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Differential Reactivity of [TpRu(κ^2P,N -*i*Pr₂PXPY)Cl] (X = NH, S) Bearing Hemilabile Coligands Towards NaBAR^F₄, Lithium Acetylide, and Acetylenes

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In contrast with [TpRu(κ^2P,N -*i*Pr₂PNHPy)Cl] (**1a**, Tp = trispyrazolylborate), [TpRu(κ^2P,N -*i*Pr₂PSPy)Cl] (**1b**) reacts with sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaBAR^F₄) in fluorobenzene under nitrogen to afford the dinuclear complex $[(\text{TpRu}(\kappa^2P,N\text{-}i\text{Pr}_2\text{PSPy}))_2(\mu\text{-Cl})][\text{BAR}^{\text{F}}_4]$ (**1b'**). Through diverse synthetic strategies, a series of neutral acetylides [TpRu(C≡CR)(κ^2P,N -*i*Pr₂PXHPy)] [X = NH; R = Ph (**2a**), SiMe₃ (**2b**); X = S; R = Ph (**2c**), *p*-C₆H₄Br (**2d**), COOMe (**2e**)], cationic vinylidene complexes [TpRu(=C=CHR)(κ^2P,N -*i*Pr₂PNHPy)]⁺ [X = NH; R = Ph (**3a**), SiMe₃ (**3b**); X = S; R = Ph (**3c**), *p*-C₆H₄Br (**3d**)] and [TpRu(=C=CH₂)(κ^2P,N -*i*Pr₂PNHPy)]⁺

(**3e**), and a cationic η^2 -alkyne complex [TpRu(η^2 -HC≡CCOOMe)(κ^2P,N -*i*Pr₂PSPy)][BAR^F₄] have been efficiently synthesized from **1a** and **1b**. The methoxy(methyl)-carbene complexes [TpRu{=C(OMe)CH₃}(κ^2P,N -*i*Pr₂PXPY)][BPh₄] [X = NH (**5a**), S (**5b**)] were isolated from the reactions of **1a** and **1b** with acetylene gas in the presence of NaBAR^F₄ in methanol. The deprotonation of the cationic vinylidenes derived from **1b** with *t*BuO affords the corresponding neutral acetylide complexes, which undergo facile protonation with CF₃SO₃H to reproduce the cationic vinylidenes quantitatively.

Introduction

The wide range of oxidation states {from -2 in [Ru(CO)₄]²⁻ to +8 in RuO₄} and coordination geometries of ruthenium complexes highlight their potential exploitation in catalytic reactions. As the coordination chemistry of ruthenium complexes has progressed, the characteristic features of ruthenium (e.g., high electron transferability and low redox potentials) and the stability of reactive metallic species such as metallacycles, metal carbenes, metal acetylides, and metal vinylidenes have allowed access to a broad variety of catalytic transformations.^[1-5] The general procedure for the synthesis of a wide range of vinylidene complexes involves protonation of metal acetylides or tautomerism of η^2 -coordinated alkynes^[6] or alkynyl-hydride species^[7] (reportedly formed by the oxidative addition of alkynes to ruthenium).^[1c] This tautomerism either involve intramolecular 1,2-H shifts for coordinated alkynes or 1,3-H shifts for alkynyl-hydride species and constitute the key step for several catalytic alkyne transformations.^[6] Recently, we have reported the tautomerism of internal alkynes to give disubstituted ruthenium vinylidene complexes. Simi-

larly to our earlier observation,^[8] this occurs both in solution and in the solid state.^[9]

In addition, interest in carbon-rich organometallic compounds has been continued owing to their potential to grant nonlinear optical,^[10] liquid crystal,^[11] mixed-valence, or conducting^[12] properties. There are reports on the unusual formation of ketonyl complexes from ruthenium acetylides bearing hydrotris(pyrazolyl)borate (Tp) and nitrosyl (NO) ligands.^[13] Further reports suggest that the introduction of the non-coordinating anion tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ([BAR^F₄]⁻) as a halide scavenger allows the isolation of a series of coordinatively unsaturated cationic complexes of the type [Cp^{*}Ru(PP)][BAR^F₄]⁺ [PP = 1,2-bis(diisopropylphosphanyl)ethane (dippe), (PMeiPr₂)₂, (PEt₃)₂, (PPhiPr₂)₂, (PPh₃)₂; Cp^{*} = pentamethylcyclopentadienyl].^[14] The {[Cp^{*}Ru(dppm)]⁺} [dppm = bis(diphenylphosphanyl)methane] and {[Cp^{*}Ru(dppe)]⁺} [dppe = 1,2-bis(diphenylphosphanyl)ethane] moieties can be generated in situ and constitute binding sites for a range of small molecules such as dihydrogen,^[15] dioxygen,^[16,17] and dinitrogen.^[18] These observations motivate constant studies on the synthesis of ruthenium precursors and their chemical reactivity towards the isolation of coordinatively unsaturated cationic complexes, σ -acetylide, π -alkyne, vinylidene, and carbene derivatives. In this perspective, the influence of the ancillary ligands is important. Other than phosphines, amines, and dienes, not many coligands have been used in TpRu complexes. Therefore, we are primarily interested in the synthesis of new TpRu^{II} precursors bearing hemilabile *P,N* coligands and the exploration of their reactivity

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towards small organic molecules. Recently, we reported the synthesis of new [TpRuCl(*i*Pr₂PXPpy)] (X = NH, CH₂) precursors bearing potential hemilabile coligands.^[8b,9] This paper describes the synthesis and characterization of a [TpRuCl(*i*Pr₂PSPy)] precursor and a series of mononuclear acetylide, cationic vinylidene, and methoxycarbene derivatives. The main emphasis has been on the differential reactivity of [TpRuCl(*i*Pr₂PXPpy)] (X = NH, S) towards NaBAR₄^F, lithium acetylide, and acetylenes.

