# Activation of 1-Alkynes by Hexamethylbenzene–Ruthenium(II) Derivatives. Synthesis and Characterization of Alkoxyalkylcarbene–Ruthenium(II) Complexes via Highly Reactive Vinylidene Intermediates

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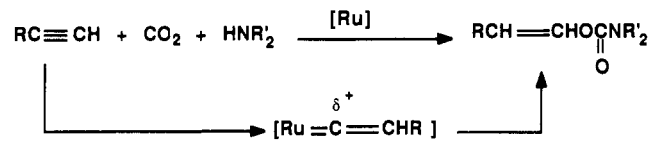
Hexamethylbenzene–ruthenium complexes $(\eta^6\text{-}C_6Me_6)(L)RuCl_2$ [L = $PMe_3$ (1), $PMe_2Ph$ (2), $PPh_3$ (3)] react with a variety of 1-alkynes RC≡CH (R = Ph, Me, *t*-Bu) in several alcohols (R'OH = MeOH, EtOH, *i*-PrOH) to produce alkoxyalkylcarbene complexes $[(\eta^6\text{-}C_6Me_6)(L)(Cl)Ru{=}C(OR')(CH_2R)]PF_6$ (4–8). Reaction of 1 with (trimethylsilyl)acetylene in methanol yields the methoxymethylcarbene complex **9a**. Treatment of 1 with 3-butyn-1-ol in methanol exclusively produces $[(\eta^6\text{-}C_6Me_6)(PMe_3)(Cl)Ru{=}\overline{COCH_2CH_2CH_2}]PF_6$ (**10a**). Carbene derivatives 4–10 are formed via an electrophilic vinylidene intermediate, which has been characterized for R = Ph: the reaction of 1 with PhC≡CLi or PhC≡CH/$Et_3N$ gives $[(\eta^6\text{-}C_6Me_6)(PMe_3)(Cl)Ru{-}C{\equiv}CPh]$ (11), which affords the vinylidene complex $[(\eta^6\text{-}C_6Me_6)(PMe_3)(Cl)(Ru{=}C{=}CHPh)]PF_6$ (12) by addition of $HBF_4{\cdot}OEt_2$ or $CF_3CO_2H$. Addition of methanol to 12 readily yields the methoxymethylcarbene complex **4a**. Cyclic voltammetry studies of complexes 1–3 and of isoelectronic ruthenium complexes $(C_5H_5)(L)(PPh_3)RuCl$ (L = $PPh_3$, CO) are reported and show that the electron deficiency of the $[(C_6Me_6)(PR_3)(Cl)Ru]$ fragments can explain the greatest reactivity of the corresponding vinylidene intermediates toward nucleophilic additions.

## Introduction

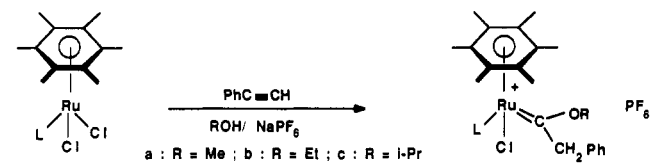
The activation of terminal alkynes by transition-metal complexes to give vinylidene metal derivatives is a well-known process.[1,2] Particularly, the stoichiometric reactions between $(\eta^5\text{-}C_5R_5)Ru(PR_3)_2Cl$ complexes (R = H, Me) and 1-alkynes have shown that cyclopentadienyl–ruthenium(II) compounds are excellent precursors of stable $\eta^1$-vinylidene compounds;[1-5] moreover, the initial formation of $\eta^2$-alkyne–ruthenium complexes followed by the rearrangement $[Ru(\eta^2\text{-}HC{\equiv}CR)] \rightarrow [Ru{=}C{=}C(H)R]$ has recently been established.[6] These ruthenium–vinylidenes have also received much attention as good precursors of σ-acetylide–,[2,6] alkoxycarbene–,[4-7] and alkyl- or acyl–ruthenium[7] complexes by reaction with bases, alcohols, and water, respectively.

By contrast, despite the increasing role of arene–ruthenium complexes in organometallic chemistry,[8] stoichiometric activation of alkynes by isoelectronic $(\eta^6\text{-}arene)Ru(PR_3)Cl_2$ was not studied. Our interest in this area was motivated by recent discoveries in our laboratory dealing with the ruthenium-catalyzed activation of terminal alkynes. Particularly, a new catalytic synthesis of vinylcarbamates from terminal alkynes was discovered[9] (Scheme I). In this reaction hexamethylbenzene–ruthenium complexes containing basic phosphines were found to be the best catalytic precursors, whereas cyclopentadienyl–ruthenium complexes were inactive. To account for the observed regioselectivity of the addition of the carbamate to the terminal carbon, the ruthenium–vinylidene intermediate was suggested as the active species. Thus, to gain insight into the mechanism, we have investigated the stoichiometric interaction between terminal alkynes and hexamethylbenzene–ruthenium dichloro phosphine complexes 1–3, for which a preliminary study was presented.[10] Here we report the results of our studies of the activation of several 1-alkynes with complexes 1–3 in alcohols. We describe an easy and general synthesis of new arene–ruthenium–carbene complexes, in one step from 1-alkynes. We show that the reaction occurs via highly reactive vinylidene intermediates and we report the characterization of the first arene–ruthenium–vinylidene complex. This paper describes an electrochemical study of several cyclopentadienyl- and hexamethylbenzene–ruthenium complexes, which demonstrates the highest electron deficiency of the $[(C_6Me_6)Ru(PR_3)Cl]$ vs the

