Carbon–Carbon and Carbon–Nitrogen Bond Formation Mediated by Ruthenium(II) Complexes: Synthesis of (1*H*)-Isoquinolinium Derivatives

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New cycloruthenated complexes can be obtained by transmetalation of $[(\eta^6\text{-arene})RuCl_2]_2$ (arene = C_6H_6 or *i*-PrC_6H_4Me-1,4) with several mercury- or zinc-metalated [(*N*,*N*-dimethylamino)-methyl]benzene derivatives. Intramolecular C—H activation using these amines with $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ affords the same cycloruthenated complexes though in lower yield. The resulting complexes are of the type $(\eta^6\text{-arene})RuCl(C,N)$ [(C,N) = $C_6H_4CH_2NMe_2$-2, (*R*)-(+)-$C_6H_4CH(Me)NMe_2$-2, $C_6H_2(OCH_2O\text{-}2,3)CH_2NMe_2$-6] and have a rigid structure containing a five-membered Ru—C—C—C—N chelate ring, both in the solid state and in solution. Reaction of the cycloruthenated complexes with internal alkynes can lead to the formation of novel Ru(0) sandwich complexes of the type $[(\eta^6\text{-arene})Ru(\eta^4\text{-}C_6H_4CH(R)NMe_2CR^1{=}CR^2\text{-}1,2)]^+[PF_6]^-$ (R = H, Me; R^1, R^2 = alkyl, aryl, or carboxyalkyl). The formation of the heterocyclic units occurs with good chemo- and regioselectivities, asymmetric alkynes being incorporated in such a way that the acetylene carbon with the sterically least demanding substituent becomes attached to the nitrogen atom of the arylamine. Oxidative demetalation induced by $CuBr_2$ allows the isolation of the free organic (1*H*)-isoquinolium derivatives $[C_6H_4CH_2NMe_2CR^1{=}CR^2\text{-}1,2]^+[PF_6]^-$ (R^1 = R^2 = Et, Ph; R^1 = CO_2Et, R^2 = Ph) under mild conditions and in reasonable yields.

Introduction

The success of metal-mediated organic synthesis is mainly due to the unique ability of a metal to activate ligands to which it is directly bound. At the same time, the metal serves as a template that directs the course of the reactions that result from ligand activation. Consequently, an organometallic reagent or homogeneous catalyst can often replace several steps of a conventional synthetic method.[1] At present, for versatility, no transition metal can compete with palladium that serves in an increasing number of processes for manufacturing either bulk or fine chemicals.[2] Currently, the application of transition metal-mediated cycloadditions of alkynes in organic synthesis is attracting much attention, and again palladium turns out to be of importance in this field.[3,4] The reactions of cyclopalladated compounds with alkynes, for instance, afford new synthetic pathways to heterocyclic compounds featuring chemo- and regioselective C–C and C–Y (Y = N, S) bond formations.[3c,4] In this palladium-mediated heterocycle synthesis, however, many examples are known of reactions that afford carbocyclic instead of heterocyclic products *via* reactions involving multiple alkyne insertions[5a-d] and undesired carbo-annulations.[5d-f]

This paper presents the first results of a project aimed at determining whether other transition metal complexes can display behavior analogous (and perhaps complementary) to that of their palladated counterparts. A possible candidate for such research may be ruthenium since several cyclometalated ruthenium complexes have already been reported[6] and in a few cases these complexes

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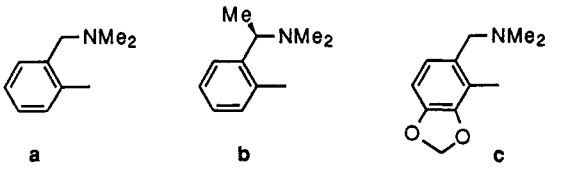
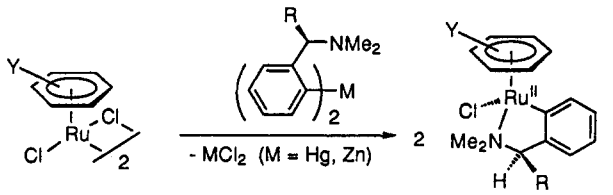
Chart I



Scheme I



1a : Y = H; R = H
1b : Y = H; R = Me
2a : Y = 1-*i*Pr, 4-Me; R = H

have even been demonstrated to react with alkynes. An example is provided by the cyclometalated phosphine complex $CpRu\{C_6H_4PPh_2\}PPh_3$ which reacts with hexafluoro-2-butyne to give a complex that results from double alkyne insertion into the Ru–σ-C bond of the starting material.[7] Only very recently, a ruthenium-mediated synthesis of a heterocycle involving the insertion of an alkyne into a Ru–C bond was reported: 2,3-diphenylindole could be prepared from diphenylacetylene and a cycloruthenated azobenzene complex.[8]

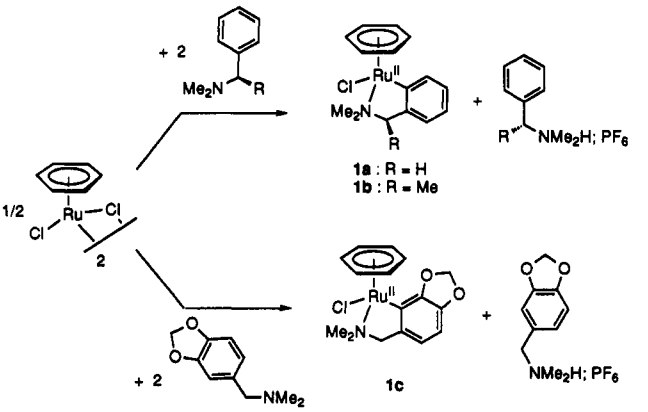
We have investigated the possibility of converting $[(\eta^6\text{-arene})RuCl_2]_2$ compounds into cycloruthenated complexes employing the arylamine systems shown in Chart I as chelating ligands. In this paper we report the full details of the synthesis and characterization of the resulting organoruthenium complexes. Their reactions with alkynes that lead to interesting organic products are also described.

Results and Discussion

Synthesis of Cyclometalated Ruthenium(II) Derivatives. $[(\eta^6\text{-arene})RuCl_2]_2$ species provide ideal starting materials for the synthesis of the new complexes described here because they are air stable and easily accessible with a wide range of arenes.[9] Furthermore, they react cleanly with dialkyl- and diarylmercury compounds affording their corresponding monoalkyl and -aryl analogues, as reported by Zelonka and Baird.[10] In our first attempts to obtain cycloruthenated complexes we have, therefore, used related transmetalation reactions. The new cycloruthenated complexes **1a,b** and **2a** are conveniently prepared from $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ or $[(\eta^6\text{-cymene})RuCl_2]_2$ (cymene = i-PrC_6H_4Me-1,4) and the mercury- or zinc-metalated derivatives of the amine ligands **a** and **b** (Scheme I).

Complexes **1a,b** and **2a** are isolated by extraction with CH_2Cl_2 and crystallize readily when Et_2O is added to the concentrated extracts; yields range from 20 to 85%. The solids can be handled in air and are thermally stable. It is noteworthy that similar reactions performed with an organolithium derivative of the ligand **a**, $[Li(C_6H_4CH_2NMe_2\text{-}2)]_4$, are not clean and do not afford the expected products **1a** or **2a** due to reduction to elemental ruthenium.

Scheme II



In an alternative approach, we have tried to synthesize the complexes **1** and **2** *via* intramolecular C–H activation starting from the corresponding $[(\eta^6\text{-arene})RuCl_2]_2$ and one of the amines **a**–**c**. When these reactions are performed with 2 equiv of the amine **a** and in the presence of 1 equiv of sodium hexafluorophosphate, the cycloruthenated complex **1a** can be obtained in 38% yield (Scheme II). Under the same conditions, only traces (<5%) of the related complex **2a** are formed. Similar reactions allowed the synthesis of **1b** (13% yield) and **1c** (52% yield).

