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Invited review

Some organometallic chemistry of ruthenium(II)

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Abstract

Stoichiometric and catalytic reactions of Ru(II) phosphine complexes with alkynes, olefins, and enynes are described. The hydride complex RuCl(CO)H(PPh$_3$)$_3$ (**1**) reacts with the double bond of a *cis*-enyne whereas it reacts with triple bonds of *trans*-enynes. Metathesis of vinyl silanes with olefins are catalyzed by **1** where β-Si elimination is the key step. Dimerizations of ^{t}Bu- and Me$_3$Si-substituted acetylenes into the corresponding butatrienes are catalyzed by Ru(II) active species as studied by isolation of the intermediates. A model reaction for the crucial step of the catalytic cycle, formation of a Ru vinylidene complex from acetylene, has been fully simulated by *ab initio*-MO calculations.

Keywords: Ruthenium; Olefins; Alkynes; Catalysis; Crystal structure; MO calculations

1. Addition of ruthenium hydride to a CC double or triple bond

Insertion of an unsaturated unit into a transition metal-hydride is one of the most important reactions in organometallic chemistry and has been recognized as the crucial step in transition metal-catalyzed hydrogenation of organic unsaturated molecules. Since the double bond is in general less reactive towards hydrogenation, partial hydrogenation of alkynes to alkenes can be achieved by use of many heterogeneous systems [1], e.g. the Lindler catalyst (Pd/BaSO$_4$), and several homogeneous catalysts, such as (arene)tricarbonylchromium [2] and cationic Rh(I) or Fe(II) complexes [3]. The hydrogenation of conjugated enynes by heterogenized homogeneous Pd(II) has been shown to give conjugated dienes in good yields [4], suggesting that triple bonds are more reactive than double bonds. The high selectivity towards formation of styrene in the hydrogenation of phenylacetylene by OsCl(CO)H(PR$_3$)$_2$/H$_2$ has been attributed to the thermodynamic stability of the metal–vinyl intermediate over the metal–alkyl species [5]. The reaction of an analogous ruthenium complex, RuCl(CO)H(PPh$_3$)$_3$ (**1**), with mono- and di-substituted alkynes has been known to give stable alkenyl complexes of the type RuCl(CO)(R′C = CHR)(PPh$_3$)$_2$ [6]. Insertion products with simple alkenes, on the other hand, are thermally unstable because β-hydrogen elimination takes place readily from alkylruthenium complexes.

The reaction of an excess of *cis*-(R)CH = CH–C≡C–R (**2**, R = SiMe$_3$) with **1** takes place smoothly in THF at room temperature to give orange crystals of (**3**), of the composition RuCl(CO)(H · RCHCHC$_2$R)(PPh$_3$)$_2$ in almost quantitative yield (Scheme 1) [7].

Its ^{1}H NMR spectrum shows signals from two of the three protons of the C4 chain in the aliphatic region, δ 1.48 and 1.26. That these two protons are attached to the same carbon atom, forming a CH$_2$ group, is further confirmed by a 2-D ^{13}C–^{1}H shift correlated NMR spectrum of the much more soluble P(p-MeOC$_6$H$_4$)$_3$ analog, RuCl(CO)(H · RCHCHC$_2$R)(P(p-MeO–C$_6$H$_4$)$_3$)$_2$ (R = SiMe$_3$).

An X-ray structure analysis of **3** revealed that the C4 skeleton lies approximately in the (Ru–P–P) plane. Three of the carbon atoms interact with the metal to form an η^3-coordination through C(2)–C(3)–C(4), while the fourth carbon is a CH$_2$ group. Thus the atoms Ru–C(2)–C(3)–C(4) are essentially coplanar, with Ru–C(2) 2.282(5) Ru–C(3) 2.192(5) and Ru–C(4) 2.366(5) Å and a C(2)–C(3)–C(4) angle of 157.1(5)°. Complexes with the "η^3-propynyl" type coordination are rare and there are only two precedents, namely [Os(η^3-PhC$_3$CHPh)(PMe$_3$)$_4$]PF$_6$ and Ru(CCPh)(η^3-Ph-C$_3$CHPh)(Cyttp), both of which were synthesized by use of a coupling reaction of phenylacetylene [8,9].