**Scheme I**




**Scheme II**




1 : L = $PMe_3$ 4a-c

2 : L = $PMe_2Ph$ 5a

3 : L = $PPh_3$ 6a

(1) For a review of metal vinylidene complexes see: Bruce, M. I.; Swincer, A. G. *Adv. Organomet. Chem.* **1983**, *22*, 59.
(2) Silvestre, J.; Hoffmann, R. *Helv. Chim. Acta* **1985**, *68*, 1461.
(3) Bruce, M. I.; Wallis, R. C. *Aust. J. Chem.* **1979**, *32*, 1471.
(4) Bruce, M. I.; Wong, F. S.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1982**, 2203.
(5) Consiglio, G.; Morandini, F.; Ciani, G. F.; Sironi, A. *Organometallics* **1986**, *5*, 1976.
(6) Bullock, R. M. *J. Chem. Soc., Chem. Commun.* **1989**, 165.
(7) Bruce, M. I.; Swincer, A. G. *Aust. J. Chem.* **1980**, *33*, 1471.
(8) Le Bozec, H.; Touchard, D.; Dixneuf, P. H. *Adv. Organomet. Chem.* **1989**, *89*, 163.
(9) (a) Mahé, R.; Dixneuf, P. H.; Lécolier, S. *Tetrahedron Lett.* **1986**, 633. (b) Mahé, R.; Sasaki, Y.; Bruneau, C.; Dixneuf, P. H. *J. Org. Chem.* **1989**, *54*, 1518.
(10) Ouzzine, K.; Le Bozec, H.; Dixneuf, P. H. *J. Organomet. Chem.* **1986**, *317*, C25.

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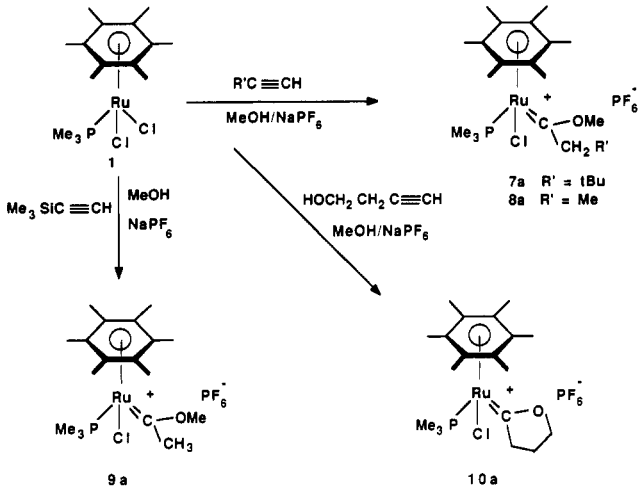
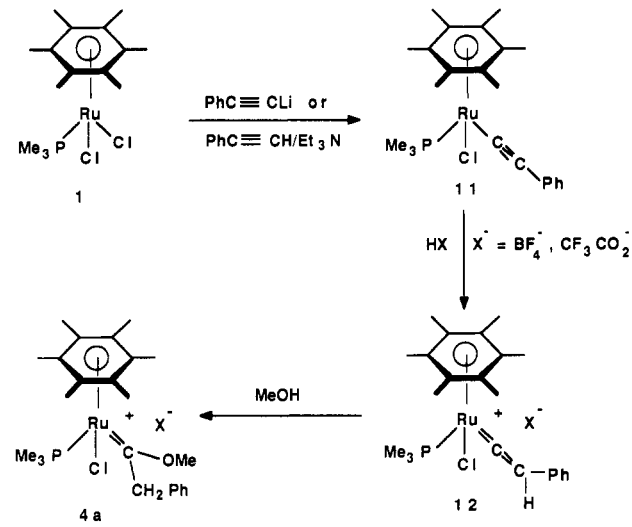
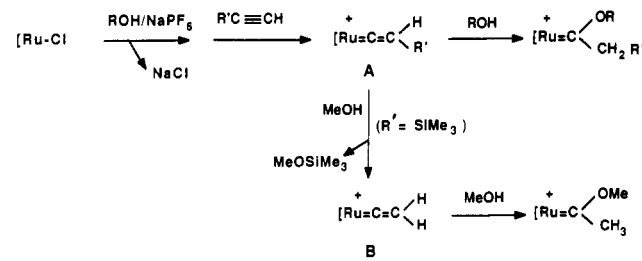
Scheme III



Scheme IV



Scheme V



$[(C_5H_5)Ru(PR_3)_2]$ fragments and thus explains the greatest electrophilic reactivity of the hexamethylbenzene vinylidene intermediates.

## Results and Discussion

**Synthesis of Alkoxyalkylcarbene–Ruthenium–Arene Complexes.** The reaction of hexamethylbenzene–ruthenium dichloro phosphine complexes **1–3** with an excess of phenylacetylene in methanol at room temperature, in presence of 1 equiv of $NaPF_6$, resulted in the rapid formation (10–15 min) of stable methoxybenzylcarbene–ruthenium complexes **4a**, **5a**, and **6a**, isolated as orange crystals from dichloromethane/ether in 60–80% yield. The same reaction occurred in ethanol and 2-propanol and gave after 20 and 30 min, respectively, the alkoxybenzylcarbene complexes **4b** and **4c** in ca. 60% yield (Scheme II). These complexes, which appeared to be the first isolated arene–ruthenium–carbene derivatives,[11] were characterized by elemental analyses and $^1H$, $^{31}P$, and $^{13}C$ NMR techniques. The presence of the carbene ligand was confirmed by low-field doublets found at ca. $\delta$ 320 ppm in the $^{13}C$ NMR spectra corresponding to the resonance of the metal-bonded (carbene) carbon nucleus coupled with the $^{31}P$ nucleus of the phosphorus ligand ($^2J_{PC} \sim 20$ Hz). The $^1H$ NMR spectra showed an AB system for the methylene protons, a signal consistent with a chiral ruthenium center.