The syntheses involving intramolecular C–H activation reactions indicate that these occur in much the same way as has been reported for palladium-mediated cyclometalations, *i.e. via* a process involving attack of an electrophilic metal center on the C–H bond of the arylamine.[11a,b] Such an electrophilic substitution obviously depends on both the electron density on the metal and that in the C–H bond that is to be activated. In this case, the process is controlled by the electronic nature of the arene ligand attached to the ruthenium center and the substituents on the arylamine, in such a way that it is promoted by the combination of a less π-electron-donating arene ligand on ruthenium together with a more electron-rich arylamine. As a consequence, $[(\eta^6\text{-benzene})RuCl_2]_2$ is a better cyclometalating agent than $[(\eta^6\text{-cymene})RuCl_2]_2$, benzene being the weaker π-electron donor.[12] The observation that the most facile cycloruthenation was that performed with $[(\eta^6\text{-benzene})RuCl_2]_2$ and the amine **c** is again consistent with the electrophilic reaction pathway since the arylamine **c** contains a dioxymethylene substituent that enhances the electron density in its aryl unit. The electron-donating dioxymethylene substituent is absent in the ligands **a** and **b**, and consequently, lower yields were obtained in the cycloruthenation of these latter ligands. It is however important to note that the site of metalation by ruthenium on this ligand **c** is notably different from that observed with palladium. In this latter case the palladation occurs at the less sterically hindered position (i.e. at position 6)[11b,c] whereas the ruthenation takes place at position 2 (ortho to the CH_2NMe_2 and the OCH_2 groups).

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(12) A nice illustration of this is the gradual increase in π-complex stability that is observed on progressive methyl substitution of benzene: Brown, H. C.; Brady, J. D. *J. Am. Chem. Soc.* **1952**, *74*, 3570. Nolan, S. P.; Martin, K. L.; Stevens, E. D.; Fagan, P. J. *Organometallics* **1992**, *11*, 3947.

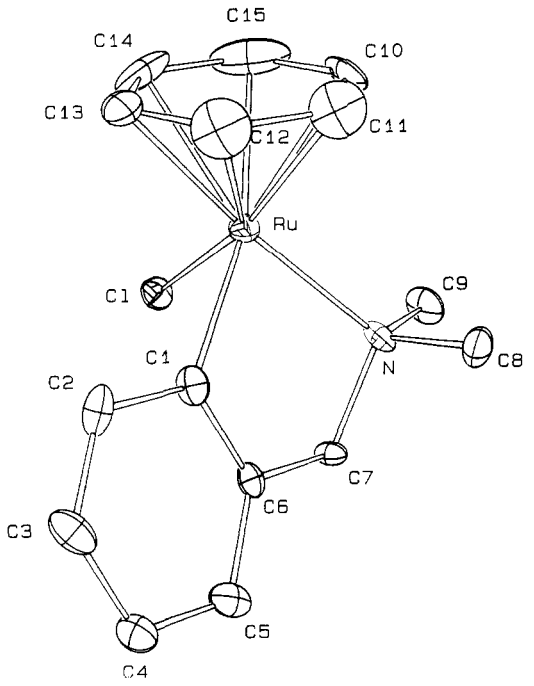


Figure 1. Structure of $(\eta^6\text{-}C_6H_6)RuCl(C_6H_4CH_2NMe_2\text{-}2)$ (**1a**) in the crystal. ORTEP drawing with 50% probability thermal ellipsoids.

Table I. Selected Bond Distances (Å) and Angles (deg) for $(\eta^6\text{-}C_6H_6)RuCl(C_6H_4CH_2NMe_2\text{-}2)$ (1a)

	Bond Distances		
Ru–C(1)	2.08(1)	Ru–N	2.148(8)
Ru–Cl	2.430(2)	Ru–C(η^6-arene)[a]	2.18
	Bond Angles		
C(1)–Ru–Cl	86.0(3)	C(1)–Ru–N	78.1(3)
N–Ru–Cl	86.6(2)		

[a] Mean value; distance range from 2.13(2) to 2.22(2) Å.

Although the route to cycloruthenated complexes *via* C–H activation instead of transmetalation has not been optimized yet, we consider it as a very important alternative since it avoids the use of stoichiometric reagents containing zinc or mercury. One should also note that no examples of the intramolecular metalation of tertiary amines by Ru(II) have been hitherto reported.[6,11b] Moreover, in combination with the reactions of these complexes with alkynes (*vide infra*), it provides a promising possibility for ruthenium-mediated C–H functionalizations.

Structure of the Cycloruthenated Complexes 1 and 2 in the Solid State and in Solution. In order to elucidate the stereochemistry of the ligand distribution around ruthenium and to serve as a reference for structural proposals based on spectroscopic experiments, an X-ray structural analysis of **1a** was carried out. Suitable crystals of **1a** were obtained from a nitromethane solution. The molecular structure involves the packing of four discrete monomeric molecules in the unit cell. An ORTEP drawing of **1a**, along with the adopted numbering scheme is shown in Figure 1; selected bond distances and angles are given in Table I. The unit cell belongs to the noncentrosymmetric space group $Pca2_1$ and as a consequence contains only one enantiomer of **1a**, the ruthenium atom providing the stereogenic element. Obviously, the complex spontaneously resolves in the crystal but the bulk material is racemic, as there is no asymmetric induction in its synthesis. The X-ray structure shows that **1a** is a mononuclear ruthenium species that has a "three-legged piano-stool" geometry, the η^6-coordinated arene is in the "stool" position while the "legs" comprise the arylamine [bonded *via* C(1) and N] and a chlorine atom. The short Ru–N bond of 2.148(8) Å is not significantly longer than the sum of the covalent radii of Ru and N, 1.42 and 0.70 Å, respectively,[13,14] which in indicative of a rigid coordinative Ru–N bond.

The ^1H and ^{13}C NMR data for the ruthenium amine complexes **1a–c** and **2a** are consistent with the structural proposals shown in Schemes I and II. All complexes provide temperature independent NMR spectra which indicate that they have a rigid structure not only in the solid state but also in solution. A useful NMR probe is provided by the unsubstituted (η^6-benzene) ligands of the complexes **1a–c** that cause characteristic upfield shifted ^1H (δ 5.56–5.34) and ^{13}C (δ 85.8–85.2) resonances. For the substituted (η^6-arene) in **2a**, more complicated, but similarly upfield shifted arene resonances are observed. For the NMe_2 unit for each of the cycloruthenated complexes, two anisochronous proton resonances are found. From this observation one can conclude that the nitrogen center is a stable tetrahedral array that is reflecting the chirality of the adjacent ruthenium center. The resulting diastereotopicity of the NMe_2 groups can only occur when pyramidal inversion of the nitrogen center is blocked, *i.e.* when the ruthenium–nitrogen interaction is stable on the NMR time scale. This observation of two NMe signals proves that in solution the complexes have a five-membered Ru–C–C–C–N chelate ring as also found in the solid state structure of **1a**.

In the case of **1b**, the ruthenium center is not the only chiral entity in the molecule since the arylamine ligand **b** also contains a stereogenic center resulting from methyl substitution at its benzylic carbon atom. Therefore, it is interesting to note that the solution NMR data for **1b** correspond to only one of the two possible diastereoisomers. Even ^1H NMR spectra of the crude reaction mixtures, from which **1b** was isolated, showed no resonances that could be attributed to the other possible diastereoisomer. This illustrates that the formation of **1b** is a reaction that is stereochemically controlled. Moreover, when solutions of **1b** are monitored in time, no trace of the other diastereoisomer emerges, a finding that provides added evidence for the ruthenium center being a chiral entity that does not easily epimerize on the NMR time scale. We assign to this complex a structure in which the methyl substituent is *endo* to the η^6-benzene ring. Such a structure minimizes the steric interference that this methyl group experiences from the chlorine atom that is present in its vicinity. Recent studies on a related imido ruthenacyclic complex indicate that this is the thermodynamically more stable complex.[6e]

Reaction of the Cycloruthenated Complexes 1 and 2 with Internal Alkynes. Since we have described in this paper two routes to cycloruthenated complexes, we are now in a position to study their reactivity with applications in mind toward metal-mediated organic synthesis. In palladium chemistry the amines **a–c** are known to be easily cyclometalated and the resulting cyclopalladated complexes have served in several studies that centered on the functionalization of C–H bonds.[4a–c,e,5a,e,f,15] One of our contributions to this field

(13) Howard, J.; Woodward, P. J. *J. Chem. Soc., Dalton Trans.* **1975**, 59.
(14) Bennett, M. J.; Mason, R. *Nature* **1965**, *205*, 760.

