C–H vs. N–H Bond Activation in Aminophosphane Ligands: Reaction of $[Cp^*Ru(MeCN)_2(PR^1{}_2NHR^2)]^+$ (R^1 = Ph, *i*Pr; R^2 = Ph, C_6F_5) with Alkynes

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Dedicated to the memory of Prof. Francisco González García (Universidad de Sevilla)[‡]

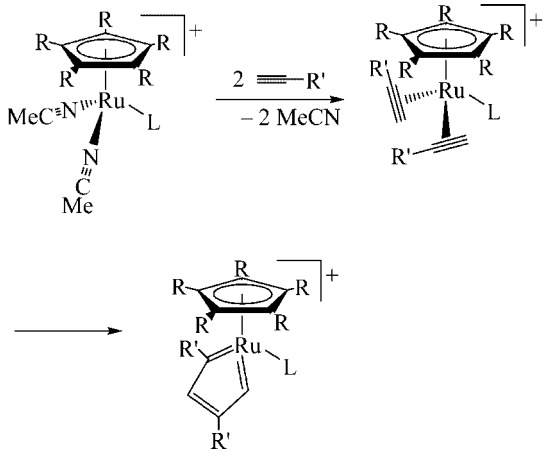
Keywords: Alkyne ligands / C–H activation / Half-sandwich complexes / Phosphane ligands / Ruthenium

The reaction of the complexes $[Cp^*Ru(MeCN)_2(PR^1{}_2NHR^2)]^+$ (R^1 = R^2 = Ph **1**; R^1 = *i*Pr, R^2 = C_6F_5 **2**; R^1 = *i*Pr, R^2 = Ph **3**) with 1-alkynes HC≡CR (R = H, *n*Bu, $SiMe_3$) or diynes $HC{\equiv}CCH_2XCH_2C{\equiv}CH$ (X = O, CH_2, CH_2CH_2) yields different products depending on the nature of the aminophosphane ligand. In some cases, alkyne coupling involving migration of the phosphane and N–H activation occurs, yielding amidobutadiene complexes of the type $[Cp^*Ru\{\eta^4\text{-}C_4H_3(R)_2\text{-}PR^1{}_2NR^2\text{-}\kappa^1N\}]^+$ or $[Cp^*Ru\{\eta^4\text{-}C_4H_3(CH_2XCH_2)PR^1{}_2NR^2\text{-}\kappa^1N\}]^+$. The complexes $[Cp^*Ru\{\eta^4\text{-}C_4H_3(CH_2OCH_2)\text{-}PPh_2NPh\text{-}\kappa^1N\}][PF_6]$ (**1a**) and $[Cp^*Ru\{\eta^4\text{-}C_4H_3(CH_2\text{-}OCH_2)PiPr_2NC_6F_5\text{-}\kappa^1N\}][PF_6]$ (**2a**) have been structurally characterized by X-ray crystallography. In other cases, for example the reaction of **3** with HC≡CR (R = *n*Bu, $SiMe_3$), C–H bond activation at the *ortho*-position of the phenyl ring of the phenylamino moiety and coupling to the alkyne fragment takes place. This results in the formation of the novel π-alkene complexes $[Cp^*Ru(MeCN)\{\eta^2\text{-}RCH{=}CH(C_6H_4)\text{-}NHPiPr_2\text{-}\kappa^1P\}]^+$ (R = *n*Bu **4**, $SiMe_3$ **5**), formally derived from the insertion of the alkyne into the *ortho*-C–H bond of the phenyl ring. The derivative $[Cp^*Ru(MeCN)\{\eta^2\text{-}nBuCH{=}CH(C_6H_4)NHPiPr_2\text{-}\kappa^1P\}][BPh_4]$ has been structurally characterized by X-ray crystallography. These compounds are related to the also structurally characterized olefin complex $[Cp^*Ru(MeCN)(\eta^2\text{-}MeOOCCH{=}CH_2)(PPh_2NHPh)][PF_6]$ (**6**), generated by reaction of **1** with methyl acrylate.

Introduction

Complexes of the type $[(C_5R_5)Ru(MeCN)_2(L)]^+$ (R = H, Me; L = CO, PR_3, $AsPh_3$, $SbPh_3$) are regarded as synthons for the corresponding cationic 14-electron fragments $[(C_5R_5)Ru(L)]^+$ due to the substitutionally labile character of the acetonitrile ligands.[1] The reactivity of these systems towards alkynes has been thoroughly studied both from the experimental and theoretical points of view.[1–5] The derivatives $[(C_5R_5)Ru(MeCN)_2(L)]^+$ react with alkynes to yield bis(π-alkyne) adducts which readily undergo oxidative alkyne coupling of the two alkyne ligands to form cationic ruthenacyclopentatriene complexes.

Ruthenacyclopentatriene complexes are key intermediates in the overall process, and the final products of the reaction are determined by the nature of L, the use of Cp or Cp* as co-ligands, and the nature of the substituents present in the alkyne.[1] When L is PR_3, migration of the phosphane from Ru to C occurs in most cases, generating



allyl carbene species.[2–4] These species behave as masked coordinatively unsaturated complexes that are capable of activating C–H bonds. In cyclopentadienyl complexes containing tertiary phosphane ligands the C–H activation process takes place at one of the aryl or alkyl substituents of the phosphane.[4,6]

At variance with this, in pentamethylcyclopentadienyl derivatives the C–H activation occurs at one of the methyl

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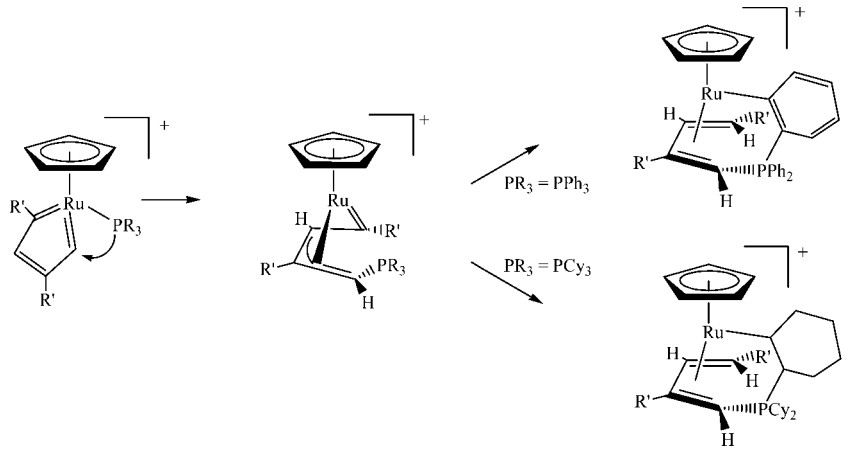
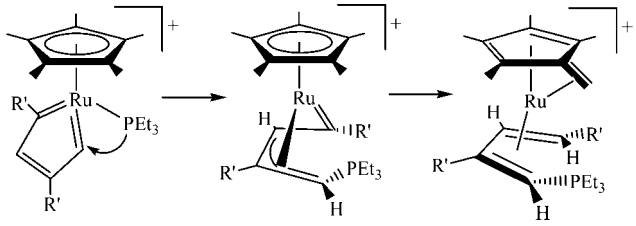
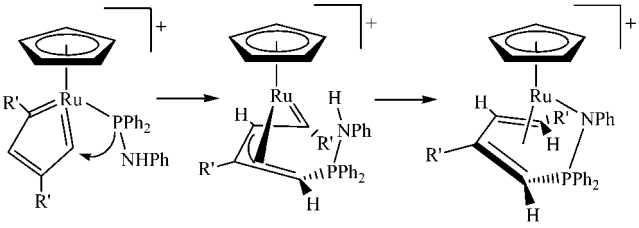


substituents of the Cp* ring to yield η^6-fulvene complexes.[6]



In all cases, the result of the phosphane migration to the organic fragment and the subsequent C–H activation process is the formation of η^4-butadiene species. Very recently, Kirchner and co-workers have reported the activation of alkynes by the aminophosphane complex $[CpRu(MeCN)_2(PPh_2NHPh)]^+$, which results in the formation of η^4-amidobutadiene complexes.[7] In this case phosphane migration also occurs, and is followed by an N–H bond activation process in the amino group rather than C–H bond activation.



Given the previously observed behavior differences between $[CpRu(MeCN)_2(PR_3)]^+$ and the homologous $[Cp^*Ru(MeCN)_2(PR_3)]^+$ complexes with respect to the C–H activation processes,[6] we have addressed the question of whether N–H or C–H activation should occur in the case of Cp* complexes containing aminophosphane ligands. Hence, we have studied the interaction of 1-alkynes with the cationic complexes $[Cp^*Ru(MeCN)_2(PR^1{}_2NHR^2)]^+$. We have found that either N–H or C–H activation may take place depending upon the aminophosphane ligand and the substituent on the alkyne. The detailed results are discussed below.

Results and Discussion

The complexes $[Cp^*Ru(MeCN)_2(PR^1{}_2NHR^2)]^+$ ($R^1 = R^2$ = Ph **1**; R^1 = *i*Pr, $R^2 = C_6F_5$ **2**; R^1 = *i*Pr, R^2 = Ph **3**) were prepared by treatment of $[Cp^*Ru(MeCN)_3][PF_6]$ with a stoichiometric amount of the corresponding aminophosphane in dichloromethane; they were isolated either as their PF_6^- (**1** and **2**) or BPh_4^- (**3**) salts.

