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New Types of (Arene)ruthenium Alkynyl Complexes[†]

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The reaction of $[\{RuCl(cym)\}_2(\mu\text{-}Cl)_2]$ (cym $= \eta^6$-4-methylisopropylbenzene) with 1,10-phenanthroline and $NaBAr'_4$ ($Ar' =$ 3,5-bis(trifluoromethyl)phenyl), followed by addition of excess sodium acetylide, yielded the complex $[Ru(CCH)(cym)(phen)]BAr'_4$ (**1**), the first cationic (arene)ruthenium alkynyl. Similar $[Ru(CCPh)(cym)(phen)]BAr'_4$ (**2**) and $[Ru(CCSiMe_3)(cym)(phen)]BAr'_4$ (**3**) complexes were prepared in an analogous manner from the corresponding lithium acetylides and in situ generated ruthenium triflate precursors. Protonation of **1** with HOTf afforded the acyl complex $[Ru(C(O)CH_3)(cym)(phen)]BAr'_4$ (**4**), presumably by reaction of an initially formed dicationic vinylidene with adventitious water. The reaction of $[RuCl_2(cym)(PMe_3)]$ with excess LiCCPh afforded the complex $[Ru(CCPh)_2(cym)(PMe_3)]$ (**5**), the first (arene)ruthenium bis(acetylide) complex. All new compounds were characterized by IR and NMR, and the crystal structures of **1**, **4**, and **5** were determined by X-ray diffraction.

Introduction

Alkynyl complexes have attracted an ongoing interest,[1] in part due to their role as precursors of vinylidene complexes, in turn highly reactive species,[2] and due to the usefulness of alkynyl complexes as building blocks in the synthesis of polymetallic compounds.[3]

Ruthenium alkynyl and vinylidene complexes have attracted much attention due to their interesting reactivity.[4,5] Ruthenium(II) alkynyls with ancillary η^5-cyclopentadienyl or related (pentamethylcyclopentadienyl or indenyl) ligands have been extensively studied. In contrast, much less is known about (arene)ruthenium (II) alkynyls, although some of these compounds have revealed an interesting reactivity. Le Bozec and Dixneuf found that protonation of the alkynyl $[RuCl(CCPh)(\eta^6\text{-}C_6Me_6)(PMe_3)]$ yielded cationic vinylidene complexes $[RuCl(CC(H)Ph)(\eta^6\text{-}C_6Me_6)(PMe_3)]^+$, which, in turn, reacted with methanol to afford methoxycarbenes $[RuCl(C(OMe)CH_2Ph)(\eta^6\text{-}C_6Me_6)(PMe_3)]^+$.[6] $[(\eta^6\text{-arene})RuCl_2(PR_3)]$ precursors were employed for the direct activation of 1-alkynes in alcohols to yield alcoxycarbenes.[6] The (arene)ruthenium complexes showed a higher efficiency than the isoelectronic $[(\eta^5\text{-}C_5H_5)RuCl(PMe_3)_2]$ compounds, a fact that is attributed mainly to the higher electrophilicity of the (arene)ruthenium vinylidene

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[†] Dedicated to Professor R. Usón on the occasion of his 75th birthday.

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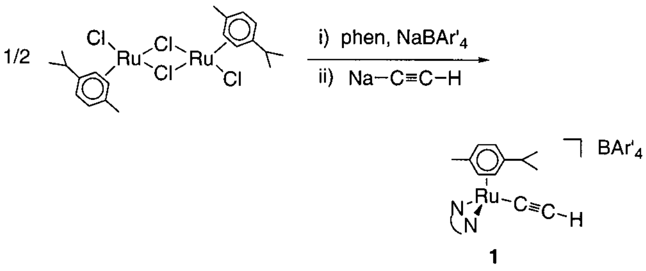
Scheme 1



intermediates.[6] The only known (arene)ruthenium alkynyls were neutral complexes with a single alkynyl ligand.[6,7] Here we report the synthesis and characterization of two new types of (arene)ruthenium alkynyl complexes: cationic alkynyls and one neutral bis(alkynyl) complex.

Results and Discussion

Synthesis, Characterization, and Reactivity of Cationic Alkynyls [Ru(CCR)(Cym)(phen)]BAr′$_4$. The complex [{RuCl(cym)}$_2$(μ-Cl)$_2$][8] reacts with 1,10-phenanthroline (phen) and the salt NaBAr′$_4$ (Ar′ = 3,5-bis(trifluoromethyl)phenyl)[9] in THF. The solution of the complex [RuCl(cym)(phen)]BAr′$_4$ obtained in this way reacts with excess sodium acetylide to yield, after workup, the alkynyl complex [Ru(CCH)(cym)(phen)]BAr′$_4$ (**1**) (Scheme 1).

The IR spectrum of **1** displays one band at 1974 cm^{-1}, assigned to the stretching of the alkynyl triple bond.[10]

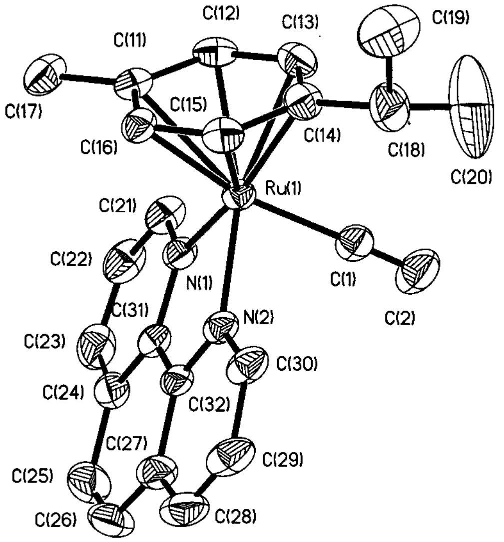


Figure 1. Thermal ellipsoid (drawn at the 30% probability level) plot of **1**.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Complex 1