Scheme III

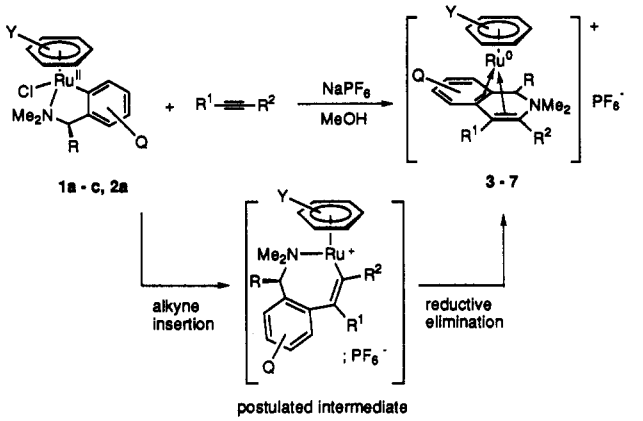
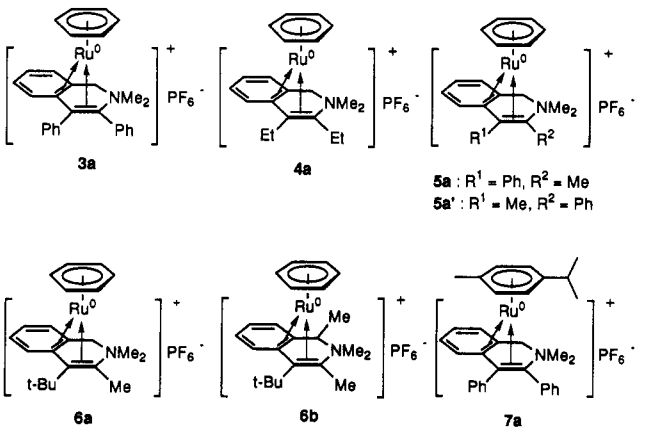


Chart II



concerns the reactions of cyclopalladated compounds with 1 equiv of an alkyne that can, under specific conditions, lead to interesting organic heterocycles.[4b,c] Reactions of the cycloruthenated complexes **1** and **2** with alkynes are therefore also worth studying: they cannot only provide information with regard to what extent cycloruthenated complexes can mimmic the reactivity of their cyclopalladated counterparts but may also demonstrate whether the scope of the heterocycle synthesis can be expanded by changing from palladium to ruthenium.

In MeOH at room temperature, complexes **1a,b** and **2a** react in the presence of 1 or more equiv of internal alkynes and a slight excess of $NaPF_6$ to afford the isoquinolinium complexes **3–7** (Scheme III and Chart II). An overview of the reactions that were performed is given in Table II; the resulting isoquinolinium derivatives along with their adopted numbering scheme are shown on Chart II.

The reactions listed in Table II provide an indication of the scope of the isoquinolinium formation. Best results are obtained with electron rich alkynes containing small substituents (entries 1–3, 7), alkynes with bulkier substituents giving rise to slower reactions with lower yields (entries 4 and 5). In the reactions with electron poor alkynes no isoquinolinium ruthenium(0) species (entry 8 and 9) could be isolated in pure form. Finally, the cycloruthenated complex **1c** that contains an arylamine with an electron-donating dioxymethylene function was found to give unclean reactions (entry 6) when the procedure described above was used.[25]

Table II. Reactions of the Cycloruthenated Complexes with Alkynes

entry	compd	$R^1C{\equiv}CR^2$	product[a]	yield (%)
1	**1a**	PhC≡CPh	**3a**	90
2	**1a**	EtC≡CEt	**4a**	90
3	**1a**	MeC≡CPh	**5a,5a'**	80[b]
4	**1a**	*t*-BuC≡CMe	**6a**	49
5	**1b**	*t*-BuC≡CMe	**6b**	20
6	**1c**	PhC≡CPh		0[c]
7	**2a**	PhC≡CPh	**7a**	80
8	**1a**	$EtO_2CC{\equiv}CPh$		*d*
9	**1a**	$MeO_2CC{\equiv}CCO_2Me$		*e*

[a] Structural formulas of the ruthenium-containing reagents are given in Scheme I, and those of the products, in Chart II. [b] Total yield of the two regioisomers **5a** and **5a'** that are obtained in a 4:1 ratio respectively. [c] The starting materials react, but no product can be isolated. [d] The free organic isoquinolinium derivative can be isolated in 10% yield; see text. [e] Product is formed (^1H NMR) in high yield but decomposes during workup.

In CH_2Cl_2 in the absence of $NaPF_6$, **1a** does not react with alkynes. However, when $NaPF_6$ is added to the reaction mixtures, slow formation of isoquinolinium complexes occurs. This indicates that a polar medium is necessary for smooth isoquinolinium formation. The reason for this probably originates in the fact that the cycloruthenated complexes must be converted to a more active cationic form, as is also mandatory for related palladium-mediated reactions.[3c,4] The solvent MeOH, in combination with $NaPF_6$, is very likely to efficiently perform this task.

In the case of asymmetric alkynes, the isoquinolinium complexes **6a** and **6b** are formed with good regioselectivities. On the basis of the structure of **6b** that was determined by X ray diffraction (*vide infra*), one can deduce that this selectivity may originate from steric factors. Since the bulkiest group is found on the carbon atom adjacent to the previously ruthenated aryl unit of **1**, with the smallest group being on the carbon atom adjacent to the NMe_2 unit, one can conclude that the incorporation of the alkyne occurs in such a way that the least steric interference occurs between the (η^6-arene)-ruthenium center and the incoming alkyne. In the reaction of **1a** with MeC≡CPh, however, the difference in the steric bulk of the alkyne substituents is much less pronounced and, consequently, two regioisomers, **5a** and **5a'**, are formed.

The isoquinolinium formations reported in this paper can be envisaged according to the pathway we have proposed for related reactions involving palladium,[3c] the regioselectivity being much the same in both cases.[4b,c] It is interesting to note that the regioselectivity that is observed in the present case is just the opposite to that observed by Larock.[3e] This important difference may be the result of a different reaction pathway in the latter case since in Larock's system *ortho*-iodinated primary or secondary arylamine derivatives have been used as starting materials.[16]

Thus the first step for the isoquinolinium formation likely involves insertion of the alkyne into the Ru–C bond[17] of complexes **1** and **2** (see Scheme III). The subsequent formation of the isoquinolinium complexes may then be rationalized as an overall reductive elimination. This

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reductive elimination has to compete with a process involving insertion of a second alkyne, a reaction that is known to limit the scope of several palladium-mediated isoquinolinium syntheses.[5,18]

Since we were never able to detect products arising from multiple alkyne insertions, the reductive elimination (from formally Ru^{2+} to Ru^0) must occur very readily. One should note that Ru^{2+} is generally difficult to reduce and that we therefore have found an interesting exception to this rule.[19]

It is interesting to note that the scope of the ruthenium-mediated method, as reported here, when the cyclometalated ligand is the *N,N*-dimethylbenzylamine (**a**), is somewhat broader than related palladium chemistry. In the latter, the obtention of the corresponding isoquinolinium derivatives using this ligand is only possible with ethyl 3-phenylpropynoate and even then only if the monoinserted organopalladium intermediate is isolated, polyinsertion occurring otherwise.[4b]

Structure of the Isoquinolinium Complexes. In order to elucidate the stereochemistry of the ligand distribution around ruthenium and to gain insight as to the way the isoquinolinium unit is bonded to the metal center, an X-ray structural analysis of **6b** was carried out. Of all the isoquinolinium complexes reported here, **6b** is likely to be the most interesting since its isoquinolinium moiety results from the combination of an optically active amine and an asymmetric alkyne. Knowledge of the exact structure of the complex therefore, may help to rationalize not only its formation but also the stereochemistry of that process. Suitable crystals of **6b** were obtained from a dichloromethane solution into which *n*-hexane was allowed to slowly diffuse. The molecular structure involves the packing of four discrete monomeric molecules in the unit cell. An ORTEP drawing of **6b**, along with the adopted numbering scheme, is shown in Figure 2; selected bond distances and angles are given in Table III. The X-ray structure shows that **6b** is a mononuclear ruthenium species that has a sandwich structure involving η^6-coordination of an arene ligand and η^4-coordination of a cationic heterocycle [*via* C(13) and C(14) of the former alkyne and C(7) and C(12) of the arylamine] to a formally zerovalent ruthenium center.