Treatment of **1**, **2**, or **3** with either propargyl ether or 1,6-heptadiyne led to the isolation after purification, in moderate yields, of the corresponding amidobutadiene complexes $[Cp^*Ru(\eta^4\text{-}C_4H_3(X)PR^1{}_2NR^2\text{-}\kappa^1N)]^+$ [$R^1 = R^2$ = Ph, X = CH_2OCH_2 **1a**, $(CH_2)_3$ **1b**; R^1 = *i*Pr, $R^2 = C_6F_5$, X = CH_2OCH_2 **2a**, $(CH_2)_3$ **2b**; R^1 = *i*Pr, R^2 = Ph, X = CH_2OCH_2 **3a**, $(CH_2)_3$ **3b**]. In analogous fashion, treatment of **1** and **3** with 1,7-octadiyne also led to the corresponding amidobutadiene complexes **1c** and **3c**, respectively, whereas the reaction of **2** with 1,7-octadiyne yielded a mixture from which no pure compound could be isolated. The reaction of **1** with HC≡CR (R = H, *n*Bu) also afforded the corresponding amidobutadiene complexes $[Cp^*Ru\{\eta^4\text{-}C_4H_3(R)_2\text{-}PPh_2NPh\text{-}\kappa^1N\}][PF_6]$ (R = H **1d**, *n*Bu **1e**). All these compounds were characterized by NMR spectroscopy. The ^1H and $^{13}C\{^1H\}$NMR spectra are consistent with those reported for the related cyclopentadienyl amidobutadiene complexes.[7] One of the most distinctive spectral features of these complexes is the resonance for H^1 and C^1 in their respective ^1H and $^{13}C\{^1H\}$ NMR spectra. Given the fact that C^1 is the carbon atom to which the phosphorus atom is bonded, its $^{13}C\{^1H\}$ resonance appears as a doublet with a rather large $^1J_{C,P}$ coupling constant in the range 100–115 Hz. The hydrogen atom attached to C^1 appears as a doublet with a value for the $^2J_{H,P}$ coupling constant of around 16 Hz. C^2 is a quaternary carbon atom in all cases except for compound **1d**. In this case, the hydrogen atom attached to C^2 displays a large $^3J_{H,P}$ coupling constant of 28 Hz with the phosphorus atom in the *trans*-position. The $^{31}P\{^1H\}$ NMR spectra consist of one singlet in all cases, which is shifted to high-field by 20 to 35 ppm with respect

to the position of the $^{31}P\{^1H\}$ NMR resonance for the corresponding bis(acetonitrile) parent compound **1**, **2**, or **3** respectively. This is fully consistent with the fact that migration of phosphorus from ruthenium to carbon has occurred.

The X-ray crystal structures of **1a** and **2a** were determined. ORTEP views of the cations $[Cp^*Ru\{\eta^4\text{-}C_4H_3(CH_2OCH_2)PPh_2NPh\text{-}\kappa^1N\}]^+$ and $[Cp^*Ru\{\eta^4\text{-}C_4H_3(CH_2OCH_2)PiPr_2NC_6F_5\text{-}\kappa^1N\}]^+$ are shown in Figures 1 and 2, respectively, together with a listing of selected bond lengths and angles.

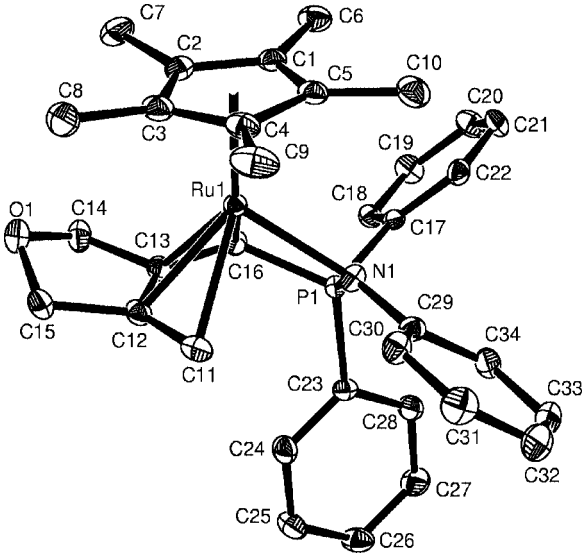


Figure 1. ORTEP drawing (50% thermal ellipsoids) of the cation $[Cp^*Ru\{\eta^4\text{-}C_4H_3(CH_2OCH_2)\text{-}PPh_2NPh\text{-}\kappa^1N\}]^+$ in complex **1a**. Hydrogen atoms have been omitted. Selected bond lengths [Å] and angles [°] with estimated standard deviations in parentheses: Ru1–C2 2.182(2), Ru1–C3 2.188(2), Ru1–C4 2.210(2), Ru1–C1 2.218(2), Ru1–C5 2.245(2), Ru1–N1 2.164(1), Ru1–C11 2.244(2), Ru1–C12 2.216(2), Ru1–C13 2.223 (2), Ru1–C16 2.217(2), P1–C16 1.766(2), C11–C12 1.401(3), C12–C13 1.420(3), C13–C16 1.413(3), N1–P1 1.599(2); Ru1–N1–P1 96.89(7), N1–Ru1–C16 72.30(7), N1–P1–C16 100.23(8), C11–C12–C13 128.1(2), C12–C13–C16 129.5(2).

The structures of the complex cations are very similar to those of the related cyclopentadienyl amidobutadiene complexes $[CpRu\{\eta^4\text{-}C_4H_3(CH_2CH_2CH_2)PPh_2NPh\text{-}\kappa^1N\}]^+$ and $[CpRu\{\eta^4\text{-}C_4H_3(n\text{Bu})_2PPh_2NPh\text{-}\kappa^1N\}]^+$.[7] The dimensions of the butadiene fragment are consistent with the delocalization of the double bonds, matching the values reported for the cyclopentadienyl complexes. The Ru1–N1 separation of 2.242(3) Å in **2a** is significantly longer than the corresponding Ru–N bond lengths observed in **1a** and in the cyclopentadienyl derivatives. This difference reflects the effect of the electron-attracting C_6F_5 group attached to the nitrogen atom in **2a**. On the other hand, all P–N and P–C separations have similar values, and are unexceptional.

The reactions of the pentamethylcyclopentadienyl bis(acetonitrile) complexes **1**–**3** with diynes or 1-alkynes examined so far seem to follow a pathway identical to that of the cyclopentadienyl derivative $[CpRu(MeCN)_2(PPh_2NHPh)]^+$, with phosphane migration, formation of an allyl carbene species, and an N–H bond activation process leading to the final amidobutadiene products.[7] However, we have found that in certain cases a different reaction pathway that leads to products other than amidobutadiene complexes is feasible.

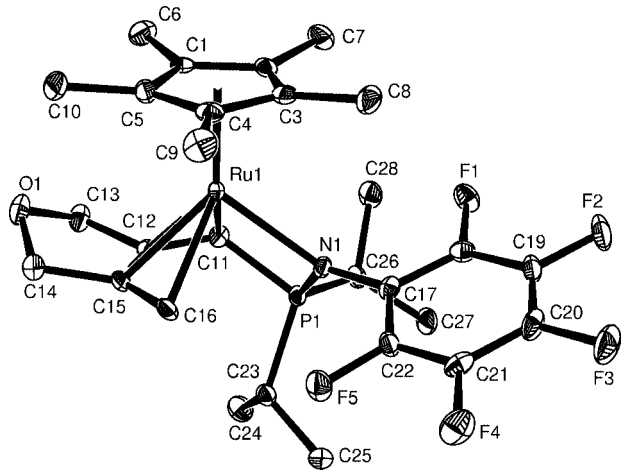
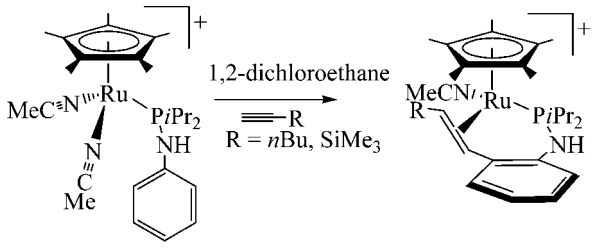


Figure 2. ORTEP drawing (50% thermal ellipsoids) of the cation $[Cp^*Ru\{\eta^4\text{-}C_4H_3(CH_2OCH_2)\text{-}PiPr_2NC_6F_5\text{-}\kappa^1N\}]^+$ in complex **2a**. Hydrogen atoms have been omitted. Selected bond lengths [Å] and angles [°] with estimated standard deviations in parentheses: Ru1–C1 2.167(4), Ru1–C5 2.189(3), Ru1–C2 2.198(4), Ru1–C4 2.216(4), Ru1–C3 2.242(4), Ru1–N1 2.242(3), Ru1–C16 2.208(4), Ru1–C15 2.227(4), Ru1–C12 2.219(4), Ru1–C11 2.208(4), P1–C11 1.771(4), C15–C16 1.392(5), C12–C15 1.425(5), C11–C12 1.410(5), N1–P1 1.605(3); Ru1–N1–P1 97.0(1), C11–Ru1–N1 70.2(1), N1–P1–C11 98.35(16), C16–C15–C12 128.1(3), C15–C12–C11 129.5(3).

The reaction of **3** with 1-hexyne or $HC{\equiv}CSiMe_3$ in dichloroethane yielded yellow materials that show one singlet in their respective $^{31}P\{^1H\}$ NMR spectra slightly above δ = 100 ppm. This indicates that migration of the aminophosphane ligands does not take place in these two cases, at variance with all the other reactions studied in this work. Furthermore, the observed patterns in the ^1H and $^{13}C\{^1H\}$ NMR spectra of these substances are remarkably different from the expected ones for amidobutadiene complexes. The NMR spectra are consistent with the presence of coordinated acetonitrile and NH groups. A series of multiplet resonances in the ^1H NMR spectra in the range δ = 2.6 to 3.9 ppm are correlated to two tertiary carbon resonances in their respective $^{13}C\{^1H\}$ NMR spectra, as inferred from DEPT and gHSQC NMR experiments, thereby suggesting the presence of an η^2-CH=CH group in the complexes. The X-ray structure analysis performed on crystals resulting from the reaction of **3** with 1-hexyne revealed the formation of the complex $[Cp^*Ru(MeCN)\{\eta^2\text{-}n\text{BuCH=CH}(C_6H_4)\text{-}NHPiPr_2\text{-}\kappa^1P\}][BPh_4]$ (**4**). The product resulting from the reaction of **3** with $HC{\equiv}CSiMe_3$ was then identified as $[Cp^*Ru(MeCN)\{\eta^2\text{-}Me_3SiCH=CH(C_6H_4)NHPiPr_2\text{-}\kappa^1P\}][BPh_4]$ (**5**).