The reaction of **1** with other 1-alkynes in methanol has also been investigated. Under similar conditions methoxyneopentyl- and methoxyethylcarbene complexes **7a** and **8a** were easily and rapidly obtained from *tert*-butylacetylene and propyne, respectively (Scheme III). Treating **1** with (trimethylsilyl)acetylene in methanol isolated the methoxymethylcarbene complex **9a** in 60% yield. The cleavage of the carbon–silicon bond by methanol in this reaction seems to be a general pathway since it has been observed in other carbene–platinum,[12] –tungsten,[13] and –ruthenium[5] complexes. Reaction of 3-butyn-1-ol with **1** in *methanol* gave exclusively the oxacyclopentylidene derivative **10a** in 61% yield, showing that the intramolecular addition of the hydroxy function of the alkynol is favored over the external addition of the methanol.[14]

**Evidence of the Ruthenium–Vinylidene Intermediates.** Arene–ruthenium–carbene derivatives **4–10** are expected to be formed via a vinylidene intermediate followed by addition of the alcohol to the electrophilic $C_\alpha$ carbon of the vinylidene ligand, as with the cyclopentadienyl–ruthenium series. However, we could never observe these arene–ruthenium–vinylidene intermediates under the reaction conditions or even at low temperature. Their reactivity toward alcohols contrasts with the stability of isoelectronic cyclopentadienyl–ruthenium–vinylidene compounds, which are generally obtained in refluxing alcohols.[7] Nevertheless, we have been able to characterize one hexamethylbenzene–ruthenium–vinylidene complex by using an indirect approach. The $\sigma$-acetylide complex **11** was obtained in 65% yield by treatment of **1** with lithium phenylacetylide in methanol or in 32% yield by reacting **1** with phenylacetylene in the presence of triethylamine (Scheme IV). Complex **11** was mainly characterized by a sharp $\nu_{C\equiv C}$ band at 2090 $cm^{-1}$ in its IR spectrum and by a doublet resonance at $\delta$ 119.5 ppm in the $^{13}C$ NMR spectrum, characteristic of the carbon $\sigma$-bonded to the ruthenium. Treatment of **11** in ether with a slight excess of $HBF_4 \cdot OEt_2$ resulted in an instantaneous color change from yellow to red, affording the phenylvinylidene complex **12** (Scheme IV). This rather unstable complex was better generated and spectroscopically characterized by reaction of $CF_3CO_2H$ with **11** in $CD_2Cl_2$. The $^{13}C\{^1H\}$ NMR spectrum revealed a doublet at $\delta$ 360 ppm characteristic of the highly electron deficient $C_\alpha$ carbon of the vinylidene ligand. The vinylidene $C_\beta$ carbon was found at $\delta$ 112 ppm with a vicinal $^1J_{CH}$ of 198 Hz in

(11) The only earlier carbene species was $[(C_6Me_6)(PMe_3)(Me)Ru{=}CH_2]PF_6$, which was suggested, but not isolated, as an intermediate by hydride elimination from $(C_6Me_6)(PMe_3)RuMe_2$. Werner, H.; Kletzin, H.; Höhn, A.; Paul, W.; Knaup, W. *J. Organomet. Chem.* **1986**, *306*, 227.

(12) Struchkov, Y. T.; Aleksandrov, G. G.; Pukhnarevich, V. B.; Sushchinskaya, S. P.; Voronkov, M. G. *J. Organomet. Chem.* **1979**, *172*, 269.

(13) Parlier, A.; Rudler, H. *J. Chem. Soc., Chem. Commun.* **1986**, 514.

(14) For use of 3-butyn-1-ol as a carbene precursor see: Dötz, K. H.; Sturm, W.; Alt, H. G. *Organometallics* **1987**, *6*, 1424 and references cited therein.

the nondecoupled $^{13}C$ NMR spectrum.

Evidence that hexamethylbenzene–ruthenium–vinylidene complexes were intermediates in the formation of carbene complexes **4–10** was provided by the addition of methanol to a THF solution of **12** ($X^- = BF_4^-$) at room temperature, which led within a few minutes to the methoxybenzyl complex **4a** ($X^- = BF_4^-$) (Scheme IV).

**Mechanism and Electrochemical Studies.** $(C_6Me_6)RuCl_2(PR_3)$ complexes **1–3** efficiently react within a few minutes under mild conditions with a variety of terminal alkynes in different alcohols to yield stable alkoxycarbene compounds **4–10**. This reaction, taking account of the transformation **11** → **12** → **4a**, is consistent with the mechanism illustrated in Scheme V: initial displacement of a chloride ligand in polar solvent and coordination of the alkyne to give $\eta^1$-vinylidene complex A should occur. The last step is expected to be the rapid nucleophilic attack of the alcohol on the electrophilic vinylidene ligand. The main observation is that A is immediately trapped by alcohol in comparison with the isoelectronic cations $[(C_5H_5)(PR_3)_2Ru{=}C{=}CHR]PF_6$, which are isolable and much less reactive toward nucleophiles:[3-7] for example $[(C_5H_5)(PPh_3)_2Ru{=}C{=}CHPh]PF_6$ was isolated after 30 min of reaction of $[(C_5H_5)(PPh_3)_2Ru\text{-}Cl]$ (**13**) and phenylacetylene in refluxing methanol and the complete addition of alcohol was only achieved after a 24-h reflux. The formation of complex **5a** from (trimethylsilyl)acetylene can be understood by a mechanism which involves the methanolysis of a (trimethylsilyl)vinylidene intermediate A to form a vinylidene B, followed by the rapid addition of methanol (Scheme V). The more stable $[(C_5H_5)(PMe_3)_2Ru{=}C{=}CH_2]PF_6$ has recently been isolated by Bullock from the reaction of $(C_5H_5)(PMe_3)_2Ru\text{–}Cl$ with (trimethylsilyl)acetylene in methanol; it slowly reacts with the solvent to give the corresponding methoxymethylcarbene–ruthenium complex.[6]

Several other relevant observations can be made. (i) All the hexamethylbenzene carbene complexes synthetized are stable whatever the nature of the phosphorus ligand. This contrasts with the relative instability of the corresponding *p*-cymene and trimethylbenzene carbene complexes, which have been isolated only with the bulky phosphine $PPh_3$.[15] The steric hindrance of the hexamethylbenzene ligand should contribute to the stabilization of the carbene complexes **4–10**. (ii) There is no significant difference of reactivity among **1–3** toward phenylacetylene in methanol: the nature of the phosphorus ligand—i.e. the bulkier but less basic $PPh_3$ vs the smaller but more basic $PMe_3$—has no apparent influence on the reaction rate. (iii) The reaction occurs more rapidly in methanol (10 min) than in ethanol (20 min) and in 2-propanol (30 min): the rate slightly decreases when the size of the sustituent R increases in ROH.