Ru(1)−C(1)	2.022(9)	Ru(1)−C(15)	2.194(8)
Ru(1)−N(2)	2.084(6)	Ru(1)−C(14)	2.232(8)
Ru(1)−N(1)	2.090(6)	Ru(1)−C(16)	2.254(7)
Ru(1)−C(13)	2.178(8)	Ru(1)−C(11)	2.263(7)
Ru(1)−C(12)	2.189(7)	C(1)−C(2)	1.151(12)
C(2)−C(1)−Ru(1)	175.7(10)	C(1)−Ru(1)−N(2)	83.8(3)
C(1)−Ru(1)−N(1)	84.2(3)	N(2)−Ru(1)−N(1)	77.7(3)

The ethynyl hydrogen occurs at 1.37 ppm in the ^{1}H NMR spectrum of **1**.[11] The ^{13}C NMR shows low-intensity signals at 99.9 and 88.9 ppm, attributable to the carbons of the ethynyl group.[3a] Integration of the ^{1}H NMR spectrum further supports the [Ru(CCH)(cym)(phen)]BAr′$_4$ composition for **1**. This was confirmed by the results of an X-ray determination carried out on a single crystal of **1**. The structure of the cation, shown in Figure 1, consists of a ruthenium atom coordinated to a η^6-cymene ligand, the two nitrogens of a 1,10-phenanthroline ligand, and one carbon of the ethynyl group. Selected distances and angles are given in Table 1. These data establish for **1** a structure in the solid state consistent with the spectroscopic data in solution, but, given the low level of accuracy of the X-ray data, further discussion of distances and angles is avoided.

The synthetic procedure outlined above involves the preparation of the nonisolated intermediate [RuCl(cym)(phen)]BAr′$_4$.[12] In this first step, the coordination of the phenanthroline ligand to the ruthenium center takes place with cleavage of the doubly chloride-bridged structure of the dimeric precursor. One chloride is abstracted out of each ruthenium and precipitates as sodium chloride. The high solubility of BAr′$_4$ salts in solvents of moderate polarity allows the use of mild conditions for the synthesis.[13,14] This first part can be

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(10) The complex [Ru(CCH)(η^5-C$_5$H$_5$)(PMe$_3$)$_2$] exhibits a C−C absorption band at 1921 cm^{-1}; see ref 3a.

(11) For the compound mentioned above the RuCC*H* resonance signal appears at 1.39 ppm.

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carried out without exclusion of air. In a second step, a metathetical reaction between the ruthenium chlorocomplex and sodium acetylide affords the ethynyl complex **1**. A long reaction time (12 h) is needed due to the low solubility of sodium acetylide.

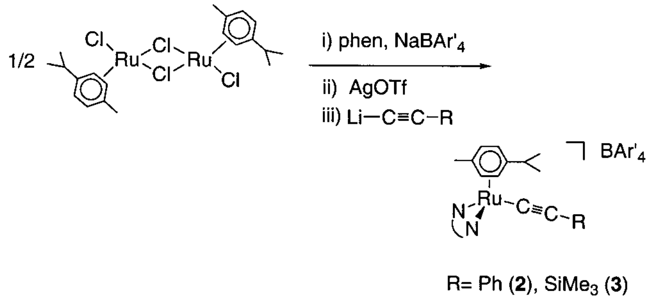
The reaction of a metal halocomplex and an alkaline-metal acetylide is perhaps the most general synthetic scheme for the preparation of alkynyl complexes.[15] However, it has been rarely employed for the direct preparation of ethynyls. Rather, most ethynyls have been synthesized by deprotection of trimethylsilylacetylide precursors[15c,16] or by deprotonation of a cationic vinylidene complex.[3a,17]

Ethynyl derivatives are relatively rare. Among the plethora of known ruthenium alkynyls, the only crystallographically characterized ethynyl complexes are, to our knowledge, the octahedral compounds *trans*-[Ru(CCH)Cl(dppm)$_2$][17b] and all-*trans*-[Ru(CCH)$_2$(CO)$_2$(PEt$_3$)$_2$].[18] Complex **1** is the first (arene)ruthenium ethynyl compound.

We aimed to extend the synthesis of alkynyls of the type [Ru(CCR)(cym)(phen)]BAr′$_4$ to derivatives with R groups other than H. For this purpose, we chose the lithium acetylides LiCCR (R = Ph, SiMe$_3$), conveniently generated in situ by the reaction of the corresponding acetylenes with *n*-BuLi. However, the lithium acetylides were not reactive toward solutions of [RuCl(cym)(phen)]BAr′$_4$. To increase the reactivity of the ruthenium complex, we sought to substitute the chloride ligand by the more labile triflate. Thus, a solution of [RuCl(cym)(phen)]BAr′$_4$ was allowed to react in the absence of light with an equimolar amount of AgOTf. The resulting [Ru(OTf)(cym)(phen)]BAr′$_4$ complex was not isolated. Instead, the filtered solutions of the triflatocomplex were transferred onto the solution of the appropriate lithium acetylide reagent. By this way we were able to prepare the complexes [Ru(CCPh)(cym)(phen)]BAr′$_4$ (**2**) and [Ru(CCSiMe$_3$)(cym)(phen)]BAr′$_4$ (**3**) (Scheme 2). In the synthesis of **2**, we found that addition of some methanol to the reaction mixture was needed. Similar use of methanol as cosolvent in the preparation of [RuCl(η^6-C$_6$Me$_6$)(CCPh)(PMe$_3$)] was reported by Dixneuf.[6]

The ^{19}F NMR spectra of complexes **2** and **3** showed only the signal of the BAr′$_4$ anion (−62.79 ppm). Therefore, BAr′$_4$/OTf exchange did not take place under the reaction conditions when the chloride ligand was substituted by triflate. The presence of the alkynyl ligands in compounds **2** and **3** was clearly indicated by their spectroscopic features. The IR spectrum of **2** shows the acetylenic C−C stretching band at 2111 cm^{-1},[19] and the two acetylenic carbons give rise to ^{13}C NMR signals at 111.2 and 105.9 ppm.[6] For complex **3**, the IR stretching of the acetylenic C−C bond[20] occurs at 2039 cm^{-1}, and, in the ^{13}C NMR, the acetylenic carbons of **3** appear as weak signals at 111.4 and 108.5 ppm.