An ORTEP view of the cation $[Cp^*Ru(MeCN)\{\eta^2\text{-}n\text{BuCH=CH}(C_6H_4)NHPiPr_2\text{-}\kappa^1P\}]^+$ is shown in Figure 3, together with a listing of selected bond lengths and angles. The ruthenium atom in the complex cation is bonded to one acetonitrile ligand, to the phosphorus atom of the aminophosphane, and to an olefin ligand η^2-*n*BuCH=CH re-



sulting formally from the insertion of the triple bond of a 1-hexyne molecule into one of the *ortho*-CH bonds of the NHPh group of the aminophosphane. The stereochemistry of the olefin ligand is *trans*. The C11–C12 separation of 1.42(1) Å, and the Ru1–C11 and Ru1–C12 bond lengths of 2.233(8) Å and 2.198(8) Å, respectively, compare well with the values found in other half-sandwich ruthenium η^2-alkene complexes, such as $[Cp^*Ru(\eta^2\text{-}CH_2{=}CH_2)(dippe)]^+$ [C–C: 1.43(2) Å; Ru–C: 2.24(1) Å and 2.25(1) Å; dippe = 1,2-bis(diisopropylphosphanyl)ethane][8] or $[Cp^*Ru(\eta^2\text{-}CH_2{=}CH_2)(CO)(PMe{i}Pr_2)]^+$ [C–C: 1.416(13) Å; Ru–C: 2.197(8) Å and 2.204(7) Å].[9]

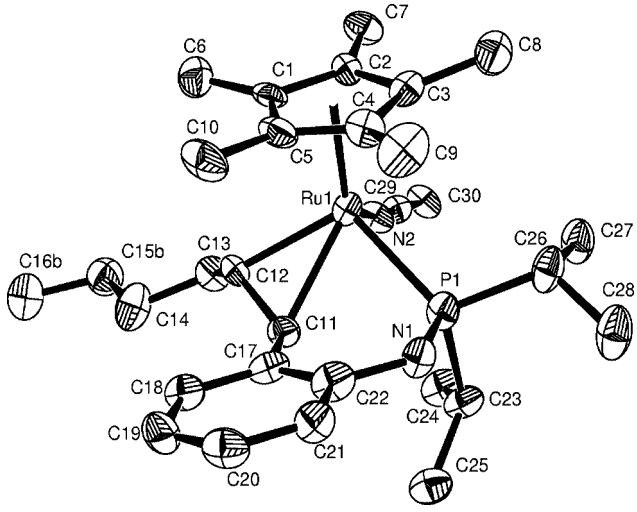


Figure 3. ORTEP drawing (50% thermal ellipsoids) of the cation $[Cp^*Ru(MeCN)\{\eta^2\text{-}n\text{BuCH=CH}(C_6H_4)NHPiPr_2\text{-}\kappa^1P\}]^+$ in complex **4**. Hydrogen atoms have been omitted. Selected bond lengths [Å] and angles [°] with estimated standard deviations in parentheses: Ru1–C1 2.227(8), Ru1–C2 2.254(8), Ru1–C3 2.247(9), Ru1–C4 2.227(8), Ru1–C5 2.208(9), Ru1–N2 2.032(7), Ru1–C11 2.233(8), Ru1–C12 2.198(8), Ru1–P1 2.327(2), P1–N1 1.688(7), C11–C12 1.42(1); Ru1–P1–N1 108.1(3), Ru1–N2–C29 169.1(7), C11–C12–C13 123.5(8), C12–C11–C17 122.7(8), C13–C12–C11–C17 139.2(9).

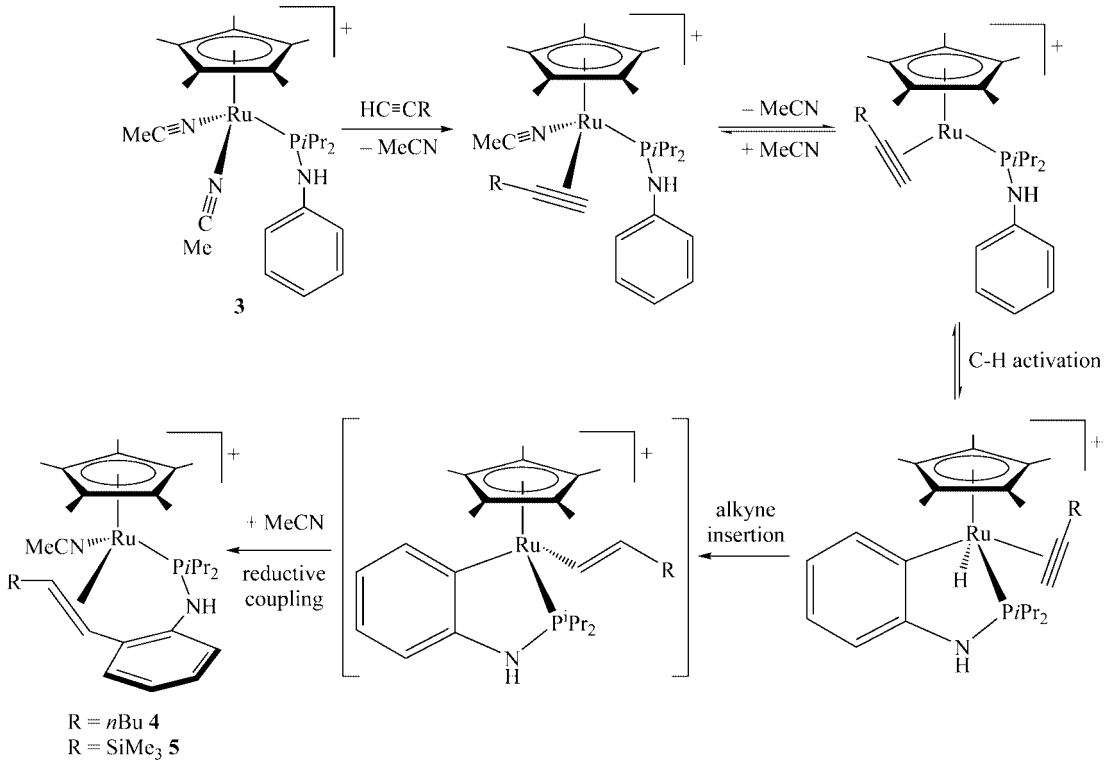
Complexes **4** and **5**, which incorporate only one alkyne molecule, are isolated even when compound **3** is allowed to react with an excess of the corresponding 1-alkyne. This fact indicates that the ruthenacyclopentatriene complex, which is a key intermediate in the process of formation of allyl carbene species, is not generated in the course of the reaction of **3** with 1-hexyne or $HC{\equiv}CSiMe_3$, and therefore an alternative reaction pathway leading to **4** and **5** is feasible.

For these processes we propose the reaction sequence shown in Scheme 1. After substitution of the first acetonitrile ligand by one alkyne molecule, the second acetonitrile molecule dissociates from the metal to generate a coordinatively unsaturated complex. If the addition of the second alkyne ligand is fast, then the resulting 18-electron bis(alkyne) complex undergoes oxidative alkyne coupling to yield a ruthenacyclopentatriene complex, and the course of the reaction would be as described previously.[1,7] However, in certain cases involving systems containing the strong electron-releasing aminophosphane iPr_2PNHPh, the metal center in the 16-electron intermediate is electron-rich enough to activate one C–H bond in the *ortho*-position of the phenyl ring to yield an orthometalated hydrido complex as a result of the oxidative addition reaction. This Ru^{IV} species is most likely in dynamic equilibrium with the 16-electron complex. Insertion of the alkyne into the ruthenium–hydride bond yields an alkenyl complex, which, upon addition of acetonitrile and reductive coupling of the alkenyl and phenyl fragments, leads to the final reaction product **4** or **5**. In the reaction of **3** with potentially chelating diynes the addition of the second alkyne to the 16-electron intermediate seems to be faster than the oxidative addition of the phenyl C–H and the subsequent alkyne insertion, and hence the amidobutadiene complexes **3a**–**c** are obtained.

The fact that reaction products similar to **4** or **5** are not observed in the course of the reaction of **1** or **2** with alkynes might be due to the following reasons: 1) in **1**, the PPh_2NHPh ligand is less basic than iPr_2PNHPh, and hence the corresponding 16-electron intermediate complex is probably not electron-rich enough to cleave *ortho*-C–H bonds prior to the entry of the second alkyne molecule, and 2) in the case of compound **2**, a final product analogous to **4** or **5** would involve C–F bond activation, a process which has a higher activation energy barrier than C–H bond activation.[10]

We must remark here that the proposed reaction sequence shown in Scheme 1, although reasonable, is only tentative. However, we must also point out the fact that spectroscopic evidence for the involvement of hydrido complexes in the formation of **4** has been obtained. In some instances, compound **4** was isolated accompanied by small amounts of other material which exhibits one hydride doublet resonance at $\delta = -10.89$ ppm, with a $^2J_{H,P}$ coupling constant of 43.9 Hz, in the ^1H NMR spectrum (Figure 4). The relatively large value of the $^2J_{H,P}$ coupling constant suggests a *transoid* disposition of the hydride and phosphane ligands. One singlet resonance at $\delta = 135.8$ ppm in the $^{31}P\{^1H\}$ NMR spectrum was attributed to this hydrido complex.

The reaction of **3** with an excess of 1-hexyne in [D_2]tetrachloroethane was monitored between 0 and 60 °C. Several intermediate species giving rise to singlets in the $^{31}P\{^1H\}$ NMR spectra were detected. One of these intermediate species is responsible for the doublet hydride resonance observed in the ^1H NMR spectrum. Although the isolation of any of these intermediate species was not possible, there is little doubt about the involvement of hydride species in the



Scheme 1. Proposed reaction sequence for the formation of **4** or **5** by C–H activation.