Results and Discussion

The treatment of [TpRuCl(PPh₃)₂] with 2-pyridyl(diisopropylphosphanyl)amine (*i*Pr₂PNHPy) or 2-pyridyl(diisopropylphosphanyl)thioether (*i*Pr₂PSPy) coligands affords the starting complexes [TpRuCl(*i*Pr₂PSPy)] (**1a**) and [TpRuCl(*i*Pr₂PSPy)] (**1b**). These compounds contain two potentially labile positions: the chlorido ligand, which is readily abstracted by NaBAR₄^F, and the pyridyl N atom of the coligands. The reactivity of **1a** and **1b** with alkynes requires the initial chloride abstraction by suitable reagents such as NaBAR₄^F and NaBPh₄. The treatment of **1b** with NaBAR₄^F in fluorobenzene under argon or nitrogen generates the dinuclear complex [{TpRu(κ²-*P,N*-*i*Pr₂PSPy)}₂(μ-Cl)][BAR₄^F] (**1b'**), as shown in Scheme 1.

The formation of the dinuclear complex [{Cp*Ru}₂(μ-Cl)(μ-dppm)₂][BAR₄^F] by the reaction of [Cp*RuCl(dppm)] with NaBAR₄^F in fluorobenzene under argon has been reported previously.^[18b] Both compounds **1b** and **1b'** have been structurally characterized. The structural information for **1b** is included in the Supporting Information. An ORTEP view of the dinuclear complex cation [{TpRu(κ²-*P,N*-*i*Pr₂PSPy)}₂(μ-Cl)]⁺ in **1b** is shown in Figure 1.

A distorted-octahedral coordination around the ruthenium center is found. In related complexes, the Ru–Ru bond lengths are below 2.980 Å, and the Ru(1)–Ru(2) separation of 4.647 Å in **1b** is even higher than that of 3.856 Å in the dinuclear Ru^{III}–Ru^{III} complex [{Cp*Ru}₂(μ-Cl)₂(μ-dppm)][CF₃SO₃]₂ and suggests that there is not a metal–metal bonding interaction.^[19] The Ru(1)–Cl(1) and Ru(2)–Cl(1) bond lengths of 2.4288(10) and 2.4328(8) Å in **1b'** are slightly shorter than those observed for chlorido-bridged Cp*Ru complexes.^[19] An angular instead of a linear bridge is frequently found in Ru–Cl–Ru complexes. As expected, the weakest *trans* influence corresponds to the chlorido

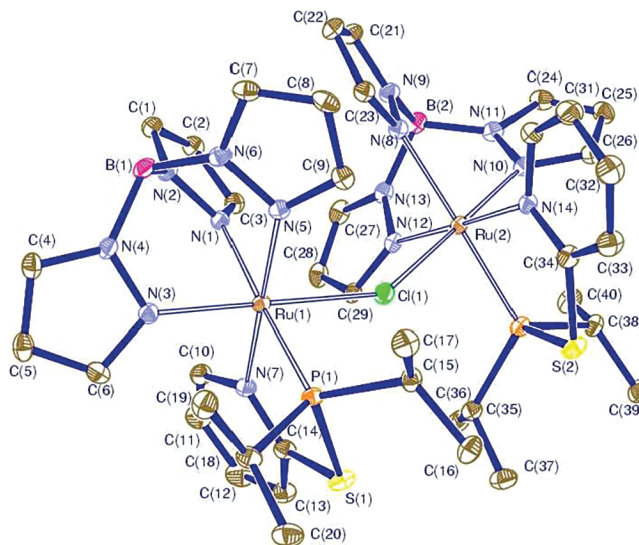
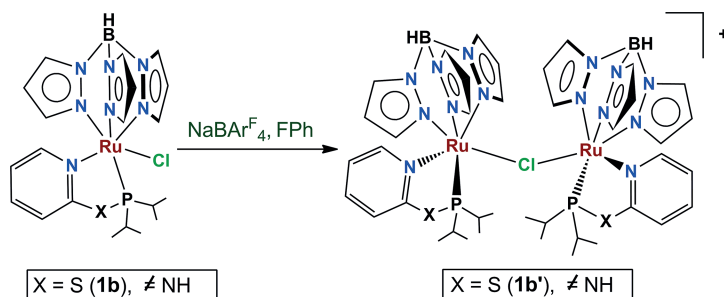


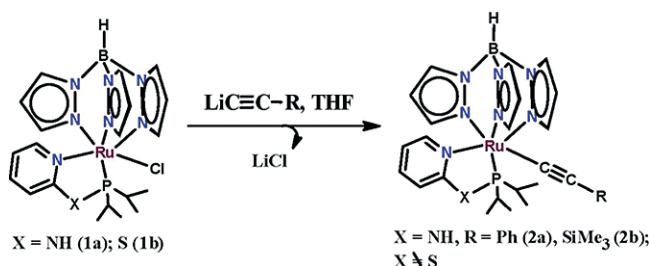
Figure 1. ORTEP view and partial numbering scheme of the cation in **1b'**. Ellipsoids are shown at 50% probability. Hydrogen atoms have been omitted for clarity.

bridging ligand and is even slightly lower than that of the pyridyl nitrogen atom. We can tentatively postulate that the removal of one chlorido ligand leads to the corresponding 16-electron species, which is attacked by the electron-rich chlorido ligand of another molecule to form the chlorido-bridged dimetallic complex **1b'**. It must be noted that no dinuclear complex was isolated from the reaction of **1b** with NaBAR₄^F under nitrogen; however, earlier observations suggest that halide abstraction from [Cp*RuCl(PP)] (PP = dppm, dppe) with NaBAR₄^F can either generate {[Cp*Ru(dppm)]⁺} and {[Cp*Ru(dppe)]⁺} moieties in situ, and these moieties offer binding sites for a range of small molecules such as dihydrogen,^[15] dioxygen,^[16,17] and dinitrogen,^[18] or generate a series of coordinatively unsaturated cationic complexes of the type [Cp*Ru(PP)][BAR₄^F] [PP = 1,2-bis(diisopropylphosphanyl)ethane (dippe), (PMe*i*Pr₂)₂, (PEt₃)₂, (PPh*i*Pr₂)₂, (PPh₃)₂].^[14] No pure product was obtained from the reaction of **1a** with NaBAR₄^F in fluorobenzene under argon or nitrogen. When the reagents were mixed, the initial blue color of the solution suggests that a 16-electron intermediate is formed. The solution promptly turned brown, and workup yielded a dark brown oil, which was not characterized.



