Yield: 0.760 g (73%). **9b:** Yield: 0.833 g (71%). **10a:** Yield: 0.897 g (85%). **10b:** Yield: 0.867 g (73%).

[Ru(=C=C(H)C(R)Ph{CH$_2$C(OMe)=M(CO)$_5$})(η^5-C$_9$H$_7$)(PPh$_3$)L][BF$_4$] (L = PPh$_3$, R = Ph, M = Cr 11a, W 11b, Mo 11c; L = PPh$_3$, R = H, M = Cr 12a, W 12b; L = PMePh$_2$, R = Ph, M = Cr 13a, W 13b; L = PMePh$_2$, R = H, M = Cr 14a, W 14b; L = PMe$_2$Ph, R = Ph, M = Cr 15a, W 15b). *General procedure.* A solution of the corresponding σ-alkynyl complex [Ru(C≡CC(R)Ph{CH$_2$C(OMe)=M(CO)$_5$})(η^5-C$_9$H$_7$)(PPh$_3$)L] **6a–c**, **7–10a**,**b** (1 mmol) in 100 cm^3 of diethyl ether at −20 °C was treated dropwise with strong stirring with a diluted solution of HBF$_4$·Et$_2$O in diethyl ether. Immediately, an insoluble brown solid precipitated but the addition was continued until no further solid was formed. The solution was then decanted and the solid washed with diethyl ether (3 × 20 cm^3) and vacuum dried. **11a:** Yield: 0.951 g (75%). **11b:** Yield: 1.007 g (72%). **11c:** Yield: 0.682 g (52%). **12a:** Yield: 0.548 g (46%). **12b:** Yield: 0.595 g (45%). **13a:** Yield: 0.783 g (55%). **13b:** Yield: 0.936 g (70%). **14a:** Yield: 0.689 g (61%). **14b:** Yield: 0.782 g (62%). **15a:** Yield: 0.617 g (54%). **15b:** Yield: 0.765 g (60%).

[(CO)$_5$W{=C(OMe)CH$_2$C(R)Ph(C≡CH)}] (R = Ph 16a, H 16b). *General procedure.* A solution of the corresponding vinylidene complex [Ru(=C=C(H)C(R)Ph{CH$_2$C(OMe)=M(CO)$_5$})(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][BF$_4$] **11b**, **12b** (1 mmol) in 40 cm^3 of acetonitrile was heated under reflux for 90 min. The solvent was then removed under vacuum and the solid residue extracted with diethyl ether (*ca.* 100 cm^3) and filtered. A yellow solid containing mainly the nitrile complex [Ru(N≡CMe)(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][BF$_4$] **17** [17g] remained insoluble. The extract was evaporated to dryness yielding complexes **16a**,**b** as red-orange oils. **16a:** Yield: 0.406 g (71%). **16b:** Yield: 0.377 g (76%).

[Ru{C≡CCPh$_2$(C≡N)}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$] 18. A solution of NaC≡N (0.049 g, 1 mmol) in 10 cm^3 of methanol was added at room temperature to a solution of the allenylidene complex [Ru(=C=C=CPh$_2$)(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][PF$_6$] **1a** (1.076 g, 1 mmol) in 50 cm^3 of THF. The mixture was stirred at room temperature for 1 h and the solvent was then removed *in vacuo*. The resulting solid residue was extracted with diethyl ether (*ca.* 60 cm^3) and filtered over Al$_2$O$_3$. Evaporation of the solvent gave the σ-alkynyl complex **18** as a yellow solid. Yield: 0.813 g (85%).

[Ru{=C=C(H)CPh$_2$(C≡N)}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][BF$_4$] 19. A solution of [Ru{C≡CCPh$_2$(C≡N)}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$] **18** (0.957 g, 1 mmol) in 100 cm^3 of diethyl ether at −20 °C was treated dropwise with strong stirring with a diluted solution of HBF$_4$·Et$_2$O in diethyl ether. Immediately, an insoluble brown solid precipitated but the addition was continued until no further solid was formed. The solution was then decanted off and the solid washed with diethyl ether (3 × 20 cm^3) and vacuum dried. Yield: 0.846 g (81%).

[Ru(C≡CCPh$_2${C≡N–M(CO)$_5$})(η^5-C$_9$H$_7$)(PPh$_3$)$_2$] (M = Cr 20a, W 20b, Mo 20c). *General procedure*. A THF solution of the corresponding [M(CO)$_5$(THF)] complex (1 mmol) was added at room temperature to a solution of [Ru{C≡CCPh$_2$-(C≡N)}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$] **18** (0.957 g, 1 mmol) in 20 cm^3 of THF, and the resulting mixture stirred for 3 h. The solvent was then removed under vacuum and the solid residue dissolved in CH$_2$Cl$_2$ (*ca.* 5 cm^3) and transferred to a SiO$_2$ chromatography column. Elution with a hexane–diethyl ether mixture (3 : 1) gave complexes **20a–c** as yellow-orange solids. **20a:** Yield: 0.816 g (71%). **20b:** Yield: 1.063 g (83%). **20c:** Yield: 0.704 g (59%).

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