The variation in reactivity, especially between the *cyclopentadienyl*- and the *arene*–ruthenium series can be explained by not only steric but also electronic effects of the ancillary ligands. Thus, the nucleophilic attack of ROH on the electrophilic $C_\alpha$ of the vinylidene will be favored by small ligands and alcohols and by a lesser electronic density at the ruthenium center.

If comparison of the steric effects between the two series seems to be difficult, the electronic factors were estimated by studying the electrochemical behavior of several complexes, assuming that the redox potential $Ru^{III}/Ru^{II}$ reflects the electron density at the metal center. Cyclic voltammetry data of complexes **1–3** and $[(C_5H_5)(PPh_3)(L)RuCl]$ (**13**, L = $PPh_3$; **14**, L = CO) are summarized in Table I. For both types of complexes a reversible $Ru^{II} \rightarrow Ru^{III}$ oxidation is observed. The increase in $Ru^{III}/Ru^{II}$ potentials of the arene–ruthenium complexes **1–3** follows the expected decrease in $\sigma$-donor ability of the phosphines $PMe_3$, $PMe_2Ph$, and $PPh_3$. The values also show that the $Ru^{III}/Ru^{II}$ potentials for **13** are 390, 300, and 240 mV less positive than those of complexes **1–3**, respectively. Thus these potentials show that the $[(C_6Me_6)(PR_3)ClRu]$ moieties are much less electron rich than the $[(C_5H_5)(PPh_3)_2Ru]$ moiety and consequently do not stabilize as much the vinylidene ligand toward nucleophilic attacks. On the contrary a decreasing of the electron density at ruthenium center is expected to increase the electrophilicity of the vinylidene ligand and to enhance its reactivity toward alcohols. In the cyclopentadienyl series, the difference in $Ru^{III}/Ru^{II}$ potentials between **13** (L = $PPh_3$) and **14** (L = CO) ($\Delta E_{1/2}$ = 490 mV) reflects the observed difference in reactivity of the corresponding vinylidene complexes.[7]

**Table I. Cyclic Voltammetric Data for Ruthenium Complexes[a]**

| complex | $E_{1/2}$ ($Ru^{III}/Ru^{II}$), V | $\Delta E_p$, mV |
|---|---|---|
| $(C_6Me_6)RuCl_2L$ | | |
| L = $PMe_3$ (**1**) | 0.77 | 80 |
| L = $PMe_2Ph$ (**2**) | 0.83 | 70 |
| L = $PPh_3$ (**3**) | 0.92 | 80 |
| $(C_5H_5)RuCl(PPh_3)L$ | | |
| L = $PPh_3$ (**13**) | 0.53 | 60 |
| L = CO (**14**) | 1.01 | 60 |
| $[(C_6Me_6)Ru(=C(OMe)CH_2Ph)Cl(PMe_3)]PF_6$ (**4a**) | 1.15 | 80 |
| $[(C_6Me_6)Ru(=C(OMe)Et)Cl(PMe_3)]PF_6$ (**8a**) | 1.13 | 70 |
| $[(C_5H_5)Ru(=C(OMe)CH_2Ph)Cl(PPh_3)_2]PF_6$ (**15**) | 1.27[b] | |

[a] *E* vs SCE, Pt working electrode, 200 mV/s. Recorded in $CH_3CN$ solution with 0.1 M $Bu_4NPF_6$ as supporting electrolyte. [b] Irreversible couple; $E_p^a$ reported.

The redox behavior of the methoxycarbenes **4a**, **8a** and $[(C_5H_5)(PPh_3)_2Ru{=}C(OMe)CH_2Ph]PF_6$ (**15**) has also been investigated (Table I). Cyclic voltammogramms of **4a** and **8a** in $CH_3CN$ solution exhibit a reversible $Ru^{II} \rightarrow Ru^{III}$ oxidation ($i_p^c/i_p^a = 1$; $\Delta E_p$ = 80 mV). By contrast, a totally irreversible anodic oxidation is observed for the cyclopentadienyl complex **15** ($E_p^a$ = 1.27 V). This suggests the possibility of generating the one-electron-oxidized carbene complexes in the arene–ruthenium series only.

## Conclusion

The present results shows that $(arene)RuCl_2(PR_3)$ complexes are much more efficient than isoelectronic $(C_5H_5)RuCl(PR_3)_2$ for the formation of alkoxycarbene complexes by activation of 1-alkynes in alcohols. They allow the formation of new chiral carbene–ruthenium complexes, in a few minutes at room temperature, via reactive arene–ruthenium–vinylidenes. A parallel can be drawn with the catalytic regioselective syntheses of vinylcarbamates from terminal alkynes: arene–ruthenium complexes **1–3** are efficient catalyst precursors whereas the cyclopentadienyl–ruthenium complex **13** is inactive. Thus, either for stoichiometric or for catalytic activation of terminal alkynes by ruthenium(II) complexes, a ruthenium–vinylidene seems to be the key intermediate, and its easy transformation into carbene is largely favored by the $(arene)RuCl(PR_3)^+$ moiety with respect to the isoelectronic $(C_5H_5)Ru(PR_3)_2^+$.

(15) Devanne, D.; Dixneuf, P. H. *J. Organomet. Chem.* **1990**, *390*, 371.