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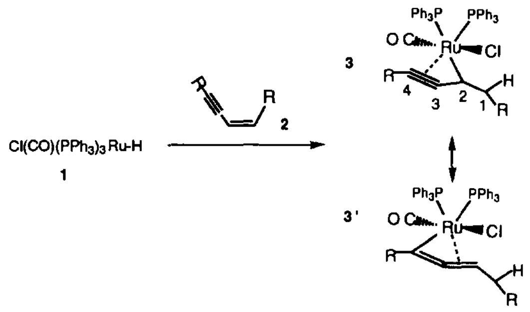
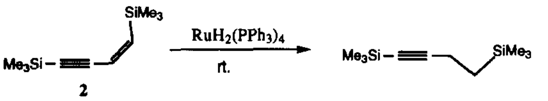


Scheme 1.

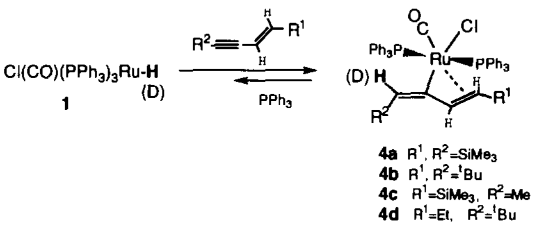
Coordination of the triple bond in **3** appears to be maintained in solution, and this should make the complex rather stable. Although it has aliphatic β-hydrogens, decomposition of **3** in benzene is negligible after 10 h at room temperature. Moreover, the very different ^{1}H NMR coupling of the methylene protons H(C1)1 and H(C1)2 with H(C2) (13 and 4 Hz) and the P atoms (1.7 and 4 Hz) suggests that rotation about Ru–C(2) and C(1)–C(2) bonds is quite restricted.

The structure may be viewed as a combination of resonance forms **3** and **3′** (Scheme 1), but the form **3** appears to be more important in an analogous reaction, involving reaction of an excess of **2** with $RuH_2(CO)(PPh_3)_3$ or $RuH_2(PPh_3)_4$, the only product observed being $Me_3SiCH_2CH_2–C≡C–SiMe_3$. To our knowledge, preferential reduction of the double bond in enynes, leading to alkynes, has not been reported previously, probably because only *trans*-enynes have been employed.



In contrast to the unexpected regioselectivity of **2** described above, a similar reaction of *trans*-(R)CH = CH–C≡C–R (R = $SiMe_3$) with **1** showed the normal pattern in which the Ru–H adds to the triple bond of the enyne [10]. Isomerization between this complex and **3** is not observed.

The reaction of an excess of *trans*-(R^1)CH = CH–C≡C–R^2 (R^1, R^2 = $SiMe_3$, ^{t}Bu, Me, Et) with **1** takes place smoothly in THF at room temperature to give orange yellow crystals (**4a–d**) of the composition $RuCl(CO)(H \cdot R^1CHCHC_2R^2)(PPh_3)_2$ in almost quantitative yield. In the ^{1}H NMR spectra the three protons of the dienyls give resonances in the olefinic region.