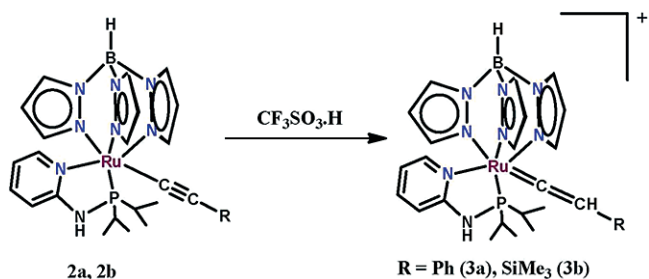
Scheme 1. Preparation of **1b'** bearing a hemilabile 2-pyridyl(diisopropylphosphanyl)thioether coligand.

On the other hand, the metathesis reaction of $[\text{Li}][\text{RC}\equiv\text{C}]$ ($\text{R} = \text{Ph}, \text{SiMe}_3$), prepared in situ by the reaction of BuLi with a tetrahydrofuran (THF) solution of phenylacetylene or trimethylsilylacetylene, and **1a** afforded the neutral acetylide complexes $[\text{TpRu}(\text{C}\equiv\text{CR})(\kappa^2P,N\text{-}i\text{Pr}_2\text{PNHpy})]$ [$\text{R} = \text{Ph}$ (**2a**), SiMe_3 (**2b**)] in 70–73% yield (Scheme 2).



Scheme 2. Synthesis of neutral TpRu^{II} -acetylide complexes **2a** and **2b** bearing hemilabile 2-pyridyl(diisopropylphosphanyl)amine coligands.

The protonation of these acetylide molecules **2a** and **2b** with $\text{CF}_3\text{SO}_3\text{H}$ in diethyl ether afforded the corresponding cationic vinylidene complexes $[\text{TpRu}(\text{C}=\text{CHR})(\kappa^2P,N\text{-}i\text{Pr}_2\text{PNHpy})][\text{CF}_3\text{SO}_3]$ [$\text{R} = \text{Ph}$ (**3a**), SiMe_3 (**3b**); Scheme 3].



Scheme 3. Protonation of TpRu^{II} -acetylide complexes bearing hemilabile 2-pyridyl(diisopropylphosphanyl)amine coligands to form the corresponding cationic vinylidene complexes **3a** and **3b**.

Attempts to deprotonate these vinylidene complexes **3a** and **3b** with $\text{K}t\text{BuO}$ produced multiple uncharacterized TpRu complexes. In the reaction with $\text{K}t\text{BuO}$, the simultaneous deprotonation of the amine $-\text{NH}$ and vinylidene groups probably prevents the reproduction of the corresponding neutral acetylides **2a** and **2b** from the vinylidene complexes **3a** and **3b**. Moreover, by the present synthetic route, we isolated SiMe_3 derivatives of the TpRu^{II} vinylidene **3b**; otherwise the reaction of $\text{HC}\equiv\text{CSiMe}_3$ with $[\text{CpRuCl}(\text{dippe})]$ apparently results in the formation of the primary vinylidene complex $[\text{TpRu}=\text{C}=\text{CH}_2(\text{dippe})][\text{BPh}_4]$ by protonolysis of the $\text{C}-\text{Si}$ bond, as in previously described cases.^[20,21]

The microanalysis and spectroscopic data were sufficient to unequivocally assign the structures of the acetylide (**2a** and **2b**) and vinylidene (**3a** and **3b**) complexes. The ^1H NMR spectra of **2a** and **2b** show three sets of nine signals, which suggests that the pyrazolyl ring protons of the ruthenium-bonded Tp ligand are nonequivalent, that is, diastereotopic. Further, the signals corresponding to py, NH,

and $i\text{Pr}$ fragments are observed. As expected, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **2a** and **2b** both show only one singlet signal at $\delta = 136.39$ and 136.61 ppm, respectively. The most characteristic signals in the ^{13}C NMR spectra of these TpRu acetylide complexes are two doublets at $\delta = 134.81/160.19$ ppm and $\delta = 109.17/109.19$ ppm with coupling constant $J_{\text{C,P}} = 23.4/18.5$ Hz and $J_{\text{C,C}} = 6.7$ Hz for **2a** and **2b** respectively. These signals are attributable to the α and β carbon atoms of acetylide moieties. Similarly to those of **2a** and **2b**, the ^1H NMR spectra of **3a** and **3b** exhibit three distinct sets of pyrazol-1-yl resonances in addition to those of the vinylidene and coligand units. The ^{13}C NMR spectra of these vinylidene complexes exhibit extremely downfield signals at $\delta = 370.84$ and 365.01 ppm, which appear as doublets with $\text{C}-\text{P}$ coupling constants of 19–20 Hz and are attributable to the α carbon atoms ($\text{Ru}=\text{C}$) of the vinylidene ligands. Single crystals of **3a** suitable for single-crystal X-ray diffraction study were grown by the slow diffusion of n -hexane into a dichloromethane solution of the complex at room temperature. An ORTEP view of the $[\text{TpRu}(\text{C}=\text{CHR})(\kappa^2P,N\text{-}i\text{Pr}_2\text{PNHpy})]^+$ cation in **3a** is shown in Figure 2.