## Experimental Section

**General Data.** All reactions were performed under argon or nitrogen atmosphere with use of Schlenk techniques. The solvents were deoxygenated and dried by standard methods. Infrared spectra were recorded on a Pye Unicam SP 1100 spectrophotometer. $^1H$ (300 MHz) and $^{13}C$ (75.47 MHz) NMR spectra were recorded on a Bruker AM 300 spectrometer at 297 K and referenced to TMS. $^{31}P$ (32.38 MHz) NMR spectra were recorded on a Bruker WP 80 instrument at 309 K and referenced to external 85% $H_3PO_4$. Elemental analyses were perfomed by the Service Central de Microanalyse du CNRS at Lyon, France.

Electrochemical measurements were recorded by using a EGG PAR Model 362 scanning potentiostat with an XY recorder. Cyclic voltammogramms were recorded in a single-compartment cell by using a 2 mm Pt-disk working electrode and a 2 mm Pt-disk auxiliary electrode. The reference electrode was an aqueous saturated calomel electrode (SCE). Purified $Bu_4NPF_6$ was used as electrolyte.

The compounds ($\eta^6$-$C_6Me_6$)$RuCl_2(PR_3)$[16] and [($\eta^5$-$C_5H_5$)Ru=C(OMe)$CH_2$Ph)$(PPh_3)_2$]$PF_6$[7] were prepared by literature methods.

**Preparation of [Ru($C_6Me_6$)(L)Cl(=C(OR)$CH_2R'$)]$PF_6$ (4a–c, 5a, 7a, 9a, 10a).** To a solution of **1** or **2** (1 mmol) in 30 mL of alcohol was added 167 mg (1 mmol) of $NaPF_6$ and 5 mmol of R′—C≡CH. The reaction mixture was stirred for 10–30 min at room temperature. Addition of 30 mL of ether led to the precipitation of a yellow powder. The precipitate was dissolved in dichloromethane (10 mL) and filtered to eliminate NaCl. Adding ether or hexane (10–20 mL) and cooling to −20 °C gave **4a–c**, **5a**, **7a**, **9a**, and **10a** as orange-red crystals.

**4a** (L = $PMe_3$, R = Me, R′ = Ph): 395 mg of **4a** (60%) was obtained from 410 mg of **1** and 0.5 mL of PhC≡CH in MeOH. Anal. Calcd for $C_{24}H_{37}ClF_6OP_2Ru$: C, 44.08; H, 5.70; Cl, 5.42. Found: C, 44.26; H, 5.66; Cl, 5.91. IR ($cm^{-1}$, Nujol): 1590 ($\nu_{Ar}$), 840 ($\nu_{P-F}$). $^1H$ NMR ($CD_2Cl_2$, δ): 7.35 (m, 5 H, $C_6H_5$), 5.04 and 4.50 (dd, 2 H, $^2J_{HH}$ = 13.0 Hz, $CH_2$), 4.59 (s, 3 H, OMe), 2.01 (s, 18 H, $C_6Me_6$), 1.44 (d, 9 H, $^2J_{PH}$ = 10.6 Hz, $PMe_3$). $^{31}P$ NMR ($CD_2Cl_2$, δ): 8.12 (s, $PMe_3$), −143.50 (sept, $PF_6^-$). $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$, δ): 323.10 (d, $^2J_{PC}$ = 20.64 Hz, Ru=C), 132.05, 131.10, 129.49, 128.22 (s, $C_6H_5$), 100.19 (s, $C_6Me_6$), 68.05 (s, OMe), 56.83 (s, $CH_2$), 16.57 (s, $C_6Me_6$), 16.24 (d, $^1J_{PC}$ = 35.1 Hz, $PMe_3$).

**4b** (L = $PMe_3$, R = Et, R′ = Ph): 384 mg of **4b** (58%) was obtained from 410 mg of **1** and 0.5 mL of PhC≡CH in EtOH. Anal. Calcd for $C_{25}H_{39}ClF_6OP_2Ru$: C, 44.95; H, 5.88; P, 9.27. Found: C, 44.27; H, 5.44; P, 8.91. IR ($cm^{-1}$, Nujol): 1590 ($\nu_{Ar}$), 840 ($\nu_{P-F}$). $^1H$ NMR ($CD_2Cl_2$, δ): 7.36 (m, $C_5H_5$), 5.03 and 4.58 (dd, 2 H, $^2J_{HH}$ = 12.7 Hz, $CH_2$), 4.87 (q, 2 H, $OCH_2$); 2.00 (s, 18 H, $C_6Me_6$), 1.60 (t, 3 H, Me), 1.45 (d, 9 H, $^2J_{PH}$ = 10.7 Hz, $PMe_3$). $^{31}P$ NMR ($CD_2Cl_2$, δ): 7.83 (s, $PMe_3$), −144.33 (sept, $PF_6^-$). $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$, δ): 342.14 (d, $^2J_{PC}$ = 21.19 Hz, Ru=C), 133.90, 132.88, 131.38, 130.08 (s, $C_6H_5$), 109.78 (s, $C_6Me_6$), 76.81 (s, $OCH_2$), 58.70 (s, $CH_2$), 18.34 (s, $C_6Me_6$), 17.77 (d, $^1J_{PC}$ = 35.0 Hz, $PMe_3$), 16.77 (s, Me).