The X-ray structural analyses of **4a** and **4d** proved that *cis*-addition of the Ru–H had occurred across the triple bond of the enyne (Fig. 1). The metal is bound to the inner carbon (C_3) and apparently lies in an ideal geometrical situation to accept conventional η^3-butadienyl coordination. In reality, however, the allylic double bond of the dienyl interacts with the metal only very weakly, the Ru–C(3), Ru–C(2) and Ru–C(1) distances being 2.044(4), 2.336(5) and 2.627(5) Å in **4a** and 2.041(5), 2.358(5) and 2.661(5) Å in **4d**. In accord with this, the C(1)–C(2) bond is shorter than C(2)–C(3), 1.339(8) vs. 1.445(6) Å in **4a** and 1.354(7) vs. 1.450(7) Å in **4d**. The dihedral angle between (Ru–Cl–CO) and (C(1)–C(2)–C(3)) is 112.7(5) in both **4a** and **4d**, indicating that the π-lobes are not directly oriented towards the metal center. The existence of an attractive interaction, albeit weak, between Ru and the allylic double bond can be shown by comparing the structures of these butadienyl complexes with that of the related stilbenyl complex $RuCl(CO)\{\eta^1\text{-}C(Ph)CHPh\}(PPh_3)_2$ [11] illustrated in Fig. 1(a); (the Ru–C(2) distance is as great as 2.74 Å. This is due to the fact that the Ru–C(3)–C(2) angle, 102.3°, is wider than those in **4a** (82.1(3)°) and **4d** (83.1(3)°)). Furthermore, the angles C(3)–Ru–Cl in **4a** and **4d**, 155.7(1) and 144.4(1)°, are much wider than

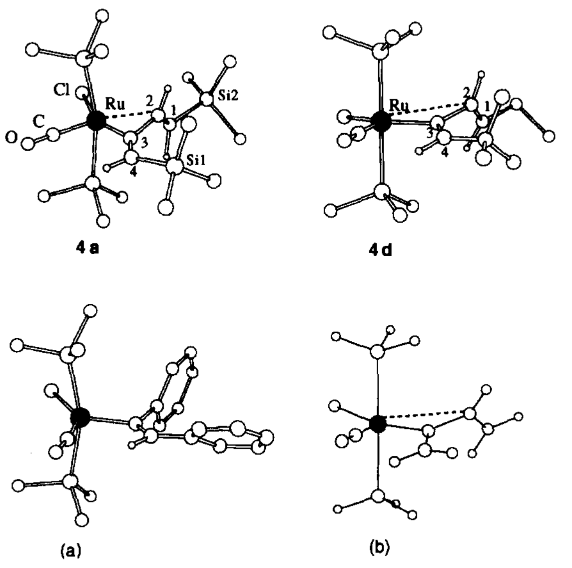


Fig. 1.

that, 132.7°, in the stilbenyl complex, owing to the interaction of Ru with C(1) = C(2) allylic double bond.

The unsubstituted enyne (vinylacetylene) also reacted readily with **1** but gave only an oily product which gradually decomposed. Geometry optimization of $RuCl(CO)(H_2C=CCHCH_2)(PH_3)_2$ carried out by ab initio MO calculations suggested that its structure (Fig. 1(b)) is similar to those of **4a** and **4d**.

It is noteworthy that η^3-allylic complexes of analogous composition, $RuCl(CO)\{\eta^3\text{-}RC(H)C(R)CHR\}(PPh_3)_2$, are known to be formed by the reaction of **1** with 1,3-dienes [12]. The metal has a discrete 18-electron configuration and the complexes are fairly stable. In contrast, an immediate consequence of the half-coordination of **4a–4d** reported here is their instability: when a solution of **4a** in benzene in the presence of an equimolar amount of triphenylphosphine is kept for 3 days, ca. 90% of the enyne is freed. The white precipitate formed was confirmed to be the hydride complex **1**. In the cases of **4b** and **4c**, the equilibria are reached when ca. 30% of the enynes are freed as indicated by ^1H NMR spectroscopy, while **4d** gives only 8% free enyne. The initial rate is not affected when an excess of phosphine is added, suggesting that the β-elimination at C(4) is the rate determining step, and so this is one of the rare examples of β-elimination of vinylic hydrogens [13].