Scheme 2



The solubility of complexes **1**−**3** in solvents of moderate polarity, such as dichloromethane, is very high, due to the presence of the BAr′$_4$ counteranion,[14] facilitating the acquisition of ^{13}C NMR spectra with a good signal-to-noise ratio. This is particularly relevant for alkynyl complexes, for which the most informative signals, those of acetylenic carbons, are of intrinsic low intensity.

Complex **1** reacted with a stoichiometric amount of trifluoromethylsulfonic acid to yield the acyl complex [Ru(C(O)CH$_3$)(cym)(phen)]BAr′$_4$ (**4**). The characterization of complex **4** is based on its spectroscopic data. The strong IR absorption at 1631 cm^{-1} is consistent with the presence of the acyl ligand, and the chemical shifts in the ^{1}H NMR (1.85 ppm) and ^{13}C NMR (252.7 ppm for the carbonylic carbon and 42.2 ppm for the methyl carbon) spectra are very close to those found for other Ru(II) acetyl complexes.[21] ^{19}F NMR of **4** showed only the signal of the BAr′$_4$ anion, indicating that no incorporation of triflate was taking place.

An X-ray determination carried out on a single crystal of **4** (Figure 2, Table 2) confirmed the [Ru(C(O)CH$_3$)(cym)(phen)]BAr′$_4$ formulation. However, again the low accuracy of the results and, in particular, the presence of disorder affecting the acetyl group (see Experimental Section) would render meaningless a discussion of the metrical parameters.

The reaction of alkynyl complexes with electrophiles typically affords vinylidenes.[2a,b] Obtention of an acyl as the product of the protonation of alkynyl complexes has been found in several instances[2a,22] and takes place by the reaction of a highly reactive vinylidene intermediate with traces of water present in the reaction mixture. For (arene)ruthenium complexes, the related reaction of the cationic vinylidene [RuCl(CC(H)Ph)(η^6-C$_6$Me$_6$)(PMe$_3$)]$^+$ with methanol to yield a methoxycarbene has been reported.[6] (Arene)ruthenium vinylidenes were

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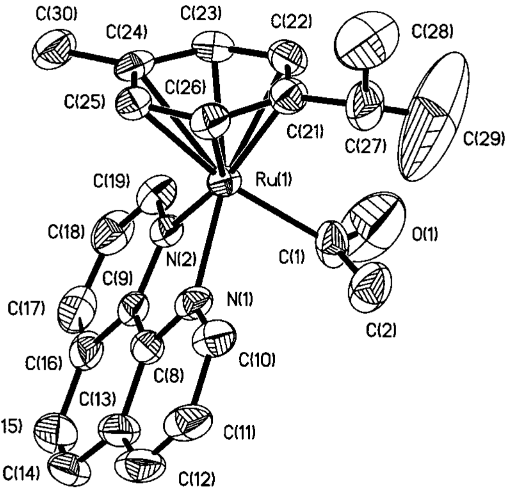
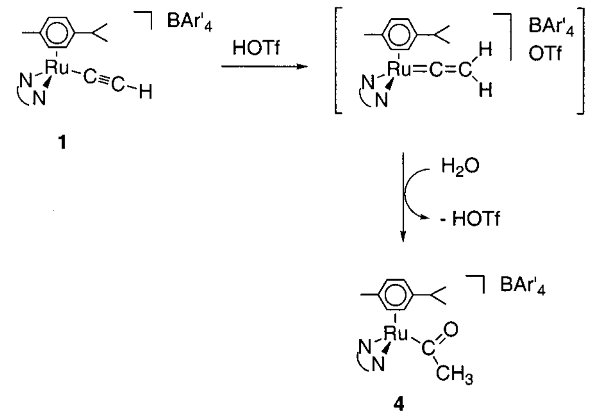


Figure 2. Thermal ellipsoid (drawn at the 30% probability level) plot of **4**.

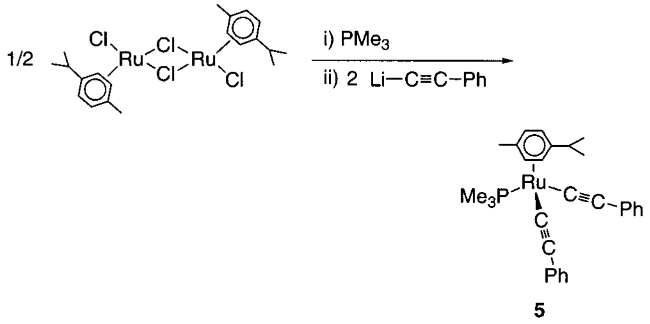
Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complex 4

Ru(1)−C(1)	2.084(11)	Ru(1)−N(2)	2.088(8)
Ru(1)−N(1)	2.088(8)	Ru(1)−C(23)	2.203(9)
Ru(1)−C(26)	2.207(10)	Ru(1)−C(22)	2.209(9)
Ru(1)−C(21)	2.256(9)	Ru(1)−C(25)	2.308(9)
Ru(1)−C(24)	2.321(8)	C(1)−O(1)	1.252(15)
C(1)−C(2)	1.312(17)		
C(1)−Ru(1)−N(2)	85.5(4)	C(1)−Ru(1)−N(1)	81.4(3)
N(2)−Ru(1)−N(1)	78.2(3)	O(1)−C(1)−C(2)	120.0(12)
O(1)−C(1)−Ru(1)	124.6(9)	C(2)−C(1)−Ru(1)	112.8(9)

Scheme 3



Scheme 4



found to be more reactive than Cp derivatives, and only the (arene)ruthenium vinylidene mentioned above could be spectroscopically detected. This enhanced reactivity has been attributed to an increase in the electrophilic character of the vinylidene group as a result of a decrease in the electronic density at the metal center. The protonation of a cationic alkynyl such as **1** would give a dicationic vinylidene complex. This species should possess a high electrophilic character, and, hence, it is not surprising that it reacts instantaneously (the acyl **4** was the only ruthenium species observed by ^{1}H NMR when the reaction of **1** with HOTf was carried out in CD_2Cl_2 in a NMR tube) with traces of water (Scheme 3). The overall reaction leading to the obtention of **4** involves the formal addition of the elements of OH^- from water. The remaining H^+ of H_2O plus the OTf anion (which would be one of the counterions in the dicationic vinylidene intermediate) would regenerate HOTf. Thus, the reaction is catalytic in triflic acid. However, attempts to carry out the reaction with less than stoichiometric amounts of triflic acid led to decreased yields. In our opinion, this reflects the need of a strongly acidic medium to achieve the initial protonation of the cationic alkynyl.