From the structure of **6b**, it is apparent that the addition of the alkyne has resulted in the formation of both C–C and C–N bonds with the arylamine ligand of **1b**. Concomitant with these bond formations is the reduction of the ruthenium center from Ru(II) to Ru(0). An analogous sandwich structure that also involves a combination of η^6- and η^4-bonded ligands has been reported for $(\eta^6\text{-}C_6H_6)$-$Ru(\eta^4\text{-}COD)$.[20]

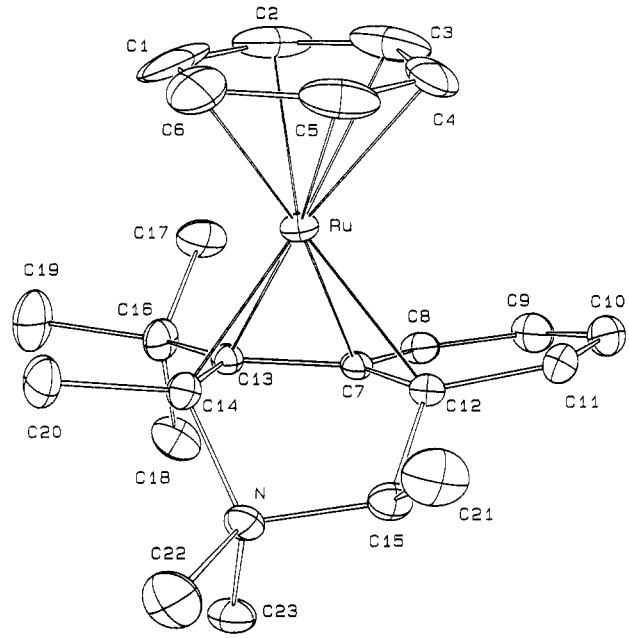

Figure 2. ORTEP plot of the cationic part of $[(\eta^6\text{-}C_6H_6)Ru\{(R)(+)\text{-}C_6H_4CH(Me)NMe_2CMe{=}C\text{-}t\text{-}Bu\text{-}1,2\}]^+[PF_6]^-$ (**6b**) (50% probability thermal ellipsoids).

Table III. Selected Bond Distances (Å) and Angles (deg) for the Cation of $[(\eta^6\text{-}C_6H_6)Ru\{(R)(+)\text{-}C_6H_4CH(Me)NMe_2\text{-}CMe{=}C\text{-}t\text{-}Bu\text{-}1,2\}]^+[PF_6]^-$ (6b)

	Bond Distances		
Ru–C(7)	2.180(5)	Ru–C(12)	2.194(6)
Ru–C(13)	2.123(6)	Ru–C(14)	2.104(6)
C(7)–C(12)	1.480(9)	C(7)–C(13)	1.465(8)
C(13)–C(14	1.465(9)	C(12)–C(15)	1.532(9)
C(14)–N	1.568(8)	C(15)–N	1.508(9)
Ru–C(η^6-arene)[a]	2.22		
	Bond Angles		
C(13)–Ru–C(14)	40.6(2)	C(7)–Ru–C(13)	39.8(2)
C(7)–Ru–C(12)	39.5(2)	C(14)–N–C(15)	109.0(5)
C(15)–C(12)–C(7)	121.6(5)	C(12)–C(7)–C(13)	115.3(5)
C(7)–C(13)–C(14)	109.1(5)	C(13)–C(14)–N	113.0(5)

[a] Mean value; distances range from 2.182(9) to 2.270(9) Å.

Demetalation of the Isoquinolinium Complexes. Initially, we have tried to liberate the heterocyclic unit from the isoquinolinium complexes by a displacement reaction with excess of a Lewis base. Surprisingly, these attempts only led to loss of the η^6-coordinated arene ligands while the isoquinolinium unit remained bonded to the ruthenium center. For instance, when dissolved in acetonitrile, complexes **3a** and **7a** quantitatively liberated benzene and cymene, respectively, in very clean reactions. Liberation of the isoquinolinium ligands, however, was not observed, regardless of whether the solutions were heated or irradiated with UV light. Attempts to perform the desired displacement with pyridine, triphenylphosphine, CO, or 1,3-cyclohexadiene were also unsuccessful. Finally, we tried to free the isoquinolinium derivatives in an oxidative fashion and found an easy procedure to achieve our goal.

In MeOH, in the presence of $CuBr_2$ or $CuCl_2$, complexes **3a** and **7a** react with virtually quantitative liberation of the respective heterocyclic products (Scheme IV, procedure

(16) The formation of the C–N bond between palladated primary or secondary amines and alkynes might well be due to a nucleophilic addition of the amine onto the alkyne coordinated to the metal center rather than to an insertion of the alkyne into the Pd–C bond followed by reductive elimination: Maassarani, F.; Pfeffer, M.; Spencer, J.; Wehman, E. *J. Organomet. Chem.*, in press.

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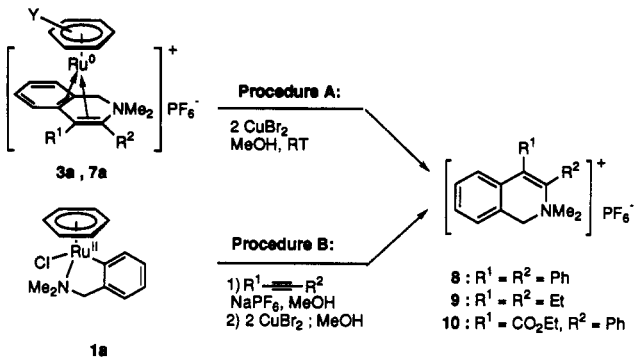
Scheme IV



A). This process has been studied in more detail using complex **3a**. Treatment of **3a** in MeOH with 2 equiv of $CuBr_2$ leads to the slow liberation of the isoquinolinium derivative **8** that could be isolated in 80% yield after workup involving extraction with CH_2Cl_2 and flash chromatography over Al_2O_3. When the same reaction is performed with only 1 equiv of $CuBr_2$, a mixture of the starting complex **3a** and **8** (in an approximately 1:1 ratio) is obtained after workup. This finding indicates that the heterocycle liberation probably involves 2e oxidation of the ruthenium starting complex to give (η^6-arene)ruthenium dihalide. The ruthenium dihalide formed could not be recovered after the reaction, probably due to its low solubility and the adopted workup procedure. However, when workup involving flash chromatography was omitted, the related reaction of the cymene complex **7a** with 2 equiv of $CuCl_2$ was shown to produce the isoquinolinium derivative **8**, this time together with $[(\eta^6\text{-cymene})RuCl_2]_2$ in about a 1:1 ratio.

An interesting aspect of the oxidative heterocycle liberation procedure is that the same solvent (MeOH) is used as that for the reaction of the cycloruthenated complexes **1** and **2** with alkynes. It is therefore possible to synthesize the organic products in a single pot procedure starting from easily accessible starting materials (Scheme IV, Procedure B), with yields that do not differ much from those obtained when the synthesis is performed starting from the isoquinolinium complexes **3–7**. For instance, the isoquinolinium complex **8** is obtained in the same yield regardless of whether it is synthesized in a one pot, two-step, procedure starting from the cycloruthenated complex **1a** or in one step from the isoquinolinium complex **3a**. No attempts have been made so far to isolate the isoquinolinium derivatives from complexes **5a–7a**.

Another interesting aspect of the one pot procedure is that it may allow the synthesis of isoquinolinium derivatives for which it is not possible to isolate the corresponding ruthenium complexes. For instance, the reaction of the cycloruthenated complex **1a** with ethyl 3-phenylpropynoate does not allow the isolation of a pure ruthenium complex. However, the isoquinolinium derivative formed can be obtained in pure form after oxidative liberation with $CuBr_2$.

The exact nature of the species involved in the oxidative heterocycle liberation, as well as the possibility of recycling the ruthenium-containing starting materials, is currently being studied in more detail.