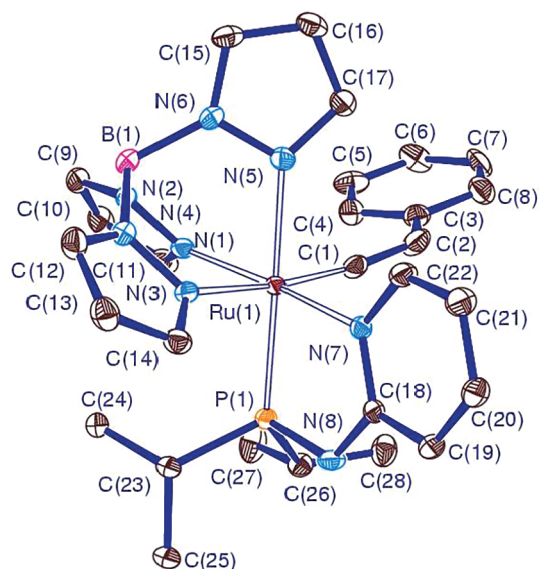
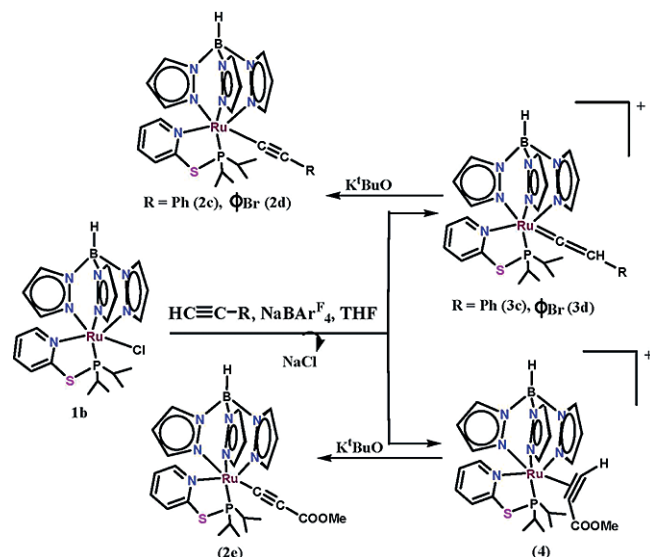


Figure 2. ORTEP view and partial numbering scheme of the cation in **3a**. Ellipsoids are shown at 50% probability. Hydrogen atoms have been omitted for clarity.

A distorted-octahedral coordination geometry around the ruthenium center is found. A short $\text{Ru}(1)-\text{C}(1)$ distance of $1.828(3)$ Å reflects the strong backbonding from the metal center and is characteristic of the vinylidene ligands. The $d\pi(\text{metal})-p\pi(\text{vinylidene})$ backbonding interaction would be essential to the stability of the vinylidene species. The $\text{C}(1)-\text{C}(2)$ bond length of $1.303(4)$ Å and the $\text{C}(1)-\text{C}(2)-\text{C}(3)$ bond angle of $126.5(3)^\circ$ fit with sp^2 hybridization at $\text{C}(2)$. The $\text{Ru}(1)-\text{C}(1)-\text{C}(2)$ bond angle of $165.2(3)^\circ$ is comparable to the structural information available for related complexes^[7,8] and confirms that the attachment of the carbon chain to the ruthenium centre is almost linear. The

trans influence of the vinylidene carbon atom C(1) is slightly stronger than that exerted by the phosphorus atom P(1) and much stronger than that shown by the pyridyl nitrogen atom N(7).

On the other hand, under similar reaction conditions, [Li][RC≡C] reacts distinctly with **1b** to give a mixture of uncharacterized complexes. The thio group present in the ancillary hemilabile 2-pyridyl(diisopropylphosphanyl)thioether ligand interacts with lithium acetylide and prevents its facile metathesis reaction with **1b**. However, the reactions of **1b** with HC≡CR in THF in the presence of NaBAR^F₄ at room temperature afford the corresponding cationic vinylidene complexes [TpRu(=C=CHR)(κ²P,N-*i*Pr₂PSPy)]-[BAR^F₄] [R = C₆H₅ (**3c**), C₆H₄Br (**3d**)] and a cationic η²-alkyne complex [TpRu(η²-HC≡CCOOMe)(κ²P,N-*i*Pr₂PSPy)][BAR^F₄] (**4**) in good yields (Scheme 4).



Scheme 4. Synthesis of cationic TpRu^{II} vinylidene (**3c** and **3d**) and TpRu^{II} η²-alkyne (**4**) complexes and their deprotonation to form the corresponding neutral acetylide complexes (**2c–2e**) bearing hemilabile 2-pyridyl(diisopropylphosphanyl)thioether coligands.

Unlike **3a** and **3b**, these vinylidene complexes **3c** and **3d** as well as the η²-alkyne complex **4** undergo facile deprotonation (Scheme 4) with K^tBuO in THF to afford another series of neutral TpRu acetylide complexes [TpRu(C≡CR)-(κ²P,N-*i*Pr₂PSPy)] [R = Ph (**2c**), *p*-C₆H₄Br (**2d**), COOMe (**2e**)] bearing 2-pyridyl(diisopropylphosphanyl)thioether ligands.

However, the protonation of these acetylide complexes **2c** and **2d** with CF₃SO₃H in diethyl ether reproduces the corresponding cationic vinylidene complexes and this is consistent with the protonation behaviors of **2a** and **2b**. The NMR spectra of **2a**-BAR^F₄/**2a**-CF₃SO₃ and **2b**-BAR^F₄/**2b**-CF₃SO₃ are very similar and fully consistent with the presence of vinylidene ligands in these complexes. In contrast to earlier reports on the protonation of monoacetylide TpRu complexes such as TpRuCl(C≡CPh)(NO),^[22] we could not observe even traces of ketonyl complex formation during the protonation reactions of **2a–2d**.