Since the reaction of (arene)ruthenium vinylidenes with alcohols is known to afford alcoxycarbenes,[5,23] we added HOTf to a solution of **1** in a mixture CH_2Cl_2/MeOH, expecting that the trapping of the initially formed vinylidene by MeOH would give a cationic methoxycarbene. No reaction took place. We believe that the presence of methanol reduces the acidity of the medium to a level that is not enough for the protonation of **1** to take place.

Synthesis and Characterization of the Bis(alkynyl) [Ru(CCPh)$_2$(cym)(PMe$_3$)] (5). The complex [RuCl$_2$(cym)(PMe$_3$)][24] reacted with excess lithium phenylacetylide to yield, after workup, the complex [Ru(CCPh)$_2$(cym)(PMe$_3$)] (**5**) (Scheme 4).

Integration of the ^{1}H NMR spectrum of **5** indicated the presence of two phenylacetylide groups in the molecule. An additional indication of the [Ru(CCPh)$_2$(cym)(PMe$_3$)] formulation for **5** is provided by the presence of a single doublet for the isopropyl CH_3 groups. A complex [RuX(CCPh)(cym)(PMe$_3$)] would be chiral, and, therefore, two doublets for the diastereotopic CH_3 groups would be seen. The ^{13}C NMR spectrum of **5** showed weak signals a 115.3 and 113.5 ppm for the acetylenic carbons of the two equivalent alkynyl ligands. The signal at 113.5 ppm showed a 35 Hz coupling with phosphorus (no resolved coupling is seen in the slightly broadened signal at 115.3 ppm) and is therefore assigned to the carbon atom directly bound to ruthenium. The IR spectrum of the bis(acetylide) **5** displays a single band at 2089 cm^{-1}. In (arene)ruthenium(II) complexes such as **5**, the angles between the monodentate ligands must be considerably less than 180°. Hence, two C−C stretching bands in the IR spectrum are expected for the two independent, active vibration modes of a bis(acetylide) complex like **5**. In octahedral dicarbonyl complexes, the presence of one or two C−O stretching bands is a safe diagnostic of the trans or cis mutual disposition of the carbonyl ligands.[25] A single C−C band,

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[23] (a) Pilette, D.; Ouzzine, K.; Le Bozec, H.; Dixneuf, P. H. *Organometallics* **1992**, *11*, 809. (b) Devanne, D.; Dixneuf, P. H. *J. Organomet. Chem.* **1990**, *390*, 371.

[24] Bennett, M. A.; Smith, K. A. *J. Chem. Soc., Dalton Trans.* **1974**, 233.

[25] Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 2nd ed; John Wiley & Sons: New York, 1994; p 259.

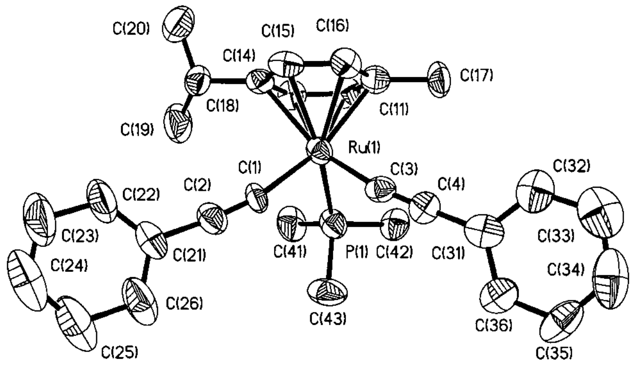

Figure 3. Thermal ellipsoid (drawn at the 30% probability level) plot of **5**.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Complex 5

Ru(1)−C(3)	2.003(9)	Ru(1)−C(1)	2.026(6)
Ru(1)−C(12)	2.242(7)	Ru(1)−C(13)	2.243(7)
Ru(1)−C(11)	2.245(8)	Ru(1)−C(16)	2.260(8)
Ru(1)−P(1)	2.267(2)	Ru(1)−C(14)	2.268(8)
Ru(1)−C(15)	2.276(8)	C(1)−C(2)	1.168(7)
C(2)−C(21)	1.474(10)	C(3)−C(4)	1.139(9)
C(4)−C(31)	1.447(11)		

C(3)−Ru(1)−C(1)	91.5(3)	C(3)−Ru(1)−P(1)	81.5(3)
C(1)−Ru(1)−P(1)	85.3(2)	C(2)−C(1)−Ru(1)	168.0(9)
C(1)−C(2)−C(21)	174.5(10)	C(4)−C(3)−Ru(1)	168.6(9)
C(3)−C(4)−C(31)	178.7(12)		

however, is observed for several *cis*-bis(acetylides),[1,26] as for complex **5**. To our knowledge, no explanation has been given for this apparent inconsistency, and we have to assume that the two stretching modes in bis(acetylide) complexes fall in a narrow wavenumber range and, due to the intrinsic width of the IR bands, the two bands often overlap.

The reaction of [$RuCl_2$(η^6-C_6Me_6)(PMe_3)] with an excess of LiCCPh in hexane/MeOH to give the alkynyl complex [RuCl(CCPh)(η^6-C_6Me_6)(PMe_3)] was reported by Le Bozec and Dixneuf.[6] We have found that the employment of THF (instead of hexane/MeOH mixtures) is needed to obtain the bis(alkynyl) product **5**. The reaction of [RuCl(CCPh)(cym)(PMe_3)] with additional LiCCPh in THF yields [$Ru(CCPh)_2$(cym)(PMe_3)], **5**, although this stepwise synthesis of **5** does not offer any advantage.