Conclusions

The results reported here nicely show the potential of cycloruthenated complexes for the formation of C–C and C–N bonds. These bond formations were shown to occur in ways related (and sometimes complementary) to that of their cyclopalladated counterparts. The insertion of alkynes into the Ru–C bond of cycloruthenated complexes combined with the oxidative liberation of the resulting organic products provides a synthetic tool for the metal-mediated synthesis of isoquinolinium derivatives with, in the particular case reported here, a scope that is larger than that for related palladium-mediated isoquinolinium synthesis. Interesting features are the strict monoinsertion of the alkyne and the facile and mild method for the isolation of the resulting organic products.

Experimental Section

General Comments. All reactions were performed in Schlenk-type flasks under oxygen- and water-free nitrogen. Solvents were dried and distilled under nitrogen: diethyl ether over benzophenone ketyl, *n*-hexane over sodium, dichloromethane over P_2O_5, acetonitrile over CaH_2, and acetone over $CaCl_2$. The ^1H NMR spectra were recorded at 200.13 or 300.13 MHz, ^{13}C NMR spectra at 50.32 or 75.47 MHz, on FT-Bruker instruments (SY200, AC200, or AC300) and externally referenced to TMS. Column chromatography was performed under N_2 by using Al_2O_3 as support (Aluminiumoxid 90, Merck). Elemental analyses were performed by the Service Central de Microanalyse du CNRS. $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$,[9] $[(\eta^6\text{-cymene})RuCl_2]_2$,[9] and $Hg(C_6H_4CH_2NMe_2\text{-}2)_2$[21] were prepared according to literature references; $Zn\{(R)\text{-}C_6H_4CH(Me)NMe_2\text{-}2\}_2$ was prepared in analogy to the literature procedure for $Zn(C_6H_4CH_2NMe_2\text{-}2)_2$.[21]

(η^6-C_6H_6)RuCl($C_6H_4CH_2NMe_2$-2) (1a). Route 1. By Transmetalation. A suspension of $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ (0.75 g, 1.5 mmol) and $Hg(C_6H_4CH_2NMe_2\text{-}2)_2$ (0.75 g, 1.6 mmol) in MeCN (10 mL) was stirred during 5 h at 20 °C. The solvent was removed *in vacuo*, and the yellow-green residue was extracted with CH_2Cl_2 (20 mL). The extract was subjected to flash chromatography over Al_2O_3 using CH_2Cl_2/MeOH (20:1). A yellow fraction was collected from which the solvent was removed *in vacuo*, leaving a yellow residue that was dissolved in CH_2Cl_2 (5 mL). From this solution, yellow product (0.88 g, 85%) can be precipitated by adding Et_2O and hexane.

Route 2. By Cyclometalation. A suspension of $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ (0.25 g, 0.50 mmol), *N,N*-dimethylbenzylamine (0.3 mL, 2 mmol), and $NaPF_6$ (0.17 g, 1.0 mmol) in CH_2Cl_2 (5 mL) was stirred at 20 °C during 18 h. The resulting dark-yellow suspension was filtered and the filtrate subjected to flash chromatography over Al_2O_3 using CH_2Cl_2/MeOH (20:1). Further workup as in route 1 yielded 0.13 g (38%) of yellow product. Anal. Calcd for $C_{15}H_{18}NRuCl$: C, 51.6; H, 5.2; N, 4.0. Found: C, 50.5; H, 5.1; N, 4.2.[22] ^1H NMR (200.13 MHz, $CDCl_3$, 298 K): δ 8.17 (d, 1H, Ar, $^3J(HH)$ = 7.3 Hz), 7.06 (m, 1H, Ar), 6.90 (m, 2H, Ar), 5.34 (s, 6H, C_6H_6), 4.32 and 2.82 (AX, 2H, CH_2N, $^2J(HH)$ = 13.0 Hz), 3.26 and 2.70 (2s, 6H, NMe_2). $^{13}C\{^1H\}$ NMR (50.32 MHz, $CDCl_3$, 298 K): δ 165.9, 146.6, 137.6, 125.9, 123.1, 122.5 (C_6H_4), 85.2 (C_6H_6), 70.9 (CH_2N), 57.9 and 55.2 (NMe_2).

(η^6-C_6H_6)RuCl{(*R*)-$C_6H_4CH(Me)NMe_2$-2} (1b). Route 1. By Transmetalation. To a stirred suspension of $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ (1.0 g, 2.0 mmol) in THF (15 mL) was dropwise added a solution of $Zn\{(R)\text{-}C_6H_4CH(Me)NMe_2\text{-}2\}_2$ (0.76 g, 2.1 mmol) in Et_2O (20 mL). The resulting orange mixture was stirred for 15 h followed by removal of the solvent in vacuo. The residue was extracted with CH_2Cl_2 (10 mL), followed by workup involving flash chromatography as described for **1a**, route 1. Yield: 0.30 g (20%) of orange product.

Route 2. By Cyclometalation. The procedure is the same as that for **1a** (route 2); yield 0.070 g (13%). ^1H NMR (200.13

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(22) We have no satisfactory explanation for the low C values found for these new ruthenium complexes.

MHz, $CDCl_3$, 298 K): δ 8.25 (d, 1H, Ar, ^3J(HH) = 7.4 Hz), 7.09 and 7.00 (2t, 2H, Ar, ^3J(HH) = 7.2 and 7.4 Hz, respectively), 6.77 (d, 1H, Ar, ^3J(HH) = 7.4 Hz), 5.34 (s, 6H, C_6H_6), 4.38 (q, 1H, C*H*(Me)N, ^3J(HH) = 6.85 Hz), 3.39 and 2.48 (2s, 6H, NMe_2), 1.19 (d, 3H, CH(*Me*)N). $^{13}C\{^1H\}$ NMR (50.32 MHz, $CDCl_3$, 298 K): δ 137.3, 126.1, 123.5, 123.2 (nonquaternary C_6H_4), 85.8 (C_6H_6), 67.4 (*C*H(Me)N), 52.3 and 49.6 (NMe_2), 9.3 (CH(*Me*)N).

(η^6-C_6H_6)RuCl{C_6H_2(OCH_2O-2,3)CH_2NMe_2-6} (1c). A suspension of [(η^6-C_6H_6)$RuCl_2$]$_2$ (0.25 g, 0.50 mmol), 1-[(*N*,*N*-dimethylamino)methyl]-3,4-(methylenedioxy)benzene (0.36, 2.0 mmol), and $NaPF_6$ (0.17 g, 1.0 mmol) in CH_2Cl_2 (6 mL) was stirred at 20 °C during 18 h. The resulting dark-brown suspension was filtered, and the filtrate was stripped *in vacuo*. The residue was washed with hexane and subsequently subjected to flash chromatography over Al_2O_3 using acetone as the eluent. Further workup as for **1a**, route 1; yield 0.20 g (52%) of orange product. Anal. Calcd for $C_{16}H_{18}NO_2RuCl$: C, 48.9; H, 4.6; N, 3.5. Found: C, 47.6; H, 4.6; N, 3.7.[22] ^1H NMR (200.13 MHz, $CDCl_3$, 298 K): δ 6.48 and 6.42 (AB pattern, 2H, Ar, ^3J(HH) = 7.6 Hz), 6.06 and 5.93 (2d, 2H, OCH_2O, ^2J(HH) = 1.5 Hz), 5.56 (s, 6H, C_6H_6), 4.28 and 2.74 (AX pattern, 2H, CH_2N, ^2J(HH) = 12.7 Hz), 3.24 and 2.67 (2s, 6H, NMe_2). $^{13}C\{H\}$NMR (75.47 MHz, $CDCl_3$, 298 K): 153.7, 143.5, 142.3, 141.5 (quaternary C_6H_2), 115.5, 103.4 (nonquaternary C_6H_2), 98.9 (OCH_2O), 84.6 (C_6H_6), 70.95 (CH_2N), 57.7 and 55.1 (NMe_2).