In contrast to the addition of ruthenium hydride to enynes described above, the treatment of **1** with simple alkenes should in general give no significant amounts of products, the expected ruthenium alkyls being unstable and reverting to alkenes via the β-hydride elimination. We have found, however, that vinylsilanes behave differently [14]. The reaction of **1** with excess of $CH_2=CH\text{–}SiMe_2R$ (R = Me, OEt) at 70°C in THF and subsequent work-up by column chromatography gave air-stable yellow crystals of $RuCl(CO)(PPh_3)_2(SiMe_2R)$ (**5a**, R = Me; **5b**, R = OEt) in 60–65% yields. Evolution of ethylene was confirmed by conducting the reaction in C_6D_6 in a sealed NMR tube. The ^{31}P NMR spectra indicate that the two phosphine ligands in both **5a** and **5b** are magnetically equivalent. That this reaction is reversible was demonstrated by the reaction of **5a** with ethylene (50 kg cm^{-2}) at 70°C in the presence of an equimolar amount of triphenylphosphine: complex **1** was isolated in 61% yield and the yield of $CH_2=CH\text{–}SiMe_3$ was determined by GLC to be 55%.

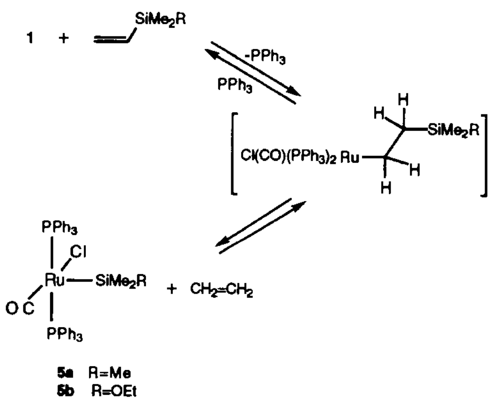
Table 1
Metathesis of olefins catalyzed by 1

$CH_2=CHSiMe_2R$ R	$CH_2=CHR'$ R'	$R'CH=CHSiMe_2R$ Yield (%) [a]	(E)/(Z)
Me	Me	74	76/24
Me	Ph	66	99/ 1
Me	CO_2Me	59	93/ 7
Me	O^nBu	75	78/22
OEt	Ph	72	99/ 1
OEt	CO_2Me	70	83/17
OEt	O^nBu	84	84/16

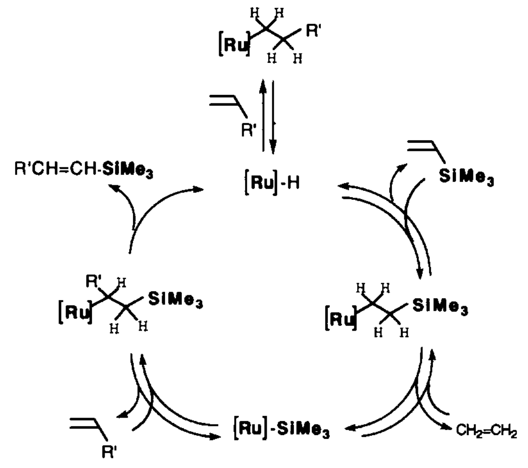
[a] GLC yields based on vinylsilane.

These reactions can reasonably be interpreted in terms of competitive β-H or β-Si elimination from the intermediate β-silylethylruthenium complex (Scheme 2). Photo-induced β-Si and competitive β-H eliminations from $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2CH_2\text{–}SiMe_3$ have been described by Randolph and Wrighton [15]. In reactions of propylene with **5a** under conditions similar to those used for ethylene, complex **1** and $MeCH=CH\text{–}SiMe_3$ ((E)/(Z) = 76/24) were obtained in almost quantitative yields.

The cross-metathesis of $CH_2=CH\text{–}SiMe_2R$ with $CH_2=CH\text{–}R'$ was carried out in the presence of a catalytic amount of **1** at 120–140°C (Table 1). The self-metathesis of vinylsilane can be suppressed completely by use of the vinylsilane and mono-substituted olefins in 1 : 2 ratio. Presumably, the presence of bulky triphenylphosphine ligands in intermediate **5** is responsible for discrimination between incoming olefinic bonds with bulky and less bulky substituents. The marked feature of the reaction is that olefins bearing electroni-



Scheme 2.