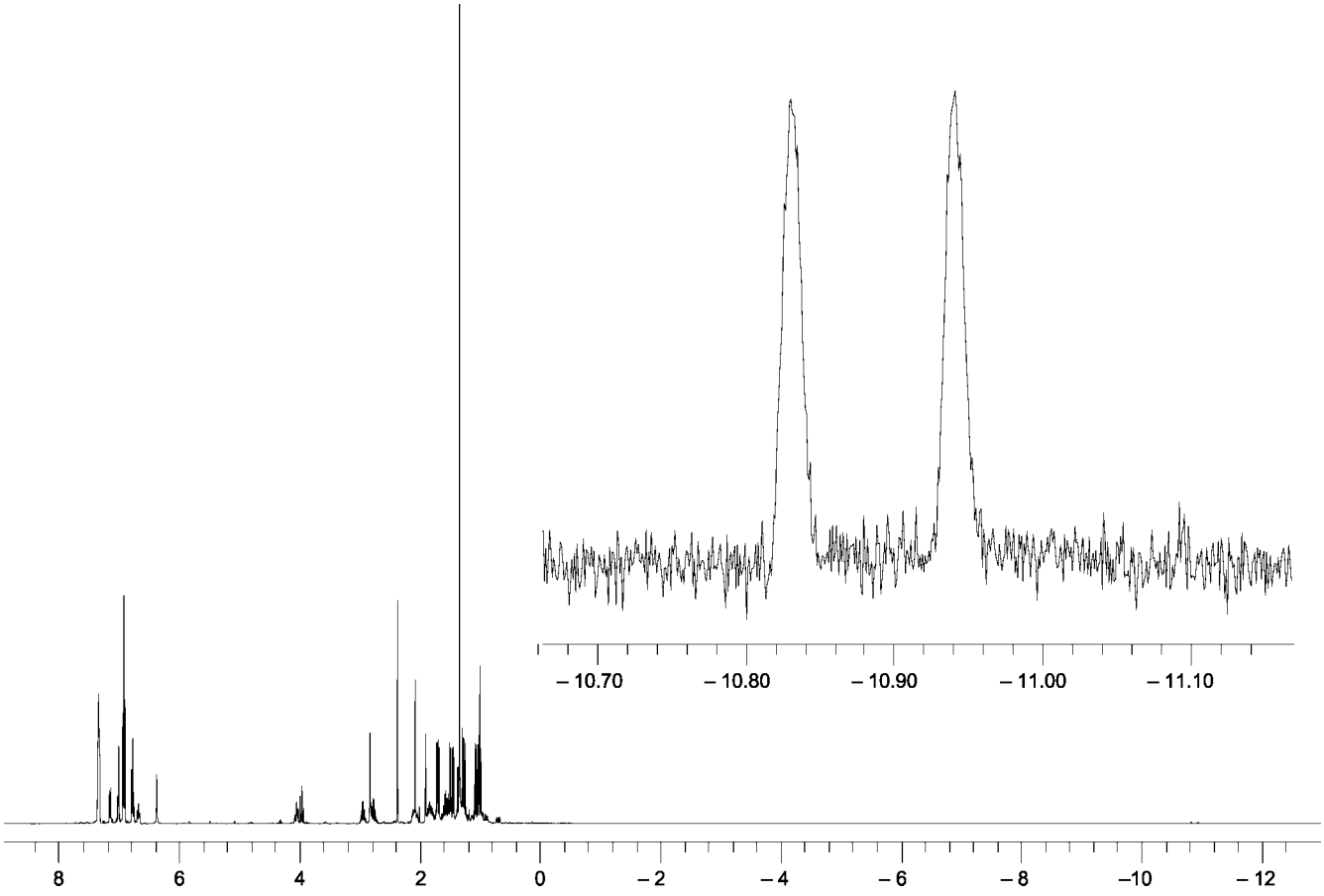


Figure 4. ^{1}H NMR spectrum (400 MHz) of crude compound **4** in [D_6]acetone, showing the presence of minor amounts of a hydrido complex.

process. Orthometalation processes at coordinatively unsaturated metal centers leading to hydrido-phenyl species have been well documented in the literature.[11–14]

We also carried out reactions of **1**, **2**, and **3** with several olefins. The only characterized product from these reactions was the η^2-alkene complex [Cp*Ru(MeOOCCH=CH_2)(MeCN)(PPh_2NHPh)][PF_6] (**6**), which was obtained from the reaction of **1** with methyl acrylate. The substitution of only one acetonitrile ligand in **1** was accomplished irrespective of the metal to methyl acrylate ratio used in the reaction. The protons of the η^2-CH=CH_2 group of the methyl acrylate ligand appear as multiplets at δ = 2.61, 3.45, and 3.52 ppm in the ^{1}H NMR spectrum, whereas the resonances for the carbon atoms appear as doublets at δ = 46.5 and 52.2 ppm, with $J_{C,P}$ coupling constant values of 5.4 Hz and 17 Hz, respectively.

The crystal structure of **6** was determined. An ORTEP view of the cation [Cp*Ru(η^2-MeOOCCH=CH_2)(MeCN)(PPh_2NHPh)]$^+$ is shown in Figure 5, together with a listing of selected bond lengths and angles. The coordination sphere around ruthenium is very similar to that of complex **4**, consisting of one Cp*, one acetonitrile ligand, one aminophosphane ligand, and the η^2-methyl acrylate ligand. The dimensions of the alkene ligand compare well with the values found for **4**, and for other compounds reported in the literature.[8,9] Only one diastereoisomer is present in the crystal. The methylcarboxylate group faces the acetonitrile ligand in an *exo*-disposition, pointing away from the Cp* group in order to minimize steric repulsions. The closest contacts between the methyl acrylate ligand and any atom from the aminophosphane ligand are around 3 Å or longer, which indicates no significant interaction between the aminophosphane and the olefin in this complex.

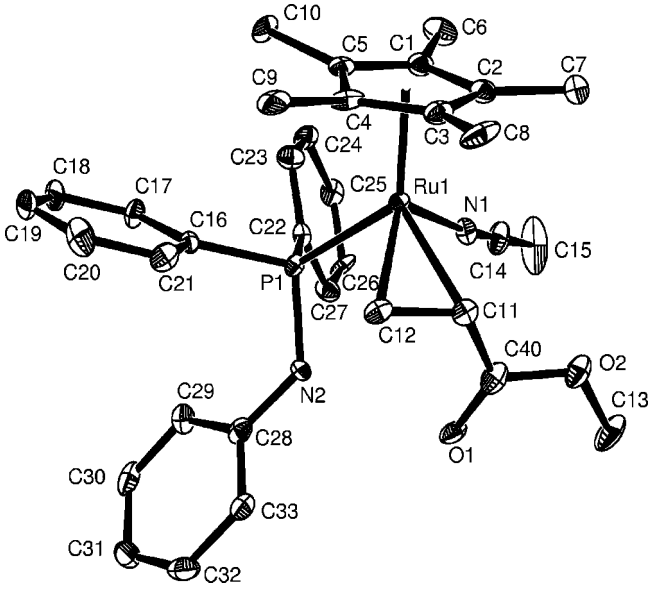


Figure 5. ORTEP drawing (50% thermal ellipsoids) of the cation [Cp*Ru(MeCN)(η^2-MeOOCCH=CH_2)(P*i*Pr_2NHPh)]$^+$ in complex **6**. Hydrogen atoms have been omitted. Selected bond lengths [Å] and angles [°] with estimated standard deviations in parentheses: Ru1–C2 2.200(5), Ru1–C1 2.215(5), Ru1–C3 2.229(5), Ru1–C4 2.245(5), Ru1–C5 2.282(6), Ru1–P1 2.342(1), Ru1–C11 2.185(5), Ru1–C12 2.181(5), Ru1–N1 2.063(4), C11–C12 1.411(7), C11–C40 1.456(8), N1–C14 1.143(7), N2–P1 1.675(5); Ru1–P1–N2 112.1(2), Ru1–N1–C14 173.0(5), C12–C11–C40 121.3(5).

We also studied the reactions of **5** with alkynes in order to check the possibility of alkene–alkyne coupling. However, this does not occur. The reaction of **5** with propargyl ether yielded red-orange crystals of the amidobutadiene complex **1a**. Likewise, the reaction with acetylene afforded the corresponding amidobutadiene derivative **1d**. Hence, the methyl acrylate and acetonitrile ligands behave as good leaving groups in these reactions, and are readily substituted by alkynes to give bis(alkyne) complexes, which follow the previously discussed reaction pathway to form amidobutadiene complexes by N–H activation.

Conclusions

We can conclude that the products of the reactions of [Cp*Ru(MeCN)$_2$(PR^1_2NHR^2)]$^+$ with alkynes are sensitive to the nature of the substituents in the aminophosphane ligand and in the alkyne. In some cases amidobutadiene complexes are generated by N–H activation, consistent with the behavior observed for their Cp counterparts. However, in other cases an alternative reaction pathway involving C–H activation is feasible. This process most likely involves orthometalation of the phenyl ring of an NHPh group and formation of Ru^{IV} hydrido species which are intermediates in the formation of the final products: η^2-alkene complexes formally derived from the insertion of one alkyne into the *ortho*-C–H bond of the NHPh group. Given the fact that the η^2-MeOOCCH=CH_2 ligand in the complex [Cp*Ru(η^2-MeOOCCH=CH_2)(MeCN)(PPh_2NHPh)]$^+$ (**6**) behaves as a good leaving group, it is reasonable to assume that the new ligands *i*Pr_2PNHC_6H_4CH=CHR (R = *n*Bu, $SiMe_3$) in complexes **4** and **5** should display a hemilabile character,[15] and hence their complexes might have potential catalytic activity, a possibility which is currently under investigation.

Experimental Section

General: All synthetic operations were performed under dry dinitrogen or argon following conventional Schlenk techniques. Tetrahydrofuran, diethyl ether, and petroleum ether (boiling point range 40–60 °C) were distilled from the appropriate drying agents. All solvents were deoxygenated immediately before use. The complex [Cp*Ru(MeCN)$_3$][PF_6] was obtained according to the literature.[16] The ligands PPh_2NHPh, P*i*Pr_2NHPh, and P*i*$Pr_2NHC_6F_5$, were prepared following suitable adaptations of published procedures.[17–21] 1-Alkynes, diynes, and methyl acrylate were purchased from Aldrich and used as received. NMR spectra were recorded on a Varian Unity 400 MHz or Varian Gemini 300 MHz spectrometer. Chemical shifts are given in ppm relative to $SiMe_4$ (^{1}H and $^{13}C\{^1H\}$), 85% H_3PO_4 ($^{31}P\{^1H\}$), or $CFCl_3$ (^{19}F). Microanalysis was performed on an elemental analyzer model LECO CHNS-932 at the Servicio Central de Ciencia y Tecnología, Universidad de Cádiz.