(η^6-cymene)RuCl($C_6H_4CH_2NMe_2$-2) (2a). An initially red solution of [(η^6-cymene)$RuCl_2$]$_2$ (2.12 g, 3.46 mmol) and Hg(C_6H_4-CH_2NMe_2-2)$_2$ (1.74 g, 3.71 mmol) in CH_2Cl_2 (30 mL) was stirred at 20 °C for 3 days. The resulting red solution with a white suspension of $HgCl_2$ was filtered and the volume of the filtrate reduced *in vacuo* to 10 mL. Addition of Et_2O (50 mL) caused the product to precipitate as an orange powder; yield 2.18 g (78%). Anal. Calcd for $C_{19}H_{28}NClRu$: C, 56.35; H, 6.47; N, 3.46. Found: C, 57.05; H, 6.40; N, 3.36. ^1H NMR (300.13 MHz, $CDCl_3$, 298 K): δ 8.04 (d, 1H, $C_6H_4CH_2$, ^3J(HH) = 7.5 Hz), 7.07 (m, 1H, $C_6H_4CH_2$), 6.87 (m, 2H, $C_6H_4CH_2$), 5.53, 5.33, 4.52, 4.49 (4d, 4H, C_6H_4, ^3J(HH) = 5.8), 4.27 and 2.84 (AX, 2H, CH_2N, ^2J(HH) = 12.8 Hz), 3.09 and 2.66 (2s, 6H, NMe_2), 2.96 (apparent septet, 1H, C*H*Me_2, ^3J(HH) = 6.9 Hz), 2.04 (s, 3H, *Me*C_6H_4), 1.30 and 1.11 (2d, 6H, CH*Me*$_2$, ^3J(HH) = 6.9 Hz). $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$, 298 K): δ 169.2, 146.6, 137.9, 126.2, 122.5, 121.6 ($C_6H_4CH_2$), 110.8, 93.9, 87.1, 87.0, 80.3, 78.3 (C_6H_4), 71.4 (CH_2N), 57.7 and 55.0 (NMe_2), 30.3 (*C*HMe_2), 23.2, 21.1 (CH*Me*$_2$), 17.9 (*Me*C_6H_4).

[(η^6-C_6H_6)Ru($C_6H_4CH_2NMe_2CPh$=CPh-1,2)]$^+$[PF_6]$^-$ (3a). An initially orange suspension of (η^6-C_6H_6)RuCl($C_6H_4CH_2NMe_2$-2) (0.35 g, 1.0 mmol), PhC≡CPh (0.20 g, 1.1 mmol), and $NaPF_6$ (0.19 g, 1.1 mmol) in MeOH (10 mL) was stirred for 1 h at 20 °C. The solvent was removed in vacuo from the resulting yellow suspension, leaving a sticky residue that was washed with Et_2O (2 × 10 mL) and extracted with CH_2Cl_2 (30 mL). The volume of the extract was reduced in vacuo to *ca.* 5 mL and Et_2O (50 mL) was added causing the precipitation of 0.57 g (90%) of yellow product that was pure by ^1H NMR spectroscopy. The compound can be obtained analytically pure by crystallization from hot MeOH. Anal. Calcd for $C_{29}H_{28}NPF_6Ru$: C, 54.72; H, 4.43; N, 2.20. Found: C, 54.55; H, 4.17; N, 2.23. ^1H NMR (200.13 MHz, $CDCl_3$, 298 K): δ 7.77 (d, 1H, Ar, ^3J(HH) = 7.5 Hz), 7.54–7.13 (m, 10H, Ar), 6.85 (m, 1H, Ar), 6.66 (m, 2H, Ar), 5.32 (s, 6H, C_6H_6), 4.33 and 3.41 (AX, 2H, CH_2N, ^2J(HH) = 14.0 Hz), 2.73 and 2.65 (2s, 6H, NMe_2). $^{13}C\{^1H\}$ NMR (50.32 MHz, CD_2Cl_2, 298 K): δ 136.9, 135.5, 131.3, 129.6, 129.2, 128.8, 128.4, 128.0, 127.3, 127.0, 122.9 (Ar and C=C), 88.2 (C_6H_6), 71.0 (CH_2N), 54.6 and 53.3 (NMe_2).

[(η^6-C_6H_6)Ru($C_6H_4CH_2NMe_2CEt$=CEt-1,2)]$^+$[PF_6]$^-$ (4a). The procedure is the same as that for **3a** except that (η^6-C_6H_6)RuCl($C_6H_4CH_2NMe_2$-2) (0.35 g, 1.0 mmol), 3-hexyne (0.12 mL, 1.1 mmol), and $NaPF_6$ (0.19 g, 1.1 mmol) reacted to give 0.49 g (90%) of a yellow product. The product was obtained analytically pure after flash chromatography over Al_2O_3 using CH_2Cl_2/MeOH (99:1) as the eluent. Anal. Calcd for $C_{21}H_{28}NPF_6Ru$: C, 46.49; H, 5.53; N, 2.58. Found: C, 46.09; H, 4.97; N, 2.65. ^1H NMR (200.13 MHz, CD_2Cl_2, 298 K): δ 7.55 (m, 1H, C_6H_4), 7.10 (m, 1H, C_6H_4), 6.75 (m, 2H, C_6H_4), 5.08 (s, 6H, C_6H_6), 3.91 and 3.27 (AX, 2H, CH_2N, ^2J(HH) = 13.2 Hz), 3.09 and 2.72 (2s, 6H, NMe_2), 2.96, 2.75, and 2.40 (3m, 4H, C$H_2$$CH_3$), 1.43 and 1.25 (2t, 6H, CH_2CH_3, ^3J(HH) = 7.5 Hz). $^{13}C\{^1H\}$ NMR (50.32 MHz, CD_2Cl_2, 298 K): δ 137.0, 126.9, 124.6, 121.5 (nonquartenary Ar), 86.2 (C_6H_6), 75.0 (CH_2N), 56.3 and 52.1 (NMe_2), 29.3 and 24.2 (CH_2CH_3), 16.3 and 15.9 (CH_2CH_3).

[(η^6-C_6H_6)Ru($C_6H_4CH_2NMe_2CMe$=CPh-1,2)]$^+$[PF_6]$^-$ (5a, 5a'). The procedure is the same as that for **3a** except that (η^6-C_6H_6)RuCl($C_6H_4CH_2NMe_2$-2) (0.35 g, 1.0 mmol), PhC≡CMe (0.14 g, 1.1 mmol), and $NaPF_6$ (0.19 g, 1.1 mmol) reacted to give 0.47 g (80%) of yellow product as a 4:1 ratio of regioisomers. ^1H NMR (200.13 MHz, $CDCl_3$, 298 K): (major isomer) δ 7.63–6.70 (m, 9H, Ar), 5.11 (s, 6H, C_6H_6), 4.05 and 3.19 (AX, 2H, CH_2N, ^2J(HH) = 13.5 Hz), 2.62 and 2.56 (2s, 6H, NMe_2), 2.47 (s, 3H, Me); (minor isomer) δ 7.68–7.10 (m, 7H, Ar), 6.75 (m, 2H, Ar), 5.30 (s, 6H, C_6H_6), 3.92 and 3.28 (AB, 2H, CH_2N, ^2J(HH) = 13.4 Hz), 3.15 and 2.90 (2s, 6H, NMe_2), 1.70 (s, 3H, Me).

[(η^6-C_6H_6)Ru($C_6H_4CH_2NMe_2CMe$=C-*t*-Bu-1,2)]$^+$[PF_6]$^-$ (6a). A suspension of (η^6-C_6H_6)RuCl($C_6H_4CH_2NMe_2$-2) (0.35 g, 1.0 mmol), 4,4-dimethyl-2-pentyne (0.34 g, 3.5 mmol), and $NaPF_6$ (0.19 g, 1.1 mmol) in MeOH (25 mL) was stirred during 1 h at 20 °C. During this period the reaction mixture changed from an orange suspension to a brown solution. Crude, brown product (0.19 g, 33%) crystallized from this solution after 18 h at −30 °C; a second batch (0.09 g, 16%) of the product could be obtained from the supernatant by concentrating this to 5 mL and storing it again at −30 °C for 18 h (total yield 0.28 g, 49%). Recrystallization from MeOH afforded a yellow product that was pure by ^1H NMR spectroscopy. Anal. Calcd for $C_{22}H_{30}NPF_6Ru$: C, 47.65; H, 5.45; N, 2.53. Found: C, 46.26; H, 5.06; N, 2.21.[22] ^1H NMR (200.13 MHz, $CDCl_3$, 298 K): δ 7.72, 7.12 (2m, 2H, C_6H_4), 6.62 (m, 2H, C_6H_4), 5.21 (s, 6H, C_6H_6), 3.81 and 3.07 (AX, 2H, CH_2N, ^2J(HH) = 13.6 Hz), 3.01 and 2.68 (2s, 6H, NMe_2), 2.15 (s, 3H, CH_3), 1.59 (s, 9H, *t*-Bu).