**4c** (L = $PMe_3$, R = *i*-Pr, R′ = Ph): 388 mg of **4c** (57%) was obtained from 410 mg of **1** and 0.5 mL of PhC≡CH in *i*-PrOH. Anal. Calcd for $C_{26}H_{41}ClF_6OP_2Ru$: C, 45.78; H, 6.07; P, 9.10. Found: C, 45.66; H, 6.10; P, 9.15. IR ($cm^{-1}$, Nujol): 1595 ($\nu_{Ar}$), 830 ($\nu_{P-F}$). $^1H$ NMR ($CD_2Cl_2$, δ): 7,.38 (m, $C_6H_5$), 5.90 (sept, 1 H, $^3J_{HH}$ = 6.1 Hz, $OCHMe_2$), 5.11 and 4.58 (dd, 2 H, $^2J_{HH}$ = 12.7 Hz, $CH_2$), 1.99 (s, $C_6Me_6$), 1.57–1.31 (dd, 6 H, $-CHMe_2$), 1.48 (d, $^2J_{PH}$ = 10.6 Hz, $PMe_3$). $^{31}P$ NMR ($CD_2Cl_2$, δ): 7.38 (s, $PMe_3$), −143.48 (sept, $PF_6^-$). $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$, δ): 317.76 (d, $^2J_{PC}$ = 22.0 Hz, Ru=C), 132.22, 130.59, 129.78, 128.27 (s, $C_6H_5$), 107.04 (s, $C_6Me_6$), 88.66 (s, $OCHMe_2$), 55.92 (s, $CH_2$), 23.21–22.72 (s, $CHMe_2$), 16.60 (s, $C_6Me_6$), 15.21 (d, $^1J_{PC}$ = 34.0 Hz, $PMe_3$).

**5a** (L = $PMe_2Ph$, R = Me, R′ = Ph): 422 mg of **5a** (59%) was obtained from 441 mg of **2** and 0.5 mL of PhC≡C—H in MeOH. Anal. Calcd for $C_{29}H_{39}ClF_6OP_2Ru$: C, 48.65; H, 5.48; P, 8.65. Found: C, 48.68; H, 5.40; P, 8.63. IR ($cm^{-1}$, Nujol): 1595 ($\nu_{Ar}$), 835 ($\nu_{P-F}$). $^1H$ NMR ($CD_2Cl_2$, δ): 7.63 (m, 5 H, $PMe_2Ph$), 7.37 (m, 5 H, $C_6H_5$), 5.49 and 4.09 (dd, 2 H, $^2J_{HH}$ = 12.0 Hz, $CH_2$), 4.60 (s, 3 H, OMe), 1.77 (s, 18 H, $C_6Me_6$), 1.69 (dd, $^2J_{PH}$ = 10.5 Hz, $PMe_2Ph$). $^{31}P$ NMR ($CD_2Cl_2$, δ): 12.65 (s, $PMe_2Ph$), −144.50 (sept, $PF_6^-$). $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$, δ): 319.27 (d, $^2J_{PC}$ = 19.74 Hz, Ru=C), 136.8, 136.0, 133.0, 132.5, 132.0, 131.0, 131.0, 130.0 (s, $PMe_2Ph$ and $C_6H_5$), 100.85 (s, $C_6Me_6$), 69.39 (s, OMe), 56.38 (s, $CH_2$), 15.60 (s, $C_6Me_6$), 18.37–14.51 (d, $^1J_{PC}$ = 37.7 and 36.8 Hz, $PMe_2Ph$).

**7a** (L = $PMe_3$, R = Me, R′ = *t*-Bu): 355 mg of **7a** (56%) was obtained from 40 mg of **1** and 0.5 mL of *t*-Bu—C≡C—H in MeOH. Anal. Calcd for $C_{22}H_{41}ClF_6OP_2Ru$: C, 41.67; H, 6.52. Found: C, 40.68; H, 6.52. IR ($cm^{-1}$, Nujol): 840 ($\nu_{P-F}$). $^1H$ NMR ($CD_2Cl_2$, δ): 4.59 (s, 3 H, OMe), 3.70 and 3.10 (dd, 2 H, $^2J_{HH}$ = 20.6 Hz, $CH_2$), 2.13 (s, 18 H, $C_6Me_6$), 1.43 (d, 9 H, $^2J_{PH}$ = 10.5 Hz, $PMe_3$), 1.00 (s, 9 H, *t*-Bu). $^{31}P$ NMR ($CD_2Cl_2$, δ): 0.7 (s, $PMe_3$), −144.5 (sept, $PF_6^-$). $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$, δ): 330.45 (d, $^2J_{PC}$ = 16.1 Hz, Ru=C), 105.69 (s, $C_6Me_6$), 66.44 (s, OMe), 29.94 (s, *C*-*t*-Bu), 17.27 (s, $C_6Me_6$), 16.73 (d, $^1J_{PC}$ = 35.0 Hz, $PMe_3$).

**9a** (L = $PMe_3$, R = Me, R′ = H): 352 mg of **9a** (61%) was obtained from 410 mg of **1** and 0.5 mL of $Me_3SiC{\equiv}CH$ in MeOH. Anal. Calcd for $C_{18}H_{33}ClF_6OP_2Ru$: C, 37.41; H, 5.76; P, 10.72. Found: C, 37.40; H, 5.68; P, 10.89. IR ($cm^{-1}$, Nujol): 840 ($\nu_{P-F}$). $^1H$ NMR ($CD_2Cl_2$, δ): 4.48 (s, 3 H, OMe), 2.98 (s, 3 H, Me), 2.11 (s, 18 H, $C_6Me_6$), 1.37 (d, 9 H, $^2J_{PH}$ = 10.7 Hz, $PMe_3$). $^{31}P$ NMR ($CD_2Cl_2$, δ): 10.50 (s, $PMe_3$), −143.33 (sept, $PF_6^-$). $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$, δ): 330.86 (d, $^2J_{PC}$ = 21.2 Hz, Ru=C), 107.02 (s, $C_6Me_6$), 66.02 (s, OMe), 40.29 (s, Me), 16.34 (s, $C_6Me_6$), 15.59 (d, $^1J_{PC}$ = 35.0 Hz, $PMe_3$).