[Cp*Ru(MeCN)$_2$(PR^1_2NHR^2)][PF_6] (R^1 = R^2 = Ph 1; R^1 = *i*Pr, R^2 = C_6F_5 2): A stoichiometric amount of either PPh_2NHPh for **1** (1.67 g, 6 mmol), or *i*$Pr_2NHC_6F_5$ for **2** (1.79 g, 6 mmol), was

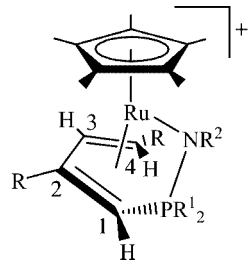
added to a solution of [Cp*Ru(MeCN)$_3$][PF$_6$] (3 g, ca. 6 mmol) in dichloromethane (25 mL). The mixture was stirred at room temperature for 1 h. The solvent was then removed in vacuo. The residue was washed with several portions of diethyl ether, and finally with one portion of petroleum ether to give a yellow powder, which was dried in vacuo.

1: Yield: 4 g, ca. 90%. $C_{32}H_{37}F_6N_3P_2Ru$: calcd. C 51.89, H 5.04, N 5.7; found C 52.1, H 5.15, N 5.4. ^{1}H NMR (CD$_3$COCD$_3$, 298 K): δ = 1.45 [d, $J_{H,P}$ = 1.5 Hz, 15 H, C$_5$(C*H*$_3$)$_5$], 2.41 (d, $J_{H,P}$ = 1.5 Hz, 6 H, C*H*$_3$CN), 5.66 (d, $J_{H,P}$ = 13.8 Hz, 1 H, N*H*), 6.74, 7.01, 7.46, 7.71 (m, 15 H, C$_6$*H*$_5$) ppm. ^{13}C{^{1}H} NMR (CD$_3$COCD$_3$, 298 K): δ = 3.6 (s, *C*H$_3$CN), 9.1 [s, C$_5$(*C*H$_3$)$_5$], 87.9 [d, $J_{C,P}$ = 2.4 Hz, *C*$_5$(CH$_3$)$_5$], 119.1, 126.6, 128.7, 129.0, 130.4, 132.2 (*C*$_6$H$_5$) ppm. ^{31}P{^{1}H} NMR (CD$_3$COCD$_3$, 298 K): δ = 78.7 ppm (s).

2: Yield: 3.4 g, ca. 75%. $C_{26}H_{36}F_{11}N_3P_2Ru$: calcd. C 40.95, H 4.76, N 5.5; found C 40.8, H 4.88, N 5.3. ^{1}H NMR (CDCl$_3$, 298 K): δ = 1.61 [s, 15 H, C$_5$(C*H*$_3$)$_5$], 1.0–1.2 [m, 12 H, P{CH(C*H*$_3$)$_2$}$_2$], 2.39 [m, 2 H, P{C*H*(CH$_3$)$_2$}$_2$], 2.41 (s, 6 H, C*H*$_3$CN), 3.41 (d, $J_{H,P}$ = 12.7 Hz, 1 H, N*H*) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$, 298 K): δ = 3.9 (s, *C*H$_3$CN), 10.3 [s, C$_5$(*C*H$_3$)$_5$], 17.4 [s, P{CH(*C*H$_3$)$_2$}$_2$], 29.0 [d, $J_{C,P}$ = 21.3 Hz, P{*C*H(CH$_3$)$_2$}$_2$], 86.0 [s, *C*$_5$(CH$_3$)$_5$] ppm. ^{19}F NMR (CDCl$_3$, 298 K): δ = –146.6, –161.0, –163.8 ppm. ^{31}P{^{1}H} NMR (CDCl$_3$, 298 K): δ = 116.5 ppm (s).

[Cp*Ru(MeCN)$_2$(P*i*Pr$_2$NHPh)][BPh$_4$] (3): This compound was prepared in a fashion analogous to that for **1** and **2**, starting from [Cp*Ru(MeCN)$_3$][PF$_6$] (1.5 g, ca. 3 mmol) and a stoichiometric amount of *i*Pr$_2$PNHPh (1.2 mL, 3 mmol) in dichloromethane (20 mL). The solvent was removed in vacuo and the residue washed with diethyl ether. Then, it was conveniently transformed into its [BPh$_4$]$^-$ salt by addition of MeOH and an excess of solid NaBPh$_4$ (1.5 g). The yellow precipitate was filtered, washed with EtOH and petroleum ether, and dried in vacuo. Yield: 2.16 g, 85%. $C_{50}H_{61}BN_3PRu$: calcd. C 70.91, H 7.26, N 5.0; found C 70.8, H 7.15, N 4.9. ^{1}H NMR (CD$_3$COCD$_3$, 298 K): δ = 1.45 [d, $J_{H,P}$ = 1.5 Hz, 15 H, C$_5$(C*H*$_3$)$_5$], 2.41 (d, $J_{H,P}$ = 1.5 Hz, 6 H, C*H*$_3$CN), 5.66 (d, $J_{H,P}$ = 13.8 Hz, 1 H, N*H*), 6.74, 7.01, 7.46, 7.71 (m, 15 H, C$_6$*H*$_5$) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$, 298 K): δ = 3.2 (s, *C*H$_3$CN), 10.8 [s, C$_5$(*C*H$_3$)$_5$], 18.2, 18.3 [s, P{CH(*C*H$_3$)$_2$}$_2$], 29.7 [d, $J_{C,P}$ = 20.6 Hz, P{*C*H(CH$_3$)$_2$}$_2$], 93.5 [s, *C*$_5$(CH$_3$)$_5$], 121.6, 126.0, 135.7 (*C*$_6$H$_5$) ppm. ^{31}P{^{1}H} NMR (CD$_3$COCD$_3$, 298 K): δ = 101.1 ppm (s).

[Cp*Ru{η^4-C$_4$H$_3$(CH$_2$OCH$_2$)PPh$_2$NPh-κ^1*N*}][PF$_6$] (1a): A slight excess over the stoichiometric amount of propargyl ether (57 μL, 0.55 mmol) was added to a solution of **1** (0.37 g, 0.5 mmol) in dichloromethane (12 mL) and the mixture was stirred for 1 h at room temperature. The solvent was then removed in vacuo, and the residue washed with two portions of diethyl ether and one portion of petroleum ether. A red-orange powder was obtained, which was filtered off and dried in vacuo. It was recrystallized from a mixture of acetone and petroleum ether. Yield: 0.16 g, 44%. $C_{34}H_{37}F_6NOP_2Ru$: calcd. C 54.26, H 4.95, N 1.9; found C 53.9, H 5.04, N 1.7. ^{1}H NMR (CD$_3$COCD$_3$, 298 K): δ = 1.67 [s, 15 H, C$_5$(C*H*$_3$)$_5$], 2.79 (d, $J_{H,H}$ = 3.1 Hz, 1 H, H^{4endo}), 4.32, 5.15 (d, $J_{H,H}$ = 13.2 Hz, 1 H each, C*H*$_2$), 4.35, 5.26 (d, $J_{H,H}$ = 12.8 Hz, 1 H each, C*H*$_2$), 4.47 (d, $J_{H,P}$ = 17.6 Hz, 1 H, H^1), 4.94 (d, $J_{H,H}$ = 3.1 Hz, 1 H, H^{4exo}), 6.68–8.00 (m, 15 H, C$_6$*H*$_5$) ppm. ^{13}C{^{1}H} NMR (CD$_3$COCD$_3$, 298 K): δ = 9.7 [s, C$_5$(*C*H$_3$)$_5$], 26.6 (d, $J_{C,P}$ = 115.5 Hz, *C*^{1}), 50.0 (s, *C*^{4}), 75.1 (s, *C*H$_2$), 75.7 (d, $J_{C,P}$ = 11.4 Hz, *C*H$_2$), 86.3 (s, *C*^{3}), 99.4 [s, *C*$_5$(CH$_3$)$_5$], 114.8 (s, *C*^{2}), 120.7, 123.6, 123.8, 129.6, 130.5, 132.4, 132.6, 132.7, 134.9, 135.1, 142.4 (*C*$_6$H$_5$) ppm. ^{31}P{^{1}H} NMR (CD$_3$COCD$_3$, 298 K): δ = 42.7 ppm (s).



[Cp*Ru{η^4-C$_4$H$_3$(CH$_2$)$_3$PPh$_2$NPh-κ^1*N*}][PF$_6$] (1b): This compound was obtained in a fashion analogous to **1a**, but using 1,6-heptadiyne instead of propargyl ether. Yield: 53%. $C_{35}H_{39}F_6NP_2Ru$: calcd. C 56.00, H 5.24, N 1.9; found C 55.8, H 5.04, N 1.8. ^{1}H NMR (CD$_3$COCD$_3$, 298 K): δ = 1.37 (m, 2 H, C*H*$_2$), 1.68 [s, 15 H, C$_5$(C*H*$_3$)$_5$], 2.42 (m, 2 H, C*H*$_2$), 2.75 (d, $J_{H,H}$ = 3.1 Hz, 1 H, H^{4endo}), 3.48 (m, 2 H, C*H*$_2$), 4.10 (d, $J_{H,P}$ = 16.9 Hz, 1 H, H^1), 4.76 (d, $J_{H,H}$ = 3.1 Hz, 1 H, H^{4exo}), 6.68–8.00 (m, 15 H, C$_6$*H*$_5$) ppm. ^{13}C{^{1}H} NMR (CD$_3$COCD$_3$, 298 K): δ = 9.6 [s, C$_5$(*C*H$_3$)$_5$], 21.1 (s, *C*H$_2$), 26.5 (d, $J_{C,P}$ = 112.7 Hz, *C*^{1}), 36.2 (s, *C*H$_2$), 38.0 (d, $J_{C,P}$ = 12 Hz, *C*H$_2$), 51.8 (s, *C*^{4}), 98.8 [s, *C*$_5$(CH$_3$)$_5$], 99.9 (s, *C*^{3}), 115.3 (s, *C*^{2}), 120.2, 120.7, 124.0, 129.5, 129.9, 130.4, 132.4, 132.6, 134.7, 134.9, 142.6 (*C*$_6$H$_5$) ppm. ^{31}P{^{1}H} NMR (CD$_3$COCD$_3$, 298 K): δ = 47.7 ppm (s).