[(η^6-C_6H_6)Ru{(*R*)-(+)-C_6H_4CH(Me)NMe_2CMe=C-*t*-Bu-1,2}]$^+$[PF_6]$^-$ (6b). A suspension of (η^6-C_6H_6)RuCl{(*R*)-C_6H_4CH(Me)NMe_2-2} (0.28 g, 0.78 mmol), 4,4-dimethyl-2-pentyne (0.096 g, 1.0 mmol), and $NaPF_6$ (0.18 g, 1.1 mmol) in CH_2Cl_2 (5 mL) was stirred during 12 h at 20 °C. Filtration followed by flash chromatography over Al_2O_3 using CH_2Cl_2/MeOH (20:1) as the eluent allowed the isolation of 0.12 g (20%) of orange product. ^1H NMR (200.13 MHz, CD_2Cl_2, 298 K): δ 7.85 (m, 1H, C_6H_4), 7.15 (m, 1H, C_6H_4), 6.66 (m, 2H, C_6H_4), 5.22 (s, 6H, C_6H_6), 2.82 (q, 1H, C*H*(Me)N, ^3J(HH) = 6.5 Hz), 2.88 and 2.60 (2s, 6H, NMe_2), 2.14 (s, 3H, Me), 1.79 (d, 3H, CH(Me)N, ^3J(HH) = 6.5 Hz), 1.62 (s, 9H, *t*-Bu).

[(η^6-cymene)Ru($C_6H_4CH_2NMe_2CPh$=CPh-1,2)]$^+$[PF_6]$^-$ (7a). An initially orange suspension of η^6-cymene)RuCl($C_6H_4CH_2$-NMe_2-2) (0.54 g, 1.3 mmol), PhC≡CPh (0.28 g, 1.6 mmol), and $NaPF_6$ (0.25 g, 1.5 mmol) in MeOH (10 mL) was stirred during 18 h at 20 °C. The solvent was removed in vacuo from the resulting yellow suspension, leaving a sticky residue that was quickly extracted with CH_2Cl_2 (30 mL). The extract was stripped *in vacuo* and the resulting brown tar was triturated and washed with Et_2O (2 × 20 mL), leaving 0.74 g (80%) of crude, yellow product. The complex can be obtained analytically pure by crystallization from CH_2Cl_2/MeOH (1:2) at −30 °C. Anal. Calcd for $C_{33}H_{36}NPF_6Ru$: C, 57.22; H, 5.24; N, 2.02. Found: C, 57.38; H, 5.15; N, 1.96. ^1H NMR (300.13 MHz, $CDCl_3$, 298 K): δ 7.76–6.7 (m, 14H, Ar), 5.06, 4.65 (AB, 2H, C_6H_4, ^3J(HH) = 6.0 Hz), 4.88, 4.78 (AB, 2H, C_6H_4, ^3J(HH) = 6.0 Hz), 4.00 and 3.46 (AB, 2H, CH_2N, ^2J(HH) = 14.0 Hz), 2.73 and 2.55 (2s, 6H, NMe_2), 2.43 (apparent septet, 1H, C*H*Me_2, ^3J(HH) = 6.9 Hz), 2.34 (s, 3H, *p*-*Me* of cymene), 1.11 and 1.08 (2d, 6H, CH*Me*$_2$, ^3J(HH) = 6.5 Hz). (No reliable ^{13}C NMR data could be obtained due to decomposition of the complex in solution.)

[($C_6H_4CH_2NMe_2CPh$=CPh-1,2)]$^+$[PF_6]$^-$ (8a) (One Pot Procedure). A suspension of (η^6-C_6H_6)RuCl($C_6H_4CH_2NMe_2$-2), **1a** (0.35 g, 1.0 mmol), PhC≡CPh (0.21 g, 1.2 mmol), and $NaPF_6$ (0.18 g, 1.1 mmol) in MeOH (5 mL) was stirred during

Table IV. Crystal Data and Details of the Structure Determinations of Compounds 1a and 6b

	(a) Crystal Data	
formula	$C_{15}H_{18}ClNRu$ (**1a**)	$C_{23}H_{32}F_6NPRu$ (**6b**)
mol wt	348.84	568.6
color	red	yellow
cryst syst	orthorhombic	orthorhombic
space group	$Pca2_1$ (No. 29)	$P2_12_12_1$ (No. 19)
a (Å)	16.735(3)	10.482(3)
b (Å)	6.554(2)	13.903(4)
c (Å)	12.826(3)	15.999(4)
V (Å^3)	1406.8	2331.5
Z	4	4
D_{calc} (g cm^{-3})	1.647	1.620
μ (cm^{-1})	12.67	7.84
cryst size (mm)	0.22 × 0.28 × 0.32	0.17 × 0.20 × 0.30
	(b) Data Collection	
T (K)	293	293
θ_{min}, θ_{max}	2, 25	2, 27
radiation	Mo Kα (graphite monochromated)	Mo Kα (graphite monochromated)
wavelength (Å)	0.709 30	0.7107
$\Delta\omega$ (deg)	1.00 + 0.343 tan θ	1.00 + 0.343 tan θ
total no. of data	1469	3042
no. of obsd data, [$I > 3\sigma(I)$]	1065	2378
octants	$+h,+k,+l$	$+h,+k,+l$
	(c) Refinement	
final $R(F)$, $R_w(F)$	0.038, 0.067	0.038, 0.052
GOF	1.56	1.13
p	0.08	0.05
min/max abs	0.85/1.11	0.94/1.00

1 h at 20 °C; $CuBr_2$ (0.47 g, 2.1 mmol) was then added, and the resulting dark brown suspension was stirred overnight. The solvent was subsequently removed *in vacuo*, and the brown residue was extracted with CH_2Cl_2 (20 mL). Addition of Et_2O (30 mL) to the extract caused the precipitation of off-white product (0.37 g, 80%) that was pure by ^1H NMR spectroscopy. The compound can be obtained analytically pure in *ca.* 60% overall yield after flash chromatography over Al_2O_3 using CH_2Cl_2/MeOH (20:1) as the eluent. Anal. Calcd for $C_{23}H_{22}NPF_6$: C, 60.40; H, 4.85; N, 3.06. Found: C, 60.11; H, 4.59; N, 3.00. ^1H NMR (200.13 MHz, $CDCl_3$, 298 K): δ 7.58–6.85 (m, 14H, Ar), 5.09 (s, 2H, CH_2N), 3.28 (s, 6H, NMe_2). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2, 298 K): δ 140.4, 137.7, 134.3, 131.8, 131.5, 130.9, 130.8, 130.6, 130.1, 129.6, 128.8, 128.2, 128.0, 126.2 (Ar and C=C), 66.9 (CH_2N), 52.5 (NMe_2).

[($C_6H_4CH_2NMe_2CEt$=CEt-1,2)]$^+$[PF_6]$^-$ (9a). The procedure is the same as that for [($C_6H_4CH_2NMe_2CPh$=CPh-1,2)]$^+$[PF_6]$^-$ (**8a**) except that (η^6-C_6H_6)RuCl($C_6H_4CH_2NMe_2$-2) (0.36 g, 1.0 mmol), 3-hexyne (0.13 mL, 1.1 mmol), $NaPF_6$ (0.19 g, 1.2 mmol), and $CuBr_2$ (0.49 g, 2.2 mmol) were reacted to produce 0.22 g (60%) of off-white, crude product that was purified by flash chromatography to afford 0.14 g (40%) of the analytically pure compound. Anal. Calcd for $C_{15}H_{22}NPF_6$: C, 49.86; H, 6.14; N, 3.88. Found: C, 49.79; H, 6.05; N, 3.67. ^1H NMR (200.13 MHz, $CDCl_3$, 298 K): δ 7.45 (m, 4H, C_6H_4), 4.71 (s, 2H, CH_2N), 3.32 (s, 6H, NMe_2), 2.66 (m, 4H, CH_2CH_3), 1.36 and 1.20 (2t, 6H, CH_2CH_3, ^3J(HH) = 7.5 Hz). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2, 298 K): δ 141.3, 134.6, 130.8, 130.4, 129.4, 128.1, 126.2, 127.7 (Ar and C=C), 66.6 (CH_2N), 51.4 (NMe_2), 22.1 and 20.2 (CH_2CH_3), 14.6 and 13.6 (CH_2CH_3).