**10a** (L = $PMe_3$, R, R′ = $CH_2CH_2$): 353 mg of **10a** (60%) was obtained from 410 mg of **1** and 0.5 mL of $HO(CH_2)_2C{\equiv}CH$ in MeOH. Anal. Calcd for $C_{19}H_{33}ClF_6OP_2Ru$: C, 38.68; H, 5.64; P, 10.50. Found: C, 37.65; H, 5.52; P, 10.31. IR ($cm^{-1}$, Nujol): 840 ($\nu_{P-F}$). $^1H$ NMR ($CD_2Cl_2$, δ): 5.17 (t, 2 H, $^3J_{HH}$ = 7.8 Hz, $OCH_2$), 3.70 and 3.29 (ddd, 2 H, $^2J_{HH}$ = 21.1 Hz, $^3J_{HH}$ = 6.85 and 9.25 Hz, Ru=C—$CH_2$), 2.17 (m, 2 H, $OCH_2$—$CH_2$–), 2.13 (s, 18 H, $C_6Me_6$), 1.39 (d, 9 H, $^2J_{PH}$ = 10.7 Hz, $PMe_3$). $^{31}P$ ($CD_2Cl_2$, δ): 8.58 (s, $PMe_3$), −144.33 (sept, $PF_6^-$). $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$, δ): 317.38 (d, $^2J_{PC}$ = 22.0 Hz, Ru=C), 106.39 (s, $C_6Me_6$), 87.98 (s, $OCH_2$–), 55.96 (s, Ru=C—$CH_2$), 21.54 (s, $CH_2$–$CH_2$–$CH_2$), 16.19 (s, $C_6Me_6$), 14.10 (d, $^1J_{PC}$ = 34.6 Hz, $PMe_3$).

**Preparation of [Ru($C_6Me_6$)($PPh_3$)Cl(=C(OMe)$CH_2$Ph)]$PF_6$ (6a).** To a solution of 300 mg of **3** (0.50 mmol) in 20 mL of dichloromethane was successively added 20 mL of methanol, 90 mg of $NaPF_6$ (0.54 mmol), and 0.25 mL of PhC≡CH. The reaction mixture was stirred at room temperature for 20 min. The solvent was removed in vacuo. The reaction mixture was dissolved in dichloromethane (10 mL) and filtered to eliminate NaCl. Adding ether and cooling to −20 °C gave 330 mg (82%) of **6a** as orange microcrystals. Anal. Calcd for $C_{39}H_{43}ClF_6OP_2Ru$: C, 55.75; H, 5.16; P, 7.37. Found: C, 56.16; H, 5.17; P, 6.75. $^1H$ NMR ($CD_2Cl_2$, δ): 7.45–7.13 (m, $C_6H_5$), 4.76 (d, 1 H, $^2J_{HH}$ = 12.7 Hz, $CH_2$), 4.50 (s, 3 H, OMe), 2.65 (d, 1 H, $^2J_{HH}$ = 13.03 Hz, $CH_2$), 1.72 (s, 18 H, $C_6Me_6$). $^{31}P$ NMR ($CD_2Cl_2$, δ): 36.06 (s, $PPh_3$), −143.40 (sept, $PF_6^-$). $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$, δ): 316.60 (d, $^2J_{PC}$ = 18.65 Hz, Ru=C), 135.02, 134.89, 131.93, 131.65, 130.90, 129.37, 129.02, 128.88, 128.20 (s, $C_6H_5$ and $P(C_6H_5)_3$), 110.57 (s, $C_6Me_6$), 68.06 (s, $OCH_3$), 53.94 (s, $CH_2$), 16.23 (s, $C_6Me_6$).

**Preparation of [Ru($C_6Me_6$)($PMe_3$)Cl(=C(OMe)-$CH_2CH_3$)]$PF_6$ (8a).** A 10-mmol sample of propyne was dissolved in 50 mL of methanol at −60 °C. Then, 820 mg (2 mmol) of complex **1** and 334 mg (2 mmol) of $NaPF_6$ were added to the solution at room temperature. The reaction mixture was stirred for 10 min at room temperature. Addition of 30 mL of ether led to precipitation of a yellow powder. The precipitate was dissolved in 15 mL of dichloromethane. The solution was filtered to eliminate NaCl, and addition of 15 mL of ether afforded, after cooling to −20 °C, 760 mg (64% yield) of **8a** as yellow microcrystals. Anal. Calcd for $C_{19}H_{35}ClF_6OP_2Ru$: C, 38.55; H, 5.96. Found: C, 38.62; H, 5.98. IR ($cm^{-1}$, Nujol): 840 ($\nu_{P-F}$). $^1H$ NMR ($CD_2Cl_2$, δ): 4.88 (s, 3 H, OMe), 2.44 (s, 18 H, $C_6Me_6$), 1.72 (d, 9 H, $^2J_{PH}$ = 10.8 Hz, $PMe_3$), 1.45 (t, 3 H, Me). $^{31}P$ ($CD_2Cl_2$, δ): 9.64 (s, $PMe_3$), −143.48 (sept, $PF_6^-$). $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$, δ): 330.39 (d, $^2J_{PC}$ = 20.6 Hz, Ru=C), 107.0 (s, $C_6Me_6$), 66.60 (s, OMe), 45.73 (s, $CH_2$), 16.64 (s, $C_6Me_6$), 16.13 (d, $^1J_{PC}$ = 34.7 Hz, $PMe_3$), 8.80 (s, Me).

**Preparation of Ru($C_6Me_6$)($PMe_3$)Cl(C≡C—Ph) (11). Method A.** A 3.2-mmol sample of *n*-butyllithium in hexane (2 mL) was added to 3 mmol of phenylacetylene (0.3 mL) at −78 °C. The reaction mixture was stirred for 5 min at −78 °C. A solution

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of 1 (410 mg, 1 mmol) in 30 mL of methanol was then transferred via cannula to the lithium phenylacetylide. The orange solution progressively turned dark yellow. After being stirred for 1 h at room temperature, 20 mL of ether was added to the reaction mixture. The solution was cooled to -20 °C for 4 h. A total of 309 mg (65% yield) of 11 was isolated as yellow microcrystals.