[Cp*Ru{η^4-C$_4$H$_3$(CH$_2$)$_4$PPh$_2$NPh-κ^1*N*}][PF$_6$] (1c): This compound was obtained in a fashion analogous to **1a**, but using 1,7-octadiyne instead of propargyl ether. Yield: 43%. $C_{36}H_{41}F_6NP_2Ru$: calcd. C 56.54, H 5.40, N 1.8; found C 56.5, H 5.33, N 1.8. ^{1}H NMR (CD$_3$COCD$_3$, 298 K): δ = 1.48 (m, 2 H, C*H*$_2$), 1.69 [s, 15 H, C$_5$(C*H*$_3$)$_5$], 1.95 (m, 2 H, C*H*$_2$), 2.23 (m, 2 H, C*H*$_2$), 2.60 (d, $J_{H,H}$ = 2.8 Hz, 1 H, H^{4endo}), 3.13 (m, 2 H, C*H*$_2$), 3.71 (d, $J_{H,P}$ = 14 Hz, 1 H, H^1), 4.62 (d, $J_{H,H}$ = 2.8 Hz, 1 H, H^{4exo}), 6.8–7.9 (m, 15 H, C$_6$*H*$_5$) ppm. ^{13}C{^{1}H} NMR (CD$_3$COCD$_3$, 298 K): δ = 10.0 [s, C$_5$(*C*H$_3$)$_5$], 22.0, 22.3 (s, *C*H$_2$), 28.2 (d, $J_{C,P}$ = 109 Hz, *C*^{1}), 31.4, 31.5 (s, *C*H$_2$), 54.1 (s, *C*^{4}), 99.7 [s, *C*$_5$(CH$_3$)$_5$], 108.7 (s, *C*^{3}), 115.8 (s, *C*^{2}), 121.5, 125.3, 129.4, 129.8, 130.5, 132.3, 132.6, 134.6, 135.0, 143.2 (*C*$_6$H$_5$) ppm. ^{31}P{^{1}H} NMR (CD$_3$COCD$_3$, 298 K): δ = 50.6 ppm (s).

[Cp*Ru(η^4-C$_4$H$_5$PPh$_2$NPh-κ^1*N*)][PF$_6$] (1d): Acetylene was bubbled through a solution of **1** (0.37 g, 0.5 mmol) in dichloromethane (15 mL) and the mixture was stirred under acetylene for 1 h at room temperature. The solution was then filtered in order to remove a black solid in suspension [most likely poly(acetylene)]. The solvent was removed in vacuo, and the residue washed with two portions of diethyl ether and one portion of petroleum ether. A red-orange powder was obtained, which was filtered off and dried in vacuo. It was recrystallized from a mixture of acetone and petroleum ether. Yield: 0.19 g, ca. 54%. $C_{32}H_{35}F_6NP_2Ru$: calcd. C 54.08, H 4.96, N 2.0; found C 53.8, H 5.06, N 1.8. ^{1}H NMR (CDCl$_3$, 298 K): δ = 1.66 [s, C$_5$(C*H*$_3$)$_5$], 2.45 (dd, $J_{H,H}$ = 11, $J_{H,H'}$ = 2.7 Hz, 1 H, H^{4endo}), 3.63 (dd, $J_{H,P}$ = 16.3, $J_{H,H}$ = 9.9 Hz, 1 H, H^1), 4.47 (dd, $J_{H,H}$ = 9.2, $J_{H,H'}$ = 2.7 Hz, 1 H, H^{4exo}), 5.41 (m, 1 H, H^3), 5.88 (ddd, $J_{H,P}$ = 28, $J_{H,H}$ = 9.9, $J_{H,H'}$ = 7.5 Hz, 1 H, H^2), 6.64–7.76 (m, C$_6$*H*$_5$) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$, 298 K): δ = 9.8 [C$_5$(*C*H$_3$)$_5$], 31.5 (d, $J_{C,P}$ = 112.2 Hz, *C*^{1}), 58.2 (s, *C*^{4}), 98.2 (s, *C*^{3}), 98.9 [*C*$_5$(CH$_3$)$_5$], 103.8 (s, *C*^{2}), 120.6, 123.4, 123.5, 128.8, 129.1, 129.2, 129.6, 129.7, 131.2, 131.3, 131.4, 133.9, 134.2, 142.6 (*C*$_6$H$_5$) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$, 298 K): δ = 41.6 ppm (s).

[Cp*Ru{η^4-C$_4$H$_3$(*n*Bu)$_2$PPh$_2$NPh-κ^1*N*}][PF$_6$] (1e): 1-Hexyne (126 μL, 1.10 mol) was added to a solution of **1** (0.37 g, 0.5 mmol) in dichloromethane (15 mL) and the mixture was stirred for 1 h at room temperature. The solvent was then removed in vacuo, and the

residue washed with two portions of diethyl ether and one portion of petroleum ether. A yellow-orange powder was obtained, which was filtered off and dried in vacuo. It was recrystallized from a mixture of acetone and petroleum ether. Yield: 0.14 g, 35%. $C_{40}H_{51}F_6NP_2Ru$: calcd. C 58.39, H 6.25, N 1.7; found C 58.2, H 6.12, N 1.6. ^{1}H NMR ($CDCl_3$, 298 K): δ = 1.58 [s, $C_5(CH_3)_5$], 3.39 (m, 1 H, H^4), 3.45 (d, $J_{H,P}$ = 15.9 Hz, 1 H, H^1), 5.10 (d, $J_{H,H}$ = 11.3 Hz, 1 H, H^3), 6.58–7.70 (m, C_6H_5) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K): δ = 9.8 [s, $C_5(CH_3)_5$], 13.7, 13.9 [s, $(CH_2)_3CH_3$], 21.7 (s), 22.4 (s), 33.5 (s), 34.5 (s), 35.8 (s), 41.7 (d, $J_{C,P}$ = 9.8 Hz) [$(CH_2)_3CH_3$], 29.6 (d, $J_{C,P}$ = 112.2 Hz, C^1), 81.9 (s, C^4), 96.5 [$C_5(CH_3)_5$], 99.5 (s, C^3), 116.1 (s, C^2), 120.6, 123.2, 123.4, 128.7, 128.9, 129.0, 129.7, 129.8, 131.0, 133.7, 134.3, 142.6 (C_6H_5) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$, 298 K): δ = 42.4 ppm (s).

[Cp*Ru{η^4-C$_4$H$_3$(CH$_2$OCH$_2$)P*i*Pr$_2$NC$_6$F$_5$-κ^1*N*}][PF$_6$] (2a): Propargyl ether (57 μL, 0.55 mmol) was added to a solution of **2** (0.38 g, ca. 0.5 mmol) in dichloromethane (12 mL) and the mixture was stirred for 1 h at room temperature. The solvent was then removed in vacuo, and the residue washed with two portions of diethyl ether and one portion of petroleum ether. A red-orange powder was obtained, which was filtered off and dried in vacuo. It was recrystallized from a mixture of acetone and petroleum ether. Yield: 0.16 g, ca. 42%. $C_{28}H_{36}F_{11}NOP_2Ru$: calcd. C 43.42, H 4.68, N 1.8; found C 43.3, H 4.77, N 1.5. ^{1}H NMR ($CDCl_3$, 298 K): δ = 0.90, 1.34, 1.54 [m, 12 H, P{CH(CH_3)$_2$}$_2$], 1.49 [s, 15 H, $C_5(CH_3)_5$], 2.49 [m, 2 H, P{CH(CH$_3$)$_2$}$_2$], 3.61 (d, $J_{H,H}$ = 4.5 Hz, 1 H, H^{4endo}), 4.11, 5.14 (d, $J_{H,H}$ = 13.2 Hz, 1 H each, CH_2), 4.29, 5.12 (d, $J_{H,H}$ = 14.2 Hz, 1 H each, CH_2), 4.38 (d, $J_{H,P}$ = 16.5 Hz, 1 H, H^1), 4.41 (d, $J_{H,H}$ = 4.5 Hz, 1 H, H^{4exo}) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K): δ = 8.9 [s, $C_5(CH_3)_5$], 14.9, 15.6, 16.4, 17.0 [s, P{CH(*C*H$_3$)$_2$}$_2$], 19.7 (d, $J_{C,P}$ = 105 Hz, C^1), 31.5 [d, $J_{C,P}$ = 44 Hz, P{*C*H(CH$_3$)$_2$}$_2$], 32.1 [d, $J_{C,P}$ = 42 Hz, P{*C*H(CH$_3$)$_2$}$_2$], 48.1 (s, C^4), 74.8 (s, *C*H$_2$), 75.2 (d, $J_{C,P}$ = 8.9 Hz, *C*H$_2$), 98.4 [s, $C_5(CH_3)_5$], 114.0 (s, C^2) ppm.^{19}F NMR ($CDCl_3$, 298 K): δ = –144.1, –162.3, –162.7 ppm. ^{31}P{^{1}H} NMR ($CDCl_3$, 298 K): δ = 84.7 ppm (s).