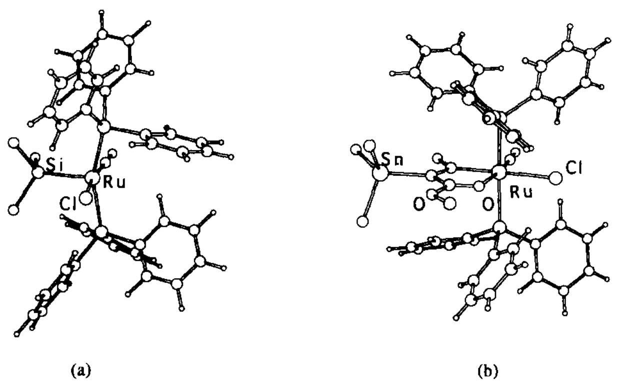
Scheme 3.

cally different kinds of substituent can be successfully employed, as listed in Table 1, pointing to the synthetic versatility of the present system. The reaction sequence in the catalytic cycle is illustrated in Scheme 3.

Alkenylsilanes have become increasingly important reagents in organic synthesis [16] but their transformation by olefin metathesis into more valuable species has been found to be difficult. Typical olefin metathesis catalysts, MoO_3/Al_2O_3 and Re_2O_7/Al_2O_3, convert trimethyl(vinyl)silane into bis(trimethylsilyl)ethylene in only 10–15% yield [17]. Recent developments have involved the use of ruthenium and rhodium complexes. Marciniec and coworkers showed that systems based on various ruthenium or rhodium complexes with a hydride-donor and O_2 can catalyze self-metathesis of alkoxy(vinyl)-silanes to give ethylene and 1,2-bis(alkoxysilyl)ethylene in good yields [18]. A reaction mechanism involving metal–carbene and metallacyclobutane intermediates was proposed. Seki and coworkers reported a similar disproportionation of trimethyl(vinyl) silane catalyzed by $Ru_3(CO)_{12}$ and $HSiR_3$ [19]. Cross-disproportionation with styrene yielded (*E*)-$PhCH=CHSiMe_3$ together with an almost equal amount of the self-disproportionation product $Me_3SiCH=CHSiMe_3$. Though no evidence was given, a mechanism was proposed in which the key step is β-silyl elimination followed by insertion of olefins into the metal–Si bond.

The present reaction provides a new route to complexes with transition metal-silyl bonds. An X-ray structural analysis of **5a** showed that this 16-electron complex has a distorted square pyramidal orientation with the trimethylsilyl group at the apical position (Fig. 2(a)) [20]. A direct extension of this reaction to vinyltrimethylstannane, which afforded ruthenium–stannane complexes via β-stannyl elimination, was reported recently by Roper and co-workers [21]. Though photolysis was used in their reactions, we independently found that an overnight reaction at room temperature yielded $RuCl(CO)(PPh_3)_2(SnMe_3)$ (**6**) in good yield: use of benzene as solvent appears to be crucial.

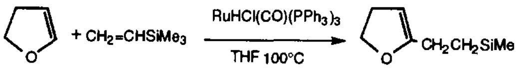
Insertion of olefins into metal–Si bonds, an important step in Scheme 3, is also of interest in connection with the dehydrogenative silylation of olefins, i.e. formation of alkenylsilanes under hydrosilation conditions [22]. Similar insertion of olefins into the Ru–Sn bond could not be confirmed, but acetylenes reacted smoothly at room temperature. The reaction of $MeC\equiv CCO_2Me$ with **6** gave the insertion product in which the carbonyl of ester is coordinated as the sixth ligand (Fig. 2(b)) [23].