In chlorinated solvents, **5** undergoes a slow (12 h in $CDCl_3$, 60 h in CD_2Cl_2) transformation to [$RuCl_2$(cym)(PMe_3)]. ^{31}P NMR monitoring of this decomposition in CD_2Cl_2 showed the presence of [RuCl(CCPh)(cym)(PMe_3)][27] as an intermediate. In contrast, **5** is indefinitely stable in THF or toluene solutions.

The molecular structure of complex **5** was determined by single-crystal X-ray diffraction (Figure 3, Table 3).

The geometry of **5** can be described as a three-legged piano stool. The Ru−$C_{alkynyl}$ distances, 2.003(9) and 2.026(6) Å, are similar to those found in other ruthenium alkynyl complexes.[18,28] Triple bond carbon−carbon distances are in the typical range of transition metal alkynyls.[1] The angle between the two metal-bonded alkynyl carbon atoms and ruthenium, 91.3(5)°, is only slightly greater than the Cl−Ru−Cl angles (88.1° and 88.18(3)°) found in [$RuCl_2(PR_3)$(arene)] complexes[29] and is almost identical to the C−Ru−C angle found in the octahedral *cis*-bis(alkynyl) [$Ru(CCPh)_2L$], L = P($CH_2CH_2PPh_2$)$_3$ (90.7(5)°).[28a]

The synthesis of bis(acetylide) transition metal complexes that can be used as metalloligands with a tweezer geometry toward a second metal center has attracted the attention of several research groups.[3c,g,k,25,30−33] Most of these bis(acetylide) complexes are based on group 4 metallocene fragments[3c,30,32] or are square-planar palladium or platinum compounds.[3d,g,30e,31a,b] As far as we know, the only ruthenium complex that was used as tweezer metalloligand is the octahedral compound *cis*-[$Ru(Ph_2PCH_2PPh_2)_2(CCFc)_2$] (Fc = ferrocenyl), which acts as a chelate toward CuI with a C−Ru−C angle of 82.6(3)°.[34] Complex **5** is the first pseudotetrahedral piano-stool ruthenium bis(alkynyl) complex, and the fact that the angle between the alkynyl groups is similar to those found in tweezer-like bimetallic complexes[35] is encouraging with regard to the use of **5** as a metalloligand.

Experimental Section

General Procedures. All manipulations were carried out under nitrogen using standard Schlenk techniques or in a drybox. Solvents were distilled from freshly wired Na (hexanes), Na/benzophenone (Et_2O and THF), NaOMe (MeOH), and CaH_2 (CH_2Cl_2). CD_2Cl_2 and $CDCl_3$ were degassed by three freeze−pump−thaw cycles, dried over molecular sieves (MS4A), and stored in the dark. Elemental analyses were obtained using a Perkin-Elmer 240-B microanalyzer. The IR and NMR spectra were recorded on Perkin-Elmer FT 1720-X and Bruker AC-200 or AC-300 spectrometers, respectively. [{RuCl(cym)}$_2$(μ-Cl)$_2$][8] and NaBAr′$_4$[9] were prepared according to literature procedures. All other chemicals were used as received from commercial sources. ^{13}C NMR signals of the BAr′$_4$ anion are almost identical in all complexes and are given only for **1**.

Synthesis of [Ru(CCH)(cym)(phen)]BAr′$_4$ (1). A mixture of [{RuCl(cym)}$_2$(μ-Cl)$_2$] (0.026 mmol, 0.016 g), 1,10-phenanthroline (0.055 mmol, 0.010 g), and NaBAr′$_4$ (0.055 mmol, 0.048 g) was dissolved in THF and stirred for 2 h. The resulting orange solution of [RuCl(cym)(phen)]BAr′$_4$ was transferred via

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(26) James, S. L.; Younus, M.; Raithby, P. R.; Lewis, J. *J. Organomet. Chem.* **1997**, *543*, 233.

(27) Spectroscopic data for [RuCl(CCPh)(cym)(PMe_3)]: IR ν(CC) (CH_2Cl_2): 2095 cm^{-1}. ^{1}H NMR ($CDCl_3$): 7.30 (m, 5H, *Ph*), 5.76 (apparent triplet $J = 5.87$ Hz), 5.16, 5.08 (d (5.87), 4H, C_6H_4), 2.85 (sep, 1H, C*H*(Pr^i)), 2.15 (s, 3H, CH_3-C_6H_4), 1.65 (d(10.75), 9H, PCH_3), 1.28 (apparent triplet $J = 6.65$, 6H, CH_3(Pr^i)). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 10.24.

(28) (a) Bianchini, C.; Frediani, P.; Masi, D.; Peruzzini, M.; Zanobini F. *Organometallics* **1994**, *13*, 4616. (b) Pedersen, A.; Tilset, M.; Folting, K.; Caulton, K. G. *Organometallics* **1995**, *14*, 875.

(29) (a) Bennett, M. A.; Robertson, G. B.; Smith, A. K. *J. Organomet. Chem.* **1972**, *43*, C41. (b) Elsegood, M. R. J.; Tocher, D. A. *Polyhedron* **1995**, *14*, 3147.

(30) (a) Lang, H.; Herres, M.; Zsolnai, L.; Imhof, W. *J. Organomet. Chem.* **1991**, *409*, C7. (b) Lang, H.; Frosch, W.; Wu, I. Y.; Blau, S.; Nuber, B. *Inorg. Chem.* **1996**, *35*, 6266. (c) Delgado, E.; Hernández, E.; Mansilla, N.; Moreno, M. T.; Sabat, M. *J. Chem. Soc., Dalton Trans.* **1999**, 533. (d) Back, S.; Rheinwald, G.; Lang, H. *J. Organomet. Chem.* **2000**, *601*, 93. (e) Frosch, W.; del Villar, A.; Lang, H. *J. Organomet. Chem.* **2000**, *602*, 91.