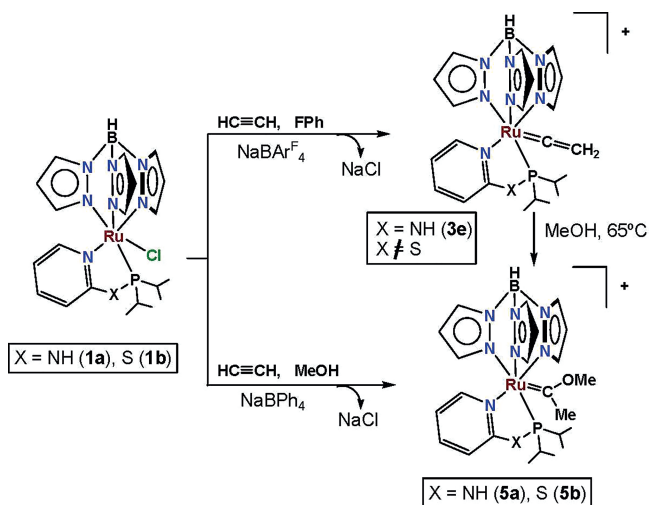
The structures of the acetylides **2c–2e**, the vinylidenes **3c** and **3d**, as well as the η²-alkyne complex **4** have been unequivocally assigned on the basis of their microanalysis and spectroscopic data. The IR spectra of TpRu acetylides **2c–2e** show characteristic bands at $\tilde{\nu}$ 2058, 2068 and 2035 cm⁻¹ and $\tilde{\nu}$ = 2471, 2464, and 2482 cm⁻¹, assignable to ν (C≡C) and ν (B–H) stretches, respectively, whereas the vinylidene complexes **3c** and **3d** exhibit a characteristic band at $\tilde{\nu}$ ≈ 1600 cm⁻¹ for the vinylidene ν (C=C) stretching vibration. A significant shift of the ν (C≡C) bands towards lower frequency ($\tilde{\nu}$ = 1929 cm⁻¹) confirms the η²-coordination mode of HC≡CCOOMe in **4**. Similarly to those of **2a–2b**, the ¹H NMR spectra of these acetylides exhibit three distinct sets of pyrazol-1-yl resonances in addition to those of the acetylide, py, and *i*Pr fragments. All of these complexes display only one singlet signal in their respective ³¹P{¹H} NMR spectra. The most characteristic signals in the ¹³C NMR spectra of acetylides **2c–2e** are the doublets at δ = 130.20, 116.0, and 106.12 ppm, respectively, with *J*_{C,P} = 12–22 Hz, which are attributed to the α carbon atoms of the acetylide moieties. Similarly to those of vinylidenes **3a** and **3b**, the most characteristic features in the ¹³C NMR spectra of **3c** and **3d** are the extremely downfield signals at δ = 375.80 and 374.80 ppm, which are doublets with *J*_{C,P} = 19 Hz, attributable to the α carbon atoms (Ru=C) of the vinylidene ligands. In addition, all of the complexes display signals corresponding to the Tp, Py, and *i*Pr molecular fragments.

Tautomerism of η²-coordinated 1-alkynes to the vinylidene form is a well-known process. The syntheses of ruthenium vinylidenes involve either η²-alkyne complexes such as [CpRu(η²-HC≡CR)(dippe)]^{+[23]} and [CpRu(η²-HC≡CR)(PR₃)₂]^{+[6,20b,24]} or hydrido-alkynyl complexes such as [Cp*^{*}RuH(C≡CR)(dippe)]^{+[7]} as intermediates; however, no intermediates have been isolated or detected in the course of the reactions of TpRu fragments with 1-alkynes. The η²-alkyne complex (**4**) is very stable and it does not undergo further rearrangement to its vinylidene isomer even after prolonged heating in THF solution. It seems more likely that the reaction of **1b** with HC≡CR (R = C₆H₅, *p*-C₆H₄Br) proceeds quickly through an intermediate η²-alkyne complex rather than a hydrido-alkynyl complex, because the latter involves an unfavorable seven-coordinate species, which has not been observed for Ru–Tp complexes.^[25,26]

Nucleophilic Addition of Methanol to Primary Vinylidenes

Unlike that of **1b**, the reaction of [TpRu(κ²P,N-*i*Pr₂PNHpy)Cl] (**1a**) with excess acetylene gas in fluorobenzene in the presence of NaBAR^F₄ affords the primary vinylidene complex [TpRu(=C=CH₂)(κ²P,N-*i*Pr₂PNHpy)]-[BAR^F₄] (**3e**, Scheme 5).

The IR spectrum of the primary vinylidene **3e** display one medium–strong band at $\tilde{\nu}$ = 1614 cm⁻¹, attributable to the ν (C=C) vibration of the vinylidene ligand, in addition to one weak ν (BH) band at $\tilde{\nu}$ = 2524 cm⁻¹, characteristic of the Tp group, and one ν (N–H) band at $\tilde{\nu}$ = 3404 cm⁻¹,



Scheme 5. Preparation of the TpRu^{II} primary vinylidene complex **3e** and the TpRu^{II} methoxy(methyl)carbene complexes **5a** and **5b**.

characteristic of the 2-pyridyl(diisopropylphosphanyl)amine coligand. Like all other complexes presented in this work, the protons of the pyrazole rings of the Tp ligand appear as three sets of nine separate resonances in the ^1H NMR spectrum, a pattern that we have previously observed and needs no further comment.^[8b,9] One doublet is observed for the hydrogen atoms attached to the β -carbon atom of the vinylidene ligand, along with one doublet for the $-\text{NH}$ proton owing to coupling with one equivalent phosphorus atom. Accordingly, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows one sharp singlet.

The most relevant feature of the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of this compound is the extremely lowfield resonance at $\delta = 361.32$ ppm for the carbon atom of the vinylidene fragment directly attached to the ruthenium center; this resonance appears as a doublet owing to coupling with one phosphorus atom with $J_{\text{C,P}} = 18.4$ Hz. This signal appears at even lower field for these Tp derivatives than for their Cp or Cp* homologs.^[7] These spectroscopic data suggest an octahedral structure around the ruthenium center with three facial coordination sites occupied by the N atoms of the Tp ligand, two other positions occupied by the P and N atoms of the 2-pyridyl(diisopropylphosphanyl)amine coligand, and the sixth position occupied by the vinylidene ligand.