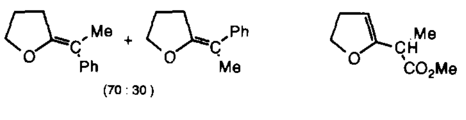
(a) (b)

Fig. 2.

With cyclic olefins, the reaction products were different from those expected from Scheme 3. The reaction of dihydrofuran with vinyl silane gave the codimerization product chemo- and regio-selectively [24].



The codimerization of dihydrofuran with styrene or acrylic ester gave similar products selectively but with a different regio chemistry.



2. Dimerization of alkynes catalyzed by ruthenium(II)

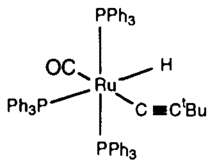
The regio- and stereo-selective dimerization of terminal acetylenes by transition metal catalysts provides a highly attractive route to C4 units involving unsaturation, which are useful for further structural elaboration. Recent developments in this field include regioselective head-to-tail coupling by a Ti or Pd catalyst to give 2,4-disubstituted (branched) enynes [25], and head to head dimerization of ethynylsilanes by Pd or Rh complexes to give exclusively (*E*)-1,4-disubstituted enynes [26]. We have observed a completely different type of dimerization in the case of t-butylacetylene, which in catalysis by ruthenium complexes gives (*Z*)-1,4-di-t-butylbutatriene (abbreviated (*Z*/)-**dbb**) in good yield and with excellent stereoselectivity [27]. Though a similar reaction takes place with trimethylsilylacetylene (vide infra), we focus first on the dimerization of t-butylacetylene, since the mechanism of this remarkable reaction can be best investigated by the reaction of $HC\equiv C^tBu$ with $Ru(CO)(PPh_3)_3(H)_2$, one of the catalysts employed, or complexes derived from it.

The dimerization leading to 2,4- and (*E*)-1,4-disubstituted enynes can easily be explained by a series of conventional reaction steps: oxidative addition of $\equiv C-H$, insertion of $C\equiv C$ of the second alkyne molecule, and then reductive elimination [28]. On the other hand, besides the strict *cis*-stereoselectivity of the two substituents, the formation of a butatriene backbone in the dimerization appeared puzzling at first, since the butatriene skeleton is thermodynamically much less stable than the enyne form according to ab initio MO calculations (Fig. 3).

Ruthenium complexes capable of generating zero-valent ruthenium species catalyze the dimerization of t-butylacetylene to butatriene under appropriate conditions. Some Ru(II) species which are related to intermediates present in the catalytic cycle also have catalytic ability. First, we studied the Ru(cod)(cot)/PR_3 (cod = 1,5-cyclooctadiene, cot = cyclooctatriene) system in order to examine the effect of tertiary phosphines. The complex Ru(cod)(cot) alone shows little ability to effect the dimerization but addition of phosphines markedly increases the catalytic activity. At least 3 moles of phosphine are required per mol of Ru. The mixture of resulting dimers consists mainly of (*Z*)-**dbb** but enymes are also present to some extent. The selectivity towards butatriene increases in the order: $P(OPh)_3 < P^nBu_3 < PPh_3 < P^iPr_3$. When 3 moles of P^iPr_3 were added, the distribution of dimers was: the branched enyne 15%, (*E*)-enyne 3%, (*Z*)-enyne 6%, (*E*)-**dbb** 3%, and (*Z*)-**dbb** 73%. Addition of a 3 molar proportion of $P(OPh)_3$ resulted in: the branched enyne 49%, (*E*)-enyne 0.5%, (*Z*)-enyne 6.5%, (*E*)-**dbb** 13%, and (*Z*)-**dbb** 31%. The above order of effectiveness of the phosphines coincides with that of their cone angle values, suggesting that a crowding around the metal center favours the selective formation of (*Z*)-**dbb**.