(31) (a) Ara, I.; Berenguer, J. R.; Forniés, J.; Lalinde, E. *Inorg. Chim. Acta* **1997**, *264*, 199. (b) Ara, I.; Berenger, J. R.; Eguizábal, E.; Forniés, J.; Lalinde, E.; Martínez, F. *Organometallics* **1999**, *18*, 4344. (c) Falvello, L. R.; Forniés, J.; Gómez, J.; Lalinde, E.; Martín, A.; Moreno, M. T.; Sacristán *Chem. Eur. J.* **1999**, *5*, 474. (d) Adams, C. J.; James, S. L.; Liu, X.; Raithby, P. R.; Yellowlees, L. J. *J. Chem. Soc., Dalton Trans.* **2000**, 63.

(32) (a) Lang, H.; Zsolnai, L. *J. Organomet. Chem.* **1991**, *406*, C5. (b) Back, S.; Pritzkow, H.; Lang, H. *Organometallics* **1998**, *17*, 41. (c) Back, S.; Rheinwald, G.; Lang, H. *Organometallics* **1999**, *18*, 4119.

(33) Lang, H.; George, D. S. A.; Rheinwald, G. *Coord. Chem. Rev.* **2000**, *206−207*, 101.

(34) Zhu, Y.; Clot, O.; Wolf, M. O.; Yap, G. P. A. *J. Am. Chem. Soc.* **1998**, *120*, 1812.

(35) For typical angles see refs 28a, 31c, and 32b,c.

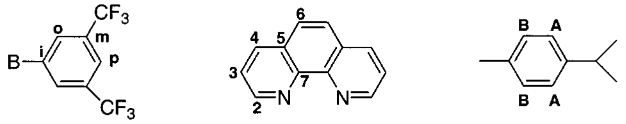

Figure 4. Atom-labeling schemes for phenanthroline, BAr′$_4$, and cym.

cannula onto sodium acetylide (0.15 mmol, 0.008 g). The best results were obtained when the commercial sodium acetylide was washed with hexanes (3 × 10 mL) and briefly dried in vacuo, leaving a loose solid that was weighted in a drybox. The resulting slurry was stirred for 12 h. After filtration (diatomaceous earth), the solvent was removed in vacuo. The residue was extracted with CH_2Cl_2 (3 × 10 mL), and the solution was filtered a second time. This second filtration in CH_2Cl_2 was found to remove traces of pyrophoric sodium acetylide. The solution was concentrated by in vacuo evaporation to a volume of 5 mL. Slow diffusion of hexane into this solution at −20 °C produced orange crystals of **1**. A single crystal obtained in this way was used for the X-ray analysis. Yield: 0.042 g, 61%. Anal. Calcd for $C_{56}H_{35}BF_{24}N_2Ru$: C, 51.57; H, 2.68; N, 2.15. Found: C, 51.31; H, 2.50; N, 2.10. IR ν(CC) (CH_2Cl_2): 1974 cm^{-1}. ^{1}H NMR (CD_2Cl_2): 9.17 (dd (5.0 and 1.0), 2H, H_2), 8.56 (dd (8.2 and 1.1), 2H, H_4), 8.02 (s, 2H, H_5), 7.88 (dd (8.45 and 5.37), 2H, H_3), 7.76 (m, 8H, H_o), 7.57 (m, 4H, H_p), 5.57, 5.73, 5.58, 5.56 (q AB, 4H, C_6H_4), 2.78 (sep, 1H, C*H*(Pr^i)), 2.25 (s, 3H, CH_3-C_6H_4), 1.37 (s, 1H, CC*H*), 1.09 (d (6.9), 6H, CH_3(Pr^i)). ^{13}C{^{1}H} NMR (CD_2Cl_2): 162.1 (q (49.9), C_i), 154.8 (s, C_2), 146.4 (s, C_7), 138.2 (s, C_4), 135.1 (s, br, C_o), 131.2 (s, C_5), 129.1 (qq, $^2J_{CF} = 31$, $^4J_{CF} = 3$, C_m), 128.1 (s, C_6), 127.9 (s, C_3), 126.1 (q(272), C_F), 119.9 (s, *C*-Pr^i), 117.8 (s, C_p), 105.9 (s, *C*-CH_3), 99.9 (s, Ru*C*C), 88.9 (s, RuC*C*), 88.9 (s, C_A), 87.1 (s, C_B), 31.8 (s, *C*H(Pr^i)), 22.4 (s, *C*H_3 of Pr^i), 19.0 (s, *C*H_3-C_6H_4).

Synthesis of [Ru(CCPh)(cym)(phen)]BAr′$_4$ (2). To a solution of [RuCl(cym)(phen)]BAr′$_4$, prepared as described for **1**, 0.05 mmol in THF (20 mL), was added AgOTf (0.055 mmol, 0.014 g), and the mixture was stirred for 2 h in the absence of light at room temperature. The color of the resulting solution was yellow, and a white solid (AgCl) precipitated. The solution of [Ru(OTf)(cym)(phen)]BAr′$_4$ obtained in this way was transferred through a cannula tipped with filter paper to a solution of LiCCPh, freshly prepared from HCCPh (0.09 mmol, 9.8 μL) and *n*-BuLi (0.09 mmol, 56 μL, 1.6 M solution in hexanes) in 10 mL of THF at −78 °C. MeOH (2 mL) was added, and the mixture was stirred at room temperature for 12 h. The color of the solution changed from yellow to brown. The solvent was evaporated under reduced pressure, and the residue was extracted with CH_2Cl_2 and filtered. A yellow solution was obtained, which was concentrated in vacuo to a volume of 5 mL. Addition of hexane (20 mL) gave **2** as a yellow microcrystalline solid, which was dried under reduced pressure. Yield: 0.040 g, 63%. Anal. Calcd for $C_{62}H_{39}BF_{24}N_2Ru$: C, 53.96; H, 2.84; N, 2.03. Found: C, 53.80; H, 2.72; N, 1.85. IR ν(CC) (CH_2Cl_2): 2111 cm^{-1}. ^{1}H NMR ($CDCl_3$): 9.22 (dd (5.1 and 1.2), 2H, H_2), 8.59 (dd (8.24 and 1.2), 2H), 8.05 (s, 2H, H_5), 7.93 (dd (8.24 and 5.50), 2H, H_3), 7.75 (m, 8H, H_o), 7.57 (m, 4H, H_p), 6.90 (m, 5H, *Ph*), 5.81, 5.78, 5.63, 5.61 (q AB, 4H, C_6H_4), 2.85 (sep, 1H, C*H*(Pr^i)), 2.28 (s, 3H, CH_3-C_6H_4), 1.16 (d (7), 6H, CH_3-(Pr^i)). ^{13}C{^{1}H} NMR ($CDCl_3$): 154.1 (s, C_2), 145.9 (s, C_7), 137.7 (s, C_4), 130.9 (s, Ph), 130.5 (s, C_5), 128.4 (s, C_6), 127.6 (s, C_3), 127.5 (s, *Ph*), 125.5 (s, *Ph*), 121.6 (s, *C*-Pr^i), 111.2 (s, Ru*C*C), 105.9 (s, RuC*C*), 102.4 (s, *C*-CH_3), 87.5 (s, C_A), 86.7 (s, C_B), 31.5 (s, *C*H(Pr^i)), 22.2 (s, *C*H_3 of Pr^i), 18.5 (s, *C*H_3-C_6H_4).