[Cp*Ru{η^4-C$_4$H$_3$(CH$_2$CH$_2$CH$_2$)P*i*Pr$_2$NC$_6$F$_5$-κ^1*N*}][PF$_6$] (2b): This compound was obtained in a fashion analogous to **2a**, but using 1,6-heptadiyne instead of propargyl ether. Yield: 50%. $C_{29}H_{38}F_{11}NP_2Ru$: calcd. C 45.08, H 4.96, N 1.8; found C 44.8, H 5.06, N 1.7. ^{1}H NMR ($CDCl_3$, 298 K): δ = 0.87, 1.32, 1.54 [m, 12 H, P{CH(CH_3)$_2$}$_2$], 1.21 (m, 2 H, CH_2), 1.45 [s, 15 H, $C_5(CH_3)_5$], 2.01, 2.16 [m, 1 H each, P{CH(CH$_3$)$_2$}], 2.62, 3.26 (m, 2 H each, CH_2) 3.59 (d, $J_{H,H}$ = 4.6 Hz, 1 H, H^{4endo}), 4.14 (d, $J_{H,P}$ = 16.4 Hz, 1 H, H^1), 4.37 (d, $J_{H,H}$ = 4.6 Hz, 1 H, H^{4exo}) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K): δ = 8.7 [s, $C_5(CH_3)_5$], 14.7, 15.8, 16.2 [s, P{CH(*C*H$_3$)$_2$}$_2$], 20.3 (s, *C*H$_2$), 21.5 (d, $J_{C,P}$ = 102.8 Hz, C^1), 31.5 [d, $J_{C,P}$ = 44.5 Hz, P{*C*H(CH$_3$)$_2$}], 34.0 [d, $J_{C,P}$ = 39.8 Hz, P{*C*H(CH$_3$)$_2$}], 35.4 (s, *C*H$_2$), 36.6 (d, $J_{C,P}$ = 7.7 Hz, *C*H$_2$), 54.6 (s, C^4), 97.0 [s, $C_5(CH_3)_5$], 116.4 (s, C^2) ppm. ^{19}F NMR ($CDCl_3$, 298 K): δ = –144.0, –162.4, –163.2 ppm. ^{31}P{^{1}H} NMR ($CDCl_3$, 298 K): δ = 85.1 ppm (s).

[Cp*Ru{η^4-C$_4$H$_3$(CH$_2$OCH$_2$)P*i*Pr$_2$NPh-κ^1*N*}][BPh$_4$] (3a): Propargyl ether (57 μL, 0.55 mmol) was added to a solution of **3** (0.42 g, ca. 0.5 mmol) in dichloromethane (15 mL) and the mixture was stirred for 1 h at room temperature. The solvent was then removed in vacuo, and the residue washed with two portions of diethyl ether and one portion of petroleum ether. A yellow-orange powder was obtained, which was filtered off and dried in vacuo. It was recrystallized from a mixture of acetone and petroleum ether. Yield: 0.22 g, 48%. $C_{57}H_{61}BNOPRu$: calcd. C 74.50, H 6.69, N 1.5; found C 74.2, H 6.58, N 1.3. ^{1}H NMR ($CDCl_3$, 298 K): δ = 0.60, 0.71, 1.10, 1.27 [m, 3 H each, P{CH(CH_3)$_2$}$_2$], 1.37 [s, 15 H, $C_5(CH_3)_5$], 1.74, 2.32 [m, 1 H each, P{CH(CH$_3$)$_2$}$_2$], 2.63 (d, $J_{H,H}$ = 3.6 Hz, 1 H, H^{4endo}), 3.20 (d, $J_{H,P}$ = 16 Hz, 1 H, H^1), 3.69, 4.64 (d, $J_{H,H}$ = 13.6 Hz, 1 H each, CH_2), 3.79, 4.75 (d, $J_{H,H}$ = 13.6 Hz, 1 H each, CH_2), 4.06 (d, $J_{H,H}$ = 3.6 Hz, 1 H, H^{4exo}), 6.36, 6.73, 7.02 (m, 5 H, C_6H_5) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K): δ = 9.5 [s, $C_5(CH_3)_5$], 16.2, 16.3, 16.8, 17.5 [s, P{CH(*C*H$_3$)$_2$}$_2$], 16.5 (d, $J_{C,P}$ = 104.3 Hz, C^1), 31.6 [d, $J_{C,P}$ = 47.7 Hz, P{*C*H(CH$_3$)$_2$}], 32.3 [d, $J_{C,P}$ = 34 Hz, P{*C*H(CH$_3$)$_2$}], 47.9 (s, C^4), 74.6 (s, *C*H$_2$), 74.9 (d, $J_{C,P}$ = 9 Hz, *C*H$_2$), 98.2 [s, $C_5(CH_3)_5$], 108.7 (s, C^3), 113.5 (s, C^2), 120.6, 122.7, 129.0, 142.2 (C_6H_5) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$, 298 K): δ = 76.7 ppm (s).

[Cp*Ru{η^4-C$_4$H$_3$(CH$_2$CH$_2$CH$_2$)P*i*Pr$_2$NPh-κ^1*N*}][BPh$_4$] (3b): This compound was obtained in a fashion analogous to **3a**, but using 1,6-heptadiyne instead of propargyl ether. Yield: 55%. $C_{58}H_{63}BNPRu$: calcd. C 75.97, H 6.92, N 1.5; found C 76.1, H 7.04, N 1.5. ^{1}H NMR ($CDCl_3$, 298 K): δ = 0.78, 0.91, 1.37, 1.49 [m, 3 H each, P{CH(CH_3)$_2$}$_2$], 1.22 (m, 2 H, CH_2), 1.53 [s, 15 H, $C_5(CH_3)_5$], 2.11 (m, 2 H, CH_2), 1.92, 2.55 [m, 1 H each, P{CH(CH$_3$)$_2$}$_2$], 2.75 (d, $J_{H,H}$ = 3.2 Hz, 1 H, H^{4endo}), 3.19 (m, 2 H, CH_2), 3.53 (d, $J_{H,P}$ = 16 Hz, 1 H, H^1), 4.21 (d, $J_{H,H}$ = 3.2 Hz, 1 H, H^{4exo}), 6.51, 7.11, 7.21 (m, 5 H, C_6H_5) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K): δ = 9.6 [s, $C_5(CH_3)_5$], 16.2, 16.7, 16.9, 17.8 [s, P{CH(*C*H$_3$)$_2$}$_2$], 17.9 (d, $J_{C,P}$ = 103 Hz, C^1), 20.3 (s, *C*H$_2$), 31.7, 32.3 [m, P{*C*H(CH$_3$)$_2$}$_2$], 36.0 (s, *C*H$_2$), 37.1 (d, $J_{C,P}$ = 7.8 Hz, *C*H$_2$), 49.9 (s, C^4), 93.5 (s, C^3), 97.4 [s, $C_5(CH_3)_5$], 113.7 (s, C^2), 119.6, 120.4, 123.1, 126.0, 135.7, 142.8 (C_6H_5) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$, 298 K): δ = 77.9 ppm (s).

[Cp*Ru{η^4-C$_4$H$_3$(CH$_2$)$_4$-P*i*Pr$_2$NPh-κ^1*N*}][BPh$_4$] (3c): This compound was obtained in a fashion analogous to **3a**, but using 1,7-octadiyne instead of propargyl ether. Yield: 48%. $C_{59}H_{65}BNPRu$: calcd. C 76.11, H 7.04, N 1.5; found C 76.1, H 6.98, N 1.4. ^{1}H NMR ($CDCl_3$, 298 K): δ = 0.64, 0.74, 1.04, 1.34 [s, 3 H each, P{CH(CH_3)$_2$}$_2$], 1.12 (m, 2 H, CH_2), 1.34 [s, 15 H, $C_5(CH_3)_5$], 1.69 (m, 2 H, CH_2), 1.72, 2.26 [m, 1 H each, P{CH(CH$_3$)$_2$}], 2.54 (m, 2 H, CH_2), 2.57 (d, $J_{H,H}$ = 3.2 Hz, 1 H, H^{4endo}), 2.74 (m, 2 H, CH_2), 2.79 (d, $J_{H,P}$ = 13.6 Hz, 1 H, H^1), 3.97 (d, $J_{H,H}$ = 3.2 Hz, 1 H, H^{4exo}), 6.45, 7.02, 7.11 (m, 5 H, C_6H_5) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K): δ = 9.8 [s, $C_5(CH_3)_5$], 14.8, 16.4, 17.6, 17.7 [P{CH(*C*H$_3$)$_2$}$_2$], 20.4 (d, $J_{C,P}$ = 98.6 Hz, C^1), 21.0, 21.4 (s, *C*H$_2$), 30.7 (d, $J_{C,P}$ = 8.1 Hz, *C*H$_2$), 30.9 (s, *C*H$_2$), 32.2 [d, $J_{C,P}$ = 48.5 Hz, P{*C*H(CH$_3$)$_2$}], 32.6 [d, $J_{C,P}$ = 43 Hz, P{*C*H(CH$_3$)$_2$}], 50.9 (s, C^4), 98.3 [s, $C_5(CH_3)_5$], 106.8 (s, C^3), 114.6 (s, C^2), 123.0, 124.4, 128.9, 135.7, 142.6 (C_6H_5) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$, 298 K): δ = 81.7 ppm (s).