**Method B.** Into a Schlenk tube containing a methanol solution (40 mL) of 410 mg of 1 (1 mmol) were successively added at room temperature 0.5 mL of phenylacetylene (5 mmol) and 2 mL of triethylamine (13.8 mmol). After the mixture was stirred for 2 h at room temperature, the solvent was evaporated to dryness. The residue was extracted with 10 mL of dichloromethane. Addition of an excess of ether led to precipitation of a yellow powder of 11 (152 mg, 32% yield). Anal. Calcd for $C_{23}H_{32}ClPRu$: C, 58.05; H, 6.77; P, 6.52. Found: C, 57.95; H, 6.68; P, 6.40. IR ($cm^{-1}$, Nujol): 2090 ($\nu_{C\equiv C}$). $^1H$ NMR ($CD_2Cl_2$, $\delta$): 7.10 (m, 5 H, $C_6H_5$), 2.09 (s, 18 H, $C_6Me_6$), 1.50 (d, 9 H, $^2J_{PH}$ = 10.4 Hz, $PMe_3$). $^{31}P$ NMR ($CD_2Cl_2$, $\delta$): 6.90 (s, $PMe_3$). $^{13}C$ NMR ($CD_2Cl_2$, $\delta$): 129.40 (m, $C_6H_5$), 119.49 (d, $^2J_{PC}$ = 41.1 Hz, Ru-C), 105.44 (s, Ph-*C*) 100.00 (s, $C_6Me_6$), 16.64 (d, $^1J_{PC}$ = 34.3 Hz, $PMe_3$), 16.35 (s, $C_6Me_6$).

**Generation and NMR Characterization of $[Ru(C_6Me_6)(PMe_3)Cl(=C=CHPh)]CF_3CO_2^-$ (12).** A solution of 330 mg (0.7 mmol) of 7 in 4 mL of $CD_2Cl_2$ in a 10-mm NMR tube was degassed with argon. The addition of a slight excess of $CF_3CO_2H$ led to the immediate formation of a red solution. $^1H$ and $^{13}C$ NMR spectra were recorded at -60 °C. $^1H$ NMR ($CD_2Cl_2$, $\delta$): 7.30 (m, 5 H, $C_6H_5$), 5.66 (s, 1 H, =C*H*Ph), 2.20 (s, 18 H, $C_6Me_6$), 1.64 (d, 9 H, $^2J_{PH}$ = 11.6 Hz, $PMe_3$). $^{13}C$ NMR ($CD_2Cl_2$, $\delta$): 360.34 (d, $^2J_{PC}$ = 20.6 Hz, Ru=C), 130 (m, $C_6H_5$), 112.30 (d, $^1J_{CH}$ = 198 Hz, =*C*HPh), 100.20 (s, $C_6Me_6$), 17.48 (q, $^1J_{CH}$ = 130 Hz), $C_6Me_6$), 16.56 (dq, $^1J_{CH}$ = 129 Hz, $PMe_3$).

**Preparation of 4a from 12.** To a suspension of 380 mg (1 mmol) of 11 in 50 mL of ether was added by syringe a slight excess of $HBF_4{\cdot}Et_2O$ (0.2 mL). The yellow reaction mixture immediately turned red. Complex 12, which was isolated as a red oil after removal of the solvent, was dissolved in 10 mL of tetrahydrofuran. Then, 1 mL of methanol was added. The red reaction mixture rapidly turned orange. After the mixture was stirred for 1 h, the solvent was removed in vacuo. Adding dichloromethane and then ether and cooling to -20 °C gave 4a ($X^- = BF_4^-$) as orange-red crystals.

# New Photochemical Routes to Germylenes and Germenes and Kinetic Evidence Concerning the Germylene–Diene Addition Mechanism†

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Upon 254-nm irradiation of phenylbis(trimethylsilyl)germanes, there is competition between two germylene-forming reactions, the unexpected elimination of phenyltrimethylsilane and the elimination of hexamethyldisilane. Irradiation of a phenylmonosilylgermane $PhGeMe_2SiMe_3$ leads to predominant elimination of $PhSiMe_3$, forming dimethylgermylene $Me_2Ge$:, accompanied by migration of $Me_3Si$ to the ortho position of the phenyl ring, forming a germene. Laser flash photolysis of $PhGeMe_2SiMe_3$ is a convenient source of $Me_3Ge$:, and rate constants are reported for $Me_2Ge$: addition to a series of dienes and other substrates. The kinetic data are in accord with 1,2-addition as the dominant pathway for addition of $Me_2Ge$: to 1,3-dienes.

The mechanistic study of germylenes, carbene analogues containing a divalent germanium atom, is currently an active field,[1] but it has been hampered by a shortage of convenient photochemical precursors. Polygermanes such as $Me_3Ge(GeMe_2)_2GeMe_3$[2] and $(PhGeMe_2)_2GeMe_2$[3] are laborious to synthesize and give clear evidence of radical side reactions. Cyclopolygermanes c-$(GeMe_2)_6$[4] and c-$(GeAr_2)_3$[5] also present synthetic hurdles, as do precursors containing a single germanium atom $(PhSe)_2GeMe_2$[6] and 7-germanorbornadiene derivatives.[7] Diazides such as $Me_2Ge(N_3)_2$ are easy to make but inefficient germylene sources.[8]

Silylgermanes, on the other hand, are readily synthesized, and disilylgermanes $(Me_3Si)_2GeRR'$ have been reported to extrude germylenes under ultraviolet irradiation.[9,10] This process parallels the well-known extrusion of silylenes from chains of three or more silicon atoms.[11]

$$(Me_3Si)_2GeRR' \xrightarrow{h\nu} Me_3SiSiMe_3 + :GeRR'$$

In scrutinizing the products from a germylene formed in such a process, $Ph_2Ge$:, some of whose reactions we have studied by kinetic spectroscopy,[12] evidence was found for

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