Synthesis of [Ru(CCSiMe$_3$)(cym)(phen)]BAr′$_4$ (3). A solution of LiCCSiMe$_3$, prepared from HCCSiMe$_3$ (0.049 mmol, 7 μL) in 10 mL of THF and *n*-BuLi (0.05 mmol, 30 μL, 1.6 M solution in hexanes) at −78 °C, was transferred onto a solution of [Ru(OTf)(cym)(phen)]BAr′$_4$ (0.05 mmol), prepared as described above, in 20 mL of THF at −78 °C. The reaction mixture was allowed to reach room temperature and stirred for 12 h. The workup was as described for **1**, affording **3** as a brown microcrystalline solid. Yield: 0.055 g, 82%. Anal. Calcd for $C_{59}H_{43}BF_{24}N_2RuSi$: C, 51.46; H, 3.12; N, 2.03. Found: C, 51.61; H, 3.25; N, 1.75. IR ν(CC) (CH_2Cl_2): 2039 cm^{-1}. ^{1}H NMR ($CDCl_3$): 9.07 (dd (5.1 and 1.2), 2H, H_2), 8.43 (dd (8.3 and 1.3), 2H, H_4), 7.91 (s, 2H, H_5), 7.84 (dd (8.45 and 5.37), 2H, H_3), 7.70 (m, 8H, H_o), 7.49 (m, 4H, H_p), 5.68, 5.66, 5.48, 5.46 (q AB, 4H, C_6H_4), 2.81 (sep, 1H, C*H*(Pr^i)), 2.13 (s, 3H, CH_3-C_6H_4), 1.11 (d (6.9), 6H, CH_3(Pr^i)), −0.37 (s, 9H, SiCH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): 154.1 (s, C_2), 146.0 (s, C_7), 137.6 (s, C_4), 130.5 (s, C_5), 127.4 (s, C_6), 126.2 (s, C_3), 118.9 (s, *C*-Pr^i), 111.4 (s, Ru*C*C), 108.5 (s, RuC*C*), 105.9 (s, *C*-CH_3), 87.5 (s, C_A), 86.9 (s, C_B), 31.5 (s, *C*H(Pr^i)), 22.2 (s, *C*H_3 of Pr^i), 18.4 (s, *C*H_3-C_6H_4), 0.7 (s, Si*C*H_3).

Synthesis of [Ru(C(O)CH$_3$)(cym)(phen)]BAr′$_4$ (4). To a solution of [Ru(CCH)(cym)(phen)]BAr′$_4$ (0.04 mmol, 0.050 g) in 10 mL of CH_2Cl_2 was added CF_3SO_3H (0.03 mmol, 3 μL). The color immediately changed from brown to orange. The solution was stirred for 10 min and filtered through diatomaceous earth, the solvent was eliminated in vacuo, and the residue was washed with hexane (3 × 10 mL). Slow diffusion of hexane in a concentrated solution of **4** in CH_2Cl_2 at −20 °C afforded orange crystals, one of which was used for the X-ray analysis. Yield: 0.065 g, 88%. Anal. Calcd for $C_{56}H_{37}BF_{24}N_2ORu$: C, 50.84; H, 2.80; N, 2.12. Found: C, 50.78; H, 2.65; N, 2.10. IR ν(CO) (CH_2Cl_2): 1631 cm^{-1}. ^{1}H NMR ($CDCl_3$): 9.27 (dd (5.0 and 1.0), 2H, H_2), 8.39 (dd (8.2 and 1.1), 2H, H_4), 7.86 (s, 2H, H_5), 7.79 (dd (8.45 and 5.37), 2H, H_3), 7.73 (m, 8H, H_o), 7.59 (m, 4H, H_p), 5.62, 5.59, 5.32, 5.29 (q AB, 4H, C_6H_4), 2.52 (sep, 1H, C*H*(Pr^i)), 2.17 (s, 3H, CH_3-C_6H_4), 1.85 (s, 3H, C(O)-CH_3), 0.88 (d (6.9), 6H, CH_3(Pr^i)). ^{13}C{^{1}H} NMR ($CDCl_3$): 252.7 (s, *CO*), 154.8 (s, C_2), 145.0 (s, C_7), 137.1 (s, C_4), 130.1 (s, C_5), 127.5 (s, C_6), 112.6 (s, C_3), 115.0 (s, *C*-Pr^i), 106.6 (s, *C*-CH_3), 76.9 (s, C_A), 76.5 (s, C_B), 42.2 (s, C(O)*C*H_3), 31.2 (s, *C*H(Pr^i)), 22.4 (s, *C*H_3 of Pr^i), 18.5 (s, *C*H_3-C_6H_4).