In the presence of a catalytic amount of the dihydride complex $Ru(CO)(PPh_3)_3(H)_2$ (**7**), t-butylacetylene dimerizes at 50–100°C in benzene to give (*Z*)-**dbb** in 85–90% selectivity and 25–50 catalytic turnovers per Ru atom. An alkynyl complex $Ru(CO)(PPh_3)_3(H)(C{\equiv}C^tBu)$ (**8**), which can readily be prepared by the reaction of $Ru(CO)(PPh_3)_3(H)Cl$ with $Li{-}C{\equiv}C^tBu$, also works as a precursor of the active species for the same dimerization. As in the case of the Ru(cod)(cot) system, addition of a 3 molar excess of P^iPr_3 increases both activity and selectivity. The reaction stops after 48 h at 50°C to give (*Z*)-**dbb** in 96% selectivity and ca. 90 catalytic turnovers per Ru. The catalytic turnover increases at higher temperatures but selectivity towards the butatriene decreases.

The reaction mechanism was studied using the precursor **7** and related model complexes. The first clue to the mechanism involved isolation of the hydride alkynyl complex **8** from the reaction mixture. Thus when the catalytic reaction using **7** was stopped at an early stage and the reaction mixture was worked up by column chromatography, complex **8** was isolated in ca. 20% yield. The two hydride ligands of **7** were presumably consumed to hydrogenate one molecule of $HC{\equiv}C^tBu$ to $H_2C = C\eta^tBu$, which was in fact detected by GLC/MS, and this was followed by the oxidative addition of the ≡C–H bond of a second alkyne molecule to the Ru(0) center. The ^1H NMR spectrum shows the hydride resonance at δ −8.23 as two triplets ($J = 87$ and 26 Hz) due to coupling with the *trans* phosphine and with the two equivalent *cis* phosphines. The ^{31}P NMR spectrum is also consistent with the structure illustrated below, since the two equivalent phosphine ligands give a doublet, $J = 17.1$ Hz (44.6 ppm), while the other phosphine (20.8 ppm) gives a triplet resonance with the same coupling constant.



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Hydride alkynyl complexes such as **8** are often proposed as active species in the dimerization of terminal alkynes to give head-to-tail or *E*-enyne type dimers. However, when an excess of $HC{\equiv}C^tBu$ is added to a benzene solution of **8** at room temperature, a slow

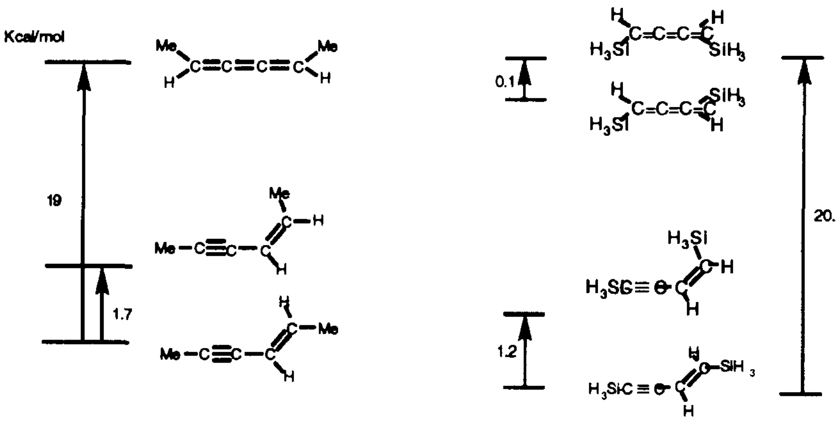
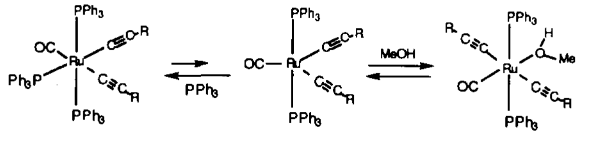


Fig. 3.