When **1a** and **1b** were treated with excess acetylene gas in methanol in the presence of NaBPh_4 , the corresponding methoxy(methyl)carbene complexes $[\text{TpRu}(\text{=C}(\text{OMe})\text{CH}_3)(\kappa^2P,N\text{-}i\text{Pr}_2\text{PXPpy})][\text{BPh}_4]$ [$\text{X} = \text{NH}$ (**5a**), S (**5b**)] were obtained (Scheme 5). Otherwise, the primary vinylidene **3e** reacts under mild reaction conditions with methanol to afford complex **5a** quantitatively as a $[\text{BAR}^{\text{F}}_4]$ salt. This indicates that the reactions of **1a** and **1b** with $\text{HC}\equiv\text{CH}$ gas in methanol and in the presence of NaBPh_4 go through intermediate primary vinylidene complexes, which simultaneously involve the nucleophilic addition of methanol to yield these methoxy(methyl)carbene complexes.

Compounds **5a** and **5b** have been characterized by elemental analysis, FTIR spectroscopy, NMR spectroscopy, and single-crystal X-ray diffraction. In their $^{13}\text{C}\{^1\text{H}\}$ NMR spectra, doublets at $\delta = 322.99$ and 324.20 ppm with $J_{\text{C,P}} = 14.6$ and 14.5 Hz, respectively, correspond to the carbon atoms of the carbene ligands directly bound to the ruthenium center.

As an illustrative example of both structures, an ORTEP view of the complex cation $[\text{TpRu}\{\text{=C}(\text{OMe})\text{CH}_3\}(\kappa^2P,N\text{-}i\text{Pr}_2\text{PNHPy})]^+$ is shown in Figure 3. The two complexes show distorted-octahedral coordination geometries around the ruthenium center. The carbene moieties are characterized by $\text{Ru}(1)\text{--C}(1)$ bond lengths of $1.920(2)$ and $1.924(3)$ Å, which correspond to $\text{Ru}=\text{C}$ double bonds in **5a** and **5b**, respectively. These bonds are slightly longer than the corresponding bond length of $1.85(2)$ Å observed in $[\text{TpRu}=\text{C}(\text{OMe})\text{CH}_2\text{COOMe}(\text{dippe})]^+$,^[27] however they are comparable to those found in other cyclopentadienyl ruthenium carbene complexes such as $[\text{CpRu}=\text{C}(\text{OMe})\text{Et}(\text{PPh}_3)_2][\text{PF}_6]$ [$1.959(6)$ Å]^[28] and $[\text{CpRu}=\text{C}(\text{OMe})\text{CH}_2\text{Ph}(\text{CHIRAPHOS})][\text{PF}_6]$ [$1.93(2)$ Å, $\text{CHIRAPHOS} = \text{Ph}_2\text{PCH}(\text{CH}_3)\text{CH}_2\text{PPh}_2$].^[29] The $\text{O}(1)\text{--C}(1)$ bond lengths of $1.335(3)$ and $1.320(4)$ Å are significantly shorter, whereas the $\text{C}(1)\text{--C}(2)$ bond lengths of $1.474(3)$ and $1.506(5)$ Å are comparable to those found in $[\text{TpRu}=\text{C}(\text{OMe})\text{CH}_2\text{COOMe}(\text{dippe})]^+$ and suggest single bonds.^[27] The $\text{O}(1)\text{--C}(1)\text{--C}(2)$ angles of $115.67(18)$ and $115.7(3)^\circ$ are significantly smaller than the similar angle observed in $[\text{TpRu}=\text{C}(\text{OMe})\text{CH}_2\text{COOMe}(\text{dippe})]^+$ but are consistent with sp^2 hybridization for $\text{C}(1)$.

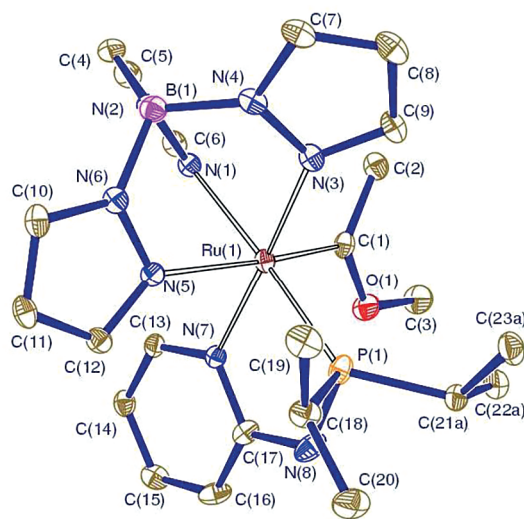


Figure 3. ORTEP view and partial numbering scheme of the cation in **5a**. Ellipsoids are shown at 50% probability. Hydrogen atoms have been omitted for clarity.

For **5a**, the *trans* influence follows the same pattern that as that for the vinylidene complex **3a**; it is slightly stronger for the carbenic carbon atom $\text{C}(1)$ than for the phosphorus atom $\text{P}(1)$ and much stronger than for the pyridyl nitrogen atom $\text{N}(7)$. Whereas for **5b**, in a manner similar to that found for the cation in **3b** and carbene complex **5a**, the *trans*

influence of the carbenic carbon atom C(1) is slightly stronger than that exerted by the phosphorus atom P(1) and much stronger than that shown by the pyridyl nitrogen atom N(7).