[($C_6H_4CH_2NMe_2CPh$=CCO_2Et-1,2)]$^+$[PF_6]$^-$ (10a). The procedure is the same as that for [($C_6H_4CH_2NMe_2CPh$=CPh-1,2)]$^+$[PF_6]$^-$ (**8a**) except that (η^6-C_6H_6)RuCl($C_6H_4CH_2NMe_2$-2) (0.37 g, 1.0 mmol), ethyl 3-phenylpropynoate (0.2 mL, 1.2 mmol), $NaPF_6$ (0.20 g, 1.2 mmol), and $CuBr_2$ (0.52 g, 2.3 mmol) reacted to give, after flash chromatography, 0.05 g (10%) of white product. The alkyne was added at −50 °C after which the reaction mixture was allowed to gradually warm to 20 °C. The spectral data of **10a** compared well with those of an authentic sample.[4b]

Structure Determination and Refinement of 1a and 6b. Crystal data and numerical details of the structure determinations are given in Table IV. The crystals were mounted on a rotation-free goniometer head and transferred to an Enraf-Nonius CAD4-F automatic diffractometer for data collection at 293 K. The resulting data sets were transferred to a VAX computer, and for all subsequent calculations the Enraf-Nonius SDP/VAX package[23] was used. Three standard reflections measured every 1 h

Table V. Positional Parameters and Their Esds of Compound 1a

atom	x	y	z	B^a (Å^2)
Ru	0.79735(4)	0.8705(1)	0.800	2.48(1)
Cl	0.8190(2)	0.6038(4)	0.6715(3)	3.18(5)
N	0.9106(6)	0.992(1)	0.7518(8)	2.9(2)
C1	0.8763(7)	0.709(2)	0.8935(8)	3.0(2)
C2	0.8580(9)	0.596(2)	0.987(1)	3.9(2)
C3	0.9163(9)	0.505(2)	1.042(1)	4.1(3)
C4	0.9960(9)	0.507(2)	1.011(1)	3.6(2)
C5	1.0147(8)	0.623(2)	0.923(1)	3.5(2)
C6	0.9533(7)	0.717(2)	0.8687(8)	2.5(2)
C7	0.9720(6)	0.823(2)	0.7658(8)	2.3(2)
C8	0.9383(8)	1.166(2)	0.819(1)	4.6(3)
C9	0.9140(9)	1.063(2)	0.640(1)	4.4(3)
C10	0.730(1)	1.148(2)	0.768(2)	10.1(5)
C11	0.750(2)	1.135(3)	0.874(2)	8.3(6)*
C12	0.729(1)	0.962(4)	0.932(2)	8.6(5)*
C13	0.6874(8)	0.802(3)	0.884(2)	5.6(4)
C14	0.6674(8)	0.815(3)	0.778(1)	6.5(4)
C15	0.689(1)	0.988(5)	0.720(2)	9.4(6)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as (4/3)[$a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)$].

Table VI. Positional Parameters and Their Esds of Compound 6b

atom	x	y	z	B^a (Å^2)
Ru	0.22311(4)	0.89100(3)	0.64659(3)	2.615(6)
P	0.2509(2)	0.4289(1)	0.6601(1)	4.04(3)
F1	0.286(1)	1.3621(6)	0.7340(4)	16.3(3)
F2	0.1364(8)	1.3629(9)	0.6542(6)	17.5(3)
F3	0.309(1)	1.3667(7)	0.5949(6)	21.1(3)
F4	0.220(1)	1.4950(6)	0.5892(4)	15.9(3)
F5	0.3734(9)	1.4885(7)	0.6648(5)	14.0(3)
F6	0.206(1)	1.4962(7)	0.7285(5)	20.6(4)
N	0.0660(5)	1.0639(4)	0.5736(3)	3.3(1)
C1	0.301(1)	0.8723(8)	0.7737(5)	9.3(3)
C2	0.3696(8)	0.8097(7)	0.7180(6)	8.9(2)
C3	0.299(1)	0.7419(6)	0.6756(6)	8.2(2)
C4	0.169(1)	0.7412(5)	0.6768(5)	5.6(2)
C5	0.1045(8)	0.7990(6)	0.7296(5)	5.7(2)
C6	0.170(1)	0.8642(7)	0.7764(5)	7.1(2)
C7	0.2704(6)	0.9452(4)	0.5225(3)	2.55(9)
C8	0.3560(6)	0.9057(5)	0.4621(4)	3.6(1)
C9	0.3238(8(	0.8263(6)	0.4158(4)	4.9(2)
C10	0.2053(9)	0.7822(5)	0.4244(4)	5.2(2)
C11	0.1173(7)	0.8208(5)	0.4742(5)	4.2(1)
C12	0.1384(6)	0.9073(4)	0.5219(4)	2.9(1)
C13	0.2978(5)	1.0159(4)	0.5879(3)	2.6(1)
C14	0.1798(6)	1.0380(4)	0.6331(3)	3.2(1)
C15	0.0228(6)	0.9741(5)	0.5291(4)	3.3(1)
C16	0.4326(6)	1.0624(6)	0.5928(5)	4.2(1)
C17	0.5368(7)	0.9860(7)	0.5991(6)	5.5(2)
C18	0.4512(8)	1.1253(6)	0.5163(6)	5.8(2)
C19	0.4512(9)	1.1258(7)	0.6706(7)	7.3(2)
C20	0.1732(9)	1.0995(6)	0.7109(4)	4.8(2)
C21	−0.0897(6)	0.9254(7)	0.5713(6)	5.5(2)
C22	−0.0445(8)	1.1140(7)	0.6146(5)	5.8(2)
C23	0.1121(8)	1.1359(5)	0.5084(4)	4.2(1)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as (4/3)[$a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)$].

(23) Frenz, B. A. The Enraf-Nonius CAD4-SPD. In *Computing in Crystallography*; Schenk, H., Olthof-Hazekamp, R., Van Koningveld, H., Bassi, G. C., Eds.; Delft University Press: Delft, Holland, 1978; pp 64–71.

during the entire data collection period showed no significant decay. The raw data were converted to intensities and corrected for Lorentz, polarization, and absorption factors, the last computed from the ψ scans of four reflections.

The structures were solved using the heavy atom method. The geometry of the benzene rings was idealized with C–C bonds of 1.39 Å and C–C–C angles of 120°; the ring was constrained to be planar. After refinement of the heavy atoms, a difference-Fourier map revealed maxima of residual electronic density close to the positions expected for hydrogen atoms. These were introduced in structure factor calculations by their computed coordinates (C–H = 0.95 Å) and isotropic temperature factors, such as $B(H) = 1.3B_{eqv}(C)$ Å^2, but were not refined. Refinement was carried out by full least-squares techniques; $\sigma^2(F^2) = \sigma^2_{counts} + (pI)^2$. The absolute structures were determined by comparing x, y, z and $-x, -y, -z$ refinements. A final difference map revealed no significant maxima. The scattering factor coefficients and anomalous dispersion coefficients come from refs 24a and 24b, respectively.

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Supplementary Material Available: Tables of bond distances and angles, H atom coordinates, and thermal parameters for **1a** and **6b** (14 pages). Ordering information is given on any current masthead page.

OM920544C

(24) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, U.K., 1974; Vol. IV, (a) Table 2.2b, (b) Table 2.3.1.

(25) Note added in proof: We found that the use of 1 equiv of $AgBF_4$ instead of $NaPF_6$ per equivalent of substrate **1c** allowed the ready isolation of **6c** in good yields (Urriolabeita, E., unpublished results).