Synthesis of [Ru(CCPh)$_2$(cym)(PMe$_3$)] (5). [{RuCl(cym)}$_2$-(μ-Cl)$_2$] (0.16 mmol, 0.10 g) and PMe$_3$ (0.32 mmol, 28 μL) in 10 mL of THF were allowed to react for 30 min. The resulting solution of [RuCl$_2$(cym)(PMe$_3$)] was transferred onto a solution of LiCCPh, freshly prepared from HCCPh (0.65 mmol, 72 μL) and *n*-BuLi (0.65 mmol, 406 μL, 1.6 M solution in hexanes) in 10 mL of THF at −78 °C. The solution was stirred for 12 h. The solvent was evaporated in a vacuum, and the residue was extracted with CH_2Cl_2 and filtered through diatomaceous earth. Recrystallization with hexane gave a brown microcrystalline solid. A crystal suitable for an X-ray determination was obtained by slow diffusion of hexane into a solution of **5** in Et_2O at −20 °C. Compound **5** is moisture sensitive. It slowly decomposes in $CDCl_3$ (12 h) and in CD_2Cl_2 (60 h) to yield [RuCl$_2$(cym)(PMe$_3$)] as the major product. Yield: 0.097 g, 59%. Anal. Calcd for $C_{29}H_{33}PRu$: C, 69.11; H, 6.55. Found: C, 69.05; H, 6.49. IR ν(CC) (CH_2Cl_2): 2089 cm^{-1}. ^{1}H NMR ($CDCl_3$): 7.30 (m, 10H, *Ph*), 5.57, 5.55, 5.53, 5.51 (q AB, 4H, C_6H_4), 2.86 (sep, 1H, C*H*(Pr^i)), 2.23 (s, 3H, CH_3-C_6H_4), 1.65 (d(11.2), 9H, PCH_3), 1.29 (d (6.9), 6H, CH_3(Pr^i)). ^{13}C{^{1}H} NMR (CD_2Cl_2): 131.3 (s, C_o and C_m, Ph), 129.9 (s, C_i, Ph), 124.2 (s, C_p, Ph), 115.3 (s, RuC*C*), 113.5 (d(35.0), Ru*C*C), 104.4 (s, *C*-Pr^i), 102.7 (s, *C*-CH_3), 94.3 (s, C_A), 91.4 (s, C_B), 32.1 (s, *C*H(Pr^i)), 24.3 (s, *C*H_3 of Pr^i), 19.6(d(36.2), P*C*H_3), 19.2 (s, *C*H_3-C_6H_4). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 15.06.

X-ray Crystal Structure Determination of Complexes 1, 4, and 5. In each case, a suitable crystal was attached to a glass fiber and transferred to a Bruker AXS SMART 1000 diffractometer with graphite-monochromatized Mo Kα X-radiation and a CCD area detector. A hemisphere of the reciprocal space was collected up to $2\theta = 48.6°$. Raw frame data were integrated with the SAINT[36] program. The structure

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[36] *SAINT+.SAX* area detector integration program, Version 6.02; Bruker AXS, Inc.: Madison, WI, 1999.

Table 4. Crystal Data and Refinement Details for Complexes 1, 4, and 5

	1	**4**	**5**
formula	$C_{61}H_{39}BF_{24}N_2Ru$	$C_{56}H_{39}BF_{24}N_2ORu$	$C_{19}H_{33}PRu$
fw	1367.82	1323.77	513.59
cryst syst	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$C2/c$
a, Å	13.083(7)	13.267(2)	25.243(7)
b, Å	13.917(7)	13.868(2)	11.725(3)
c, Å	16.421(8)	16.370(3)	18.631(5)
α, deg	73.54(1)	74.013(4)	90
β, deg	85.12(1)	87.625(5)	106.644(5)
γ, deg	74.64(1)	75.313(5)	90
V, Å^3	2765(2)	2799.5(9)	5284(2)
Z	2	2	8
T, K	293	293	295
ρ_{calc}, g cm^{-3}	1.64	1.57	1.29
F(000)	1368	1324	2128
λ (Mo Kα), Å	0.71073	0.71073	0.71073
cryst size, mm; color	0.37 × 0.25 × 0.2, yellow	0.2 × 0.2 × 0.2, yellow	0.13 × 0.12 × 0.1, yellow
μ, mm^{-1}	0.409	1.570	0.667
scan range, deg	$1 \leq \theta \leq 21$	$1 \leq \theta \leq 21$	$1 \leq \theta \leq 21$
abs corr	SADABS	SADABS	SADABS
corr factors (min., max.)	1.000, 0.847	1.000, 0.7845	1.000, 0.7904
no. of reflns measured	12694	12874	11144
no. of indep reflns	5741	5841	2762
no. of data/restraints/params	5741/0/760	5841/0/771	2762/0/286
goodness-of-fit on F^2	1.053	1.056	0.783
no of reflns obsd, $I \geq 2\sigma(I)$	4975	4891	1397
R1 (obsd reflns)	0.0669	0.0771	0.0406
wR2 (all data)	0.1862	0.2291	0.0703

was solved by direct methods with SHELXTL.[37] An empirical absorption correction was applied with the program SADABS.[38] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were set in calculated positions and refined as riding atoms with a common thermal parameter. All calculations were made with SHELXTL. In the structure of **4** several peaks were found in the region of the acetyl group, suggesting the existence of several disordered positions which arise from rotation of the acetyl group around the Ru−C(1) bond. Unfortunately, it was not possible to construct a satisfactory model for this situation, and only the main orientation has been included. Moreover, the final model must be considered as an average which contains disordered O(1) and C(2) interchanging positions.

Additional material is available from the Cambridge Crystallographic Data Center, including atomic coordinates, thermal parameters, and a full list of bond lengths and angles.

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Supporting Information Available: Tables giving positional and thermal parameters, bond distances, and bond angles for **1**, **4**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[37] Sheldrick, G. M. *SHELXTL*, An integrated system for solving, refining and displaying crystal structures from diffraction data, Version 5.1; Bruker AXS, Inc.: Madison, WI, 1998.

[38] Sheldrick, G. M. *SADABS*, Empirical Absorption Correction Program; University of Göttingen, 1997.