The formation of these carbenes is more facile than the formation of $[\text{TpRu}=\text{C}(\text{OMe})\text{CH}_2\text{COOMe}(\text{dippe})][\text{BPh}_4]$, which requires harsh reaction conditions at reflux temperature. However, the syntheses of these methoxy(methyl)carbenes are consistent with other cases in which such compounds are readily derived from the attacks of alcohols at the electrophilic R carbon atom of monosubstituted vinylidenes.^[1a,28–32] However, such reactivity patterns are rarely seen with monosubstituted vinylidene complexes of their Cp or Cp* homologs. Furthermore, these methoxycarbene complexes **5a** and **5b** are quite stable and do not undergo facile deprotonation with *Kt*BuO to yield the corresponding acetylide complexes. This is in contrast to our earlier observation^[27] that the methoxycarbene derivative $[\text{TpRu}=\text{C}(\text{OMe})\text{CH}_2\text{COOMe}(\text{dippe})][\text{BPh}_4]$ reacts with *Kt*BuO to afford the neutral alkynyl $[\text{TpRu}(\text{C}\equiv\text{CCOOMe})(\text{dippe})]$ by elimination of MeOH. This procedure has been extensively used in the deprotonation of cationic vinylidene complexes for the preparation of neutral acetylide complexes.

Further, none of the secondary vinylidene complexes, including that with $\text{R}=\text{COOMe}$, reacts with MeOH or EtOH to afford alkoxycarbene complexes, unlike $[\text{TpRu}=\text{C}=\text{CHCOOMe}(\text{dippe})]^+$. It has been determined that the attack of an alcohol at the α -carbon atom of a vinylidene group is influenced by both steric and electronic factors. Thus, bulky phosphine ligands seem to inhibit such processes, as indicated by the inverse relationship between the relative reaction rates of $[\text{CpRu}=\text{C}=\text{CHPh}(\text{PPh}_3)(\text{PR}_3)]^+$ with MeOH and the cone angle of the phosphine PR_3 .^[30]

Conclusions

Contrasting reactivity patterns for $[\text{TpRu}(\kappa^2P,N\text{-}i\text{Pr}_2\text{PNHPy})\text{Cl}]$ (**1a**) and $[\text{TpRu}(\kappa^2P,N\text{-}i\text{Pr}_2\text{PSPy})\text{Cl}]$ (**1b**) towards $\text{NaBAR}^{\text{F}_4}$, lithium acetylide, and acetylenes have been elaborated. The use of diverse synthetic strategies enabled us to isolate a series of neutral acetylides **2a–2e**, cationic vinylidenes **3a–3e**, a cationic η^2 -alkyne complex $[\text{TpRu}(\eta^2\text{-HC}\equiv\text{CCOOMe})(\kappa^2P,N\text{-}i\text{Pr}_2\text{PSPy})][\text{BAR}^{\text{F}_4}]$, and methoxy(methyl)carbenes **5a** and **5b**.

The unambiguous structures of the cationic vinylidene **3a**, methoxy(methyl)carbenes **5a** and **5b**, and dinuclear complex **1b'** have been established by single-crystal X-ray diffraction studies. The presence of hemilabile *P,N* coligands prevents the hydrolysis of the acetylide complexes during the protonation reactions of mononuclear acetylide complexes. Notably, it is possible to protonate the mononuclear acetylides (**2c** and **2d**) and deprotonate the vinylidenes (**3c** and **3d**); however, the deprotonation of the vinylidene complexes (**3a** and **3b**) bearing 2-pyridyl(diisopropylphosphanyl)amine coligands could not reproduce the corresponding metal acetylides and instead led to a mixture of complexes, which could not be characterized.

Experimental Section

General: The reagents and solvents were purchased from commercial sources. All synthetic operations were performed under dry Ar or N_2 by conventional Schlenk techniques. Tetrahydrofuran, diethyl ether, and petroleum ether (boiling point range 40–60 °C) were obtained oxygen- and water-free from an Innovative Technology, Inc., solvent purification apparatus. Fluorobenzene, methanol, and other solvents were of anhydrous quality and were used as received. All solvents were deoxygenated immediately before use. The coligands *iPr*₂PNHPy and *iPr*₂PSPy^[33] were prepared as described in previous papers by our group, by following suitable modifications of published procedures.^[34] The complex $[\text{TpRu}(\kappa^2P,N\text{-}i\text{Pr}_2\text{PNHPy})\text{Cl}]$ ^[8b] and the $\text{NaBAR}^{\text{F}_4}$ salt^[35] were synthesized by reported methods. All alkynes were purchased from Aldrich and directly employed without further purification. The IR spectra were recorded from Nujol mulls with a Perkin–Elmer FTIR Spectrum 1000 spectrophotometer. The NMR spectra were recorded with Varian Inova 400 and 600 MHz and Varian Gemini 300 MHz spectrometers. Chemical shifts are given in parts per million relative to SiMe_4 (¹H and ¹³C{¹H}) or 85% H_3PO_4 (³¹P{¹H}). The ¹H and ¹³C{¹H} NMR signal assignments were confirmed by ¹H gCOSY, 135-DEPT, and ¹H–¹³C gradient heteronuclear single quantum coherence (gHSQC) experiments. Microanalysis was performed with a LECO CHNS-932 elemental analyzer at the Servicio Central de Ciencia y Tecnología, Universidad de Cadiz.

Chlorido Complexes $[\text{TpRu}(\kappa^2P,N\text{-}i\text{Pr}_2\text{PSPy})\text{Cl}]$ (1b**) and $\{[\text{TpRu}(\kappa^2P,N\text{-}i\text{Pr}_2\text{PSPy})]_2(\mu\text{-Cl})\}[\text{BAR}^{\text{F}_4}]$ (**1b')**:** A toluene solution of $[\text{TpRu}(\text{PPh}_3)_2\text{Cl}]$ and *iPr*₂PSPy was used to obtain **1b**. The dimer **1b'** was prepared by the addition of $\text{NaBAR}^{\text{F}_4}$ to a solution of $[\text{TpRu}(\kappa^2P,N\text{-}i\text{Pr}_2\text{PSPy})\text{Cl}]$ in fluorobenzene.