[Cp*Ru(MeCN){η^2-*n*BuCH=CH(C$_6$H$_4$)NHP*i*Pr$_2$-κ^1*P*}][BPh$_4$] (4): 1-Hexyne (65 μL, ca. 0.57 mmol) was added to a solution of **3** (0.42 g, 0.5 mmol) in 1,2-dichloroethane (8 mL). The mixture was stirred for 5 min at 60 °C and then for 1 h at room temperature. The solvent was removed in vacuo, and the residue washed with diethyl ether and petroleum ether until a yellow-orange powder was obtained. This material was filtered off and dried in vacuo. Yellow crystals of **4**·Me$_2$CO were obtained by recrystallization of the crude material from acetone/petroleum ether. Yield: 0.18 g, 40%. $C_{57}H_{74}BN_2OPRu$: calcd. C 72.36, H 7.88, N 3.0; found C 72.2, H 7.73, N 2.9. ^{1}H NMR ($CDCl_3$, 298 K): δ = 1.15 (s, 3 H, CH_3CN), 1.19 [d, $J_{H,P}$ = 1.5 Hz, 15 H, $C_5(CH_3)_5$], 0.87, 1.20, 1.33, 1.54 [m, 3 H each, P{CH(CH_3)$_2$}$_2$], 0.92, 1.51, 1.76 [m, 2 H each, (CH_2)CH_3], 1.00 [t, $J_{H,H}$ = 7.3 Hz, 3 H, (CH$_2$)CH_3], 2.45, 2.70 [m, 1 H each, P{CH(CH$_3$)$_2$}$_2$], 3.80 (m, 1 H, =CH*n*Bu), 3.84 (m, 1 H, =CHC$_6$H$_4$), 4.89 (s, 1 H, NH), 6.64, 6.70, 7.02, 7.21 (m, 1 H each, C_6H_4) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K): δ = 2.8 (s, *C*H$_3$CN), 8.9 [s, $C_5(CH_3)_5$], 14.2 [s, $(CH_2)_3CH_3$], 16.6, 18.2, 20.4, 21.5

[P{CH(CH_3)$_2$}$_2$], 22.5, 33.6, 35.7 [s, (CH_2)$_3CH_3$], 32.5 [t, $J_{C,P}$ = 21.9 Hz, P{CH(CH_3)$_2$}$_2$], 57.4 (d, $J_{C,P}$ = 11 Hz, =CH*n*Bu), 67.1 (s, =CHC_6H_4), 93.8 [s, $C_5(CH_3)_5$], 116.5, 118.7, 128.1, 128.2, 135.7, 142.9 (C_6H_4) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K): δ = 101.7 ppm (s).

[Cp*Ru(MeCN){η^2-Me$_3$SiCH=CH(C$_6$H$_4$)NHP*i*Pr$_2$-κ^1*P*}][BPh$_4$] (5): This compound was obtained in a fashion analogous to **4**, but using HC≡CSiMe$_3$ instead of 1-hexyne. Yield: 53%. $C_{53}H_{68}BN_2PRuSi$: calcd. C 70.41, H 7.58, N 3.1; found C 70.2, H 7.64, N 3.0. ^1H NMR ($CDCl_3$, 298 K): δ = 0.01 [s, 9 H, Si(CH_3)$_3$], 0.93 (d, $J_{H,P}$ = 1 Hz, 3 H, CH_3CN), 1.07 [d, $J_{H,P}$ = 1.5 Hz, 15 H, C_5(CH_3)$_5$], 0.90, 1.04, 1.28, 1.42 [m, 3 H each, P{CH(CH_3)$_2$}$_2$], 2.27, 2.61 [m, 1 H each, P{CH(CH_3)$_2$}$_2$], 2.61 (m, 1 H, =CHSiMe$_3$), 3.91 (m, 1 H, =CHC_6H_4), 4.81 (s, 1 H, N*H*), 6.53, 6.60, 6.83, 6.92 (m, 1 H each, C_6H_4) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K): δ = 0.7 [s, Si(CH_3)$_3$], 2.5 (s, CH_3CN), 9.3 [s, C_5(CH_3)$_5$], 17.0 (d), 19.0 (d), 20.6 (s), 21.1 [s, P{CH(CH_3)$_2$}$_2$], 32.9, 34.5 [d, $J_{C,P}$ = 24.4 Hz, P{CH(CH_3)$_2$}$_2$], 54.0 [s, =$CHSi(CH_3)_3$], 62.1 (d, $J_{C,P}$ = 9.8 Hz, =CHC_6H_4), 94.4 [s, $C_5(CH_3)_5$], 116.4, 118.8, 127.8, 128.2, 129.8, 143.3 (C_6H_4) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K): δ = 107.7 ppm (s).

[Cp*Ru(MeCN)(η^2-MeOOCCH=CH$_2$)(PPh$_2$NHPh)][PF$_6$] (6): An excess of methyl acrylate (180 μL, ca. 1 mmol) was added to a solution of **1** (0.37 g, 0.5 mmol) in dichloromethane (10 mL) and the mixture was stirred for 30 min at room temperature. It was then filtered through celite and layered with petroleum ether. Yellow crystals of **6** were obtained after 3–4 days. The crystals were separated from the liquor, washed with petroleum ether, and dried in vacuo. Yield: 0.22 g, 56%. $C_{34}H_{40}F_6N_2O_2P_2Ru$: calcd. C 51.97, H 5.13, N 3.6; found C 51.9, H 5.14, N 3.5. IR: ν(C=O) = 1687 cm^{-1}. ^1H NMR ($CDCl_3$, 298 K): δ = 1.34 [d, $J_{H,P}$ = 1.5 Hz, 15 H, C_5(CH_3)$_5$], 2.44 (d, $J_{H,P}$ = 1.5 Hz, 3 H, CH_3CN), 3.78 (s, COOCH_3), 2.61, 3.45, 3.52 (m, 1 H each, CH=CH_2), 6.78 (d, $J_{H,P}$ = 15.9 Hz, 1 H, N*H*), 6.43, 6.68, 6.91 (m, 5 H, NHC_6H_5), 7.40–7.62 [m, 10 H, P(C_6H_5)$_2$] ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K): δ = 3.7 (s, CH_3CN), 8.3 [s, C_5(CH_3)$_5$], 46.6 (d, $J_{C,P}$ = 5.4 Hz, =CH_2), 52.1 (d, $J_{C,P}$ = 17 Hz, =$CHCOOCH_3$), 52.3 (s, COOCH_3), 98.0 [s, C_5(CH_3)$_5$], 118.3, 120.8, 128.8, 128.9, 129.0, 129.1, 131.4, 131.7, 132.0, 132.1, 142.7 (C_6H_5), 178.1 ($COOCH_3$) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K): δ = 76.4 ppm (s).

X-ray Structure Determinations: Crystal data and experimental details are given in Table 1. X-ray diffraction data were collected on a Bruker SMART APEX three-circle diffractometer (graphite-monochromated Mo-K_α radiation, λ = 0.71073 Å) with a CCD area detector at the Servicio Central de Ciencia y Tecnología de la Universidad de Cádiz. Hemispheres of the reciprocal space were measured by omega scan frames with $\delta(\omega)$ 0.30°. Corrections for absorption and crystal decay (insignificant) were applied by semi-empirical methods from equivalents using the program SADABS.[22] The structures were solved by direct methods, completed by subsequent difference Fourier synthesis, and refined on F^2 by full-matrix least-squares procedures using the program SHELXTL.[23] The ligand *i*Pr$_2$PNH(C_6H_4)CH=CH*n*Bu in compound **4** showed orientation disorder at the end of the *n*Bu group. The set C(15)H$_2$ and C(16)H$_3$ was refined as two ethyl groups in complementary positions. Final refinements gave approximately 50% of each position. In this compound all non-hydrogen atoms except C15 and C15b were refined anisotropically, and hydrogen atoms were included at idealized positions and refined using a riding model. In the case of compounds **1a**, **2a**, and **6**, all non-hydrogen atoms were refined with anisotropic displacement coefficients, and all the remaining hydrogen atoms were refined using the SHELX riding model. The program ORTEP-3[24] was used for plotting.

CCDC260375 (for **1a**), -260376 (for **2a**), -260377 (for **4**), and -260378 (for **6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The

Table 1. Summary of crystallographic data for **1a, 2a**, **4**, and **6**.

Compound	**1a**	**2a**	**4**	**6**
Formula	$C_{34}H_{37}F_6NOP_2Ru$	$C_{28}H_{36}F_{11}NOP_2Ru$	$C_{57}H_{74}BN_2OPRu$	$C_{34}H_{40}F_6N_2O_2P_2Ru$
Mol. mass	752.66	774.59	946.03	785.69
T [K]	100(2)	100(2)	100(2)	100(2)
Crystal size [mm]	0.44×0.31×0.28	0.41×0.15×0.03	0.23×0.22×0.06	0.32×0.15×0.06
Crystal system	orthorhombic	triclinic	monoclinic	orthorhombic
Space group	$Pna2_1$ (no. 33)	$P\bar{1}$ (no. 2)	$P2_1/c$ (no.14)	$Pna2_1$ (no. 33)
a [Å]	17.193(1)	8.378(2)	12.366(2)	21.133(1)
b [Å]	10.3496(6)	10.031(2)	17.846(2)	12.5882(7)
c [Å]	17.812(1)	17.976(4)	23.178(3)	12.9869(7)
α [°]		88.35(3)		
β [°]		86.22(3)	99.166(3)	
γ [°]		85.71(3)		
V [Å^3]	3169.4(3)	1502.9(5)	5049.8(1)	3454.8(3)
Z	4	2	4	4
ρ_{calc} [g cm^{-3}]	1.577	1.712	1.243	1.511
μ(Mo-K_α) [cm^{-1}]	6.61	7.22	3.83	6.12
F(000)	1536	784	2008	1608
Max. and min. transmission factors	1.04–0.93	1–0.83	0.98–0.73	1.18–0.91
Theta range for data collection	$2.28 < \theta < 27.56$	$2.04 < \theta < 25.06$	$1.67 < \theta < 23.27$	$1.88 < \theta < 27.52$
Reflections collected	27732	12886	30663	30365
Unique reflections	7085 (R_{int} = 0.0210)	5265 (R_{int} = 0.0337)	7221 (R_{int} = 0.1075)	7385 (R_{int} = 0.0532)
No. of observed reflections [$I > 2\sigma(I)$]	7007	4986	5948	7117
No.of parameters	411	409	592	431
Final $R1$, $wR2$ values [$I > 2\sigma(I)$]	0.0206, 0.0529	0.0413, 0.0821	0.0959, 0.1743	0.0524, 0.1171
Final $R1$, $wR2$ values (all data)	0.0210, 0.0531	0.0447, 0.0836	0.1237, 0.1890	0.0554, 0.1189
Residual electron density peaks (e Å^{-3})	+0.508, –0.286	+0.573, –0.785	+0.611, –1.191	+0.921, –1.287

Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

We thank the Ministerio de Educación y Ciencia (DGI, Project CTQ2004-00776/BQU) and the Junta de Andalucía (PAI FQM188) for financial support, and Johnson Matthey plc for generous loans of ruthenium trichloride.

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Received: January 12, 2005
Published Online: May 24, 2005