Neutral Acetylide Complexes $[\text{TpRu}(\text{C}\equiv\text{CR})(\kappa^2P,N\text{-}i\text{Pr}_2\text{PNHPy})]$ [$\text{X}=\text{NH}$, $\text{R}=\text{Ph}$ (2a**), SiMe_3 (**2b**); $\text{X}=\text{S}$, $\text{R}=\text{Ph}$ (**2c**), *p*- $\text{C}_6\text{H}_4\text{Br}$ (**2d**), COOMe (**2e**):** Different synthetic strategies were used to obtain derivatives bearing $[\text{TpRu}(\kappa^2P,N\text{-}i\text{Pr}_2\text{PNHPy})]$ or $[\text{TpRu}(\kappa^2P,N\text{-}i\text{Pr}_2\text{PSPy})]$ fragments. For **2a** and **2b**, the starting material was a THF solution of $[\text{TpRu}(\kappa^2P,N\text{-}i\text{Pr}_2\text{PNHPy})\text{Cl}]$, which was treated with a freshly prepared THF solution of $\text{LiC}\equiv\text{CPh}$ or $\text{LiC}\equiv\text{CSiMe}_3$. On the other hand, **2c**, **2d**, and **2e** were obtained by the reactions of excess *Kt*BuO with the corresponding THF solution of $[\text{TpRu}(\text{C}=\text{CHR})(\kappa^2P,N\text{-}i\text{Pr}_2\text{PSPy})][\text{BAR}^{\text{F}_4}]$ or $[\text{TpRu}(\eta^2\text{-HC}\equiv\text{CCOOMe})(\kappa^2P,N\text{-}i\text{Pr}_2\text{PSPy})][\text{BAR}^{\text{F}_4}]$.

Cationic Vinylidene Complexes $[\text{TpRu}(\text{C}=\text{CHR})(\kappa^2P,N\text{-}i\text{Pr}_2\text{PNHPy})][\text{CF}_3\text{SO}_3]$ { $\text{R}=\text{Ph}$ (3a**), SiMe_3 (**3b**):** Diethyl ether solutions of $[\text{TpRu}(\text{C}\equiv\text{CPh})(\kappa^2P,N\text{-}i\text{Pr}_2\text{PNHPy})]$ or $[\text{TpRu}(\text{C}\equiv\text{CSiMe}_3)(\kappa^2P,N\text{-}i\text{Pr}_2\text{PNHPy})]$ were treated with a slight excess of $\text{CF}_3\text{SO}_3\text{H}$ to obtain vinylidene complexes **3a** or **3b**.

Cationic Vinylidene Complexes $[\text{TpRu}(\text{C}=\text{CHR})(\kappa^2P,N\text{-}i\text{Pr}_2\text{PSPy})][\text{BAR}^{\text{F}_4}]$ { $\text{R}=\text{Ph}$ (3c**), *p*- $\text{C}_6\text{H}_4\text{Br}$ (**3d**)}** and **Primary Vinylidene $[\text{TpRu}(\text{C}=\text{CH}_2)(\kappa^2P,N\text{-}i\text{Pr}_2\text{PNHPy})][\text{BAR}^{\text{F}_4}]$ (**3e**):** In a typical preparation, a solution of $[\text{TpRu}(\kappa^2P,N\text{-}i\text{Pr}_2\text{PSPy})\text{Cl}]$ in fluorobenzene was treated with a slight excess of the corresponding 1-alkyne. To this mixture was added $\text{NaBAR}^{\text{F}_4}$ to obtain vinylidene complexes **3c** and **3d**.

A solution of $[\text{TpRu}(\kappa^2P,N\text{-}i\text{Pr}_2\text{PNHPy})\text{Cl}]$ in fluorobenzene was treated with excess acetylene to prepare the primary vinylidene complex **3e**.

η^2 -Alkyne Complex $[\text{TpRu}(\eta^2\text{-HC}\equiv\text{CCOOMe})(\kappa^2P,N\text{-}i\text{Pr}_2\text{PSPy})][\text{BAR}^{\text{F}_4}]$ (4**):** A solution of $[\text{TpRu}(\kappa^2P,N\text{-}i\text{Pr}_2\text{PSPy})\text{Cl}]$ in fluorobenzene was treated with a slight excess of $\text{HC}\equiv\text{CCOOMe}$. To this mixture was added $\text{NaBAR}^{\text{F}_4}$ to prepare η^2 -alkyne complex **4**.

Methoxycarbenes [TpRu(=C(OMe)CH₃)(κ²P,N-*i*Pr₂PXPpy)] [BPh₄] [X = NH (**5a**), S (**5b**): A solution/suspension of [TpRu(κ²P,N-*i*Pr₂PNHPy)Cl] or [TpRu(κ²P,N-*i*Pr₂PSPy)Cl] in methanol was treated with excess acetylene. To this mixture was added NaBPh₄ under an acetylene atmosphere to afford **5a** or **5b**. Alternatively, **5a** can be obtained as a [BARF₄] salt by the reaction of primary vinylidene **3e** with methanol.

Crystal Structure Analysis: Crystals of **1b**, **1b'**, **3a**, **5a**, and **5b** suitable for X-ray structural determination were mounted on glass fibers and then transferred to the cold nitrogen gas stream of a Bruker Smart APEX CCD three-circle diffractometer (*T* = 100 K) with a sealed-tube source and graphite-monochromated Mo-*K*_α radiation (λ = 0.71073 Å) at the Servicio Central de Ciencia y Tecnología de la Universidad de Cadiz. In each case, four sets of frames were recorded over a hemisphere of reciprocal space by ω scans with $\delta(\omega)$ = 0.30° and an exposure of 10 seconds per frame. Corrections for absorption were applied by scans of equivalents with the SADABS program.^[36] Insignificant crystal decay corrections were also applied. The structures of **1b**, **1b'**, **3b**, **5a**, and **5b** were solved by direct methods. All of the structures were refined on *F*² by full-matrix least-squares techniques (SHELX97)^[37] by using all unique data. All non-hydrogen atoms were refined anisotropically with hydrogen atoms included at calculated positions (riding model). The program ORTEP-3 was used to produce the plots.^[38] CCDC-968974 (for **1b**), -968975 (for **1b'**), -968976 (for **3a**), -968977 (for **5a**), and -968978 (for **5b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Details of the preparations, elemental analysis data, and spectroscopic data.

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