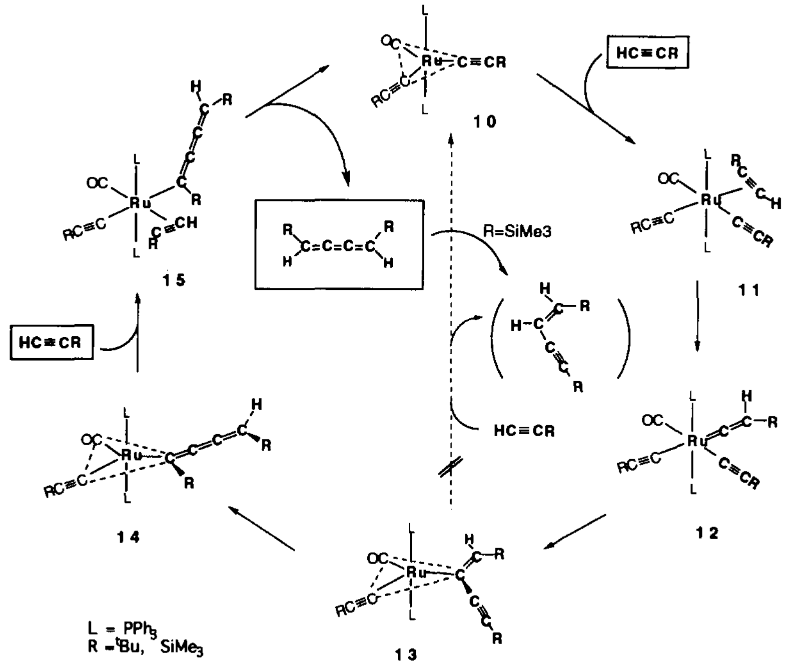
dimerization to (*Z*)-**dbb** (15 turnovers in 70 h) begins after an induction phase of a few hours. Concentration of this mixture after 24 h and addition of hexane afforded a colorless crystalline complex of the formula $Ru(CO)(PPh_3)_3(C_2^tBu)_2$ (**9**) in 60–70% yield. A single-crystal X-ray analysis of **9** confirmed its solid state structure to be as indicated in the equation below, which is consistent with the NMR spectra in solution: the ^1H NMR spectrum (C_6D_6) showed ^{t}Bu resonances at δ 0.96 and 1.28, and the ^{31}P NMR spectrum ($CDCl_3$) showed a triplet and a doublet at δ 19.34 and 29.64 ($J = 21.5$Hz) in 1:2 ratio. Complex **9** catalyzes dimerization of ^{t}BuC≡CH to (*Z*)-**dbb** at room temperature. Since the equatorial triphenylphosphine ligand is easily replaced by trimethylphosphine at room temperature, it is likely that the equatorial triphenylphosphine in complex **9** dissociates in solution to give a five-coordinate species **10**.



9 **10**

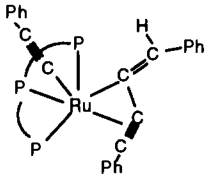
The concentration of **10** must be very low, since its presence was not detected in ^1H or ^{31}P NMR spectroscopy. When **9** was recrystallized from a benzene/methanol solution, a new colorless complex was isolated in 52% yield. An X-ray structure analysis revealed this to be a methanol complex with two *trans*-C≡C^{t}Bu units [29]. Addition of triphenylphosphine to this complex in benzene immediately regenerated the original **9** with two *cis* C≡C^{t}Bu ligands. The interchange between complexes with *cis* and *trans* C≡C^{t}Bu ligands must proceed via **10**. We thus assume that intermediate **10** is the active species involved in the catalytic cycle for the production of (*Z*)-**dbb**.

Starting from intermediate **10**, the reaction sequence illustrated in Scheme 4 depicts the cycle we adopt to explain the catalytic and stereoselective (*Z*)-**dbb** formation. Coordination of an alkyne molecule to **10** will give **11**, which is an intermediate on the way to a vinylidene complex **12** by an intraligand H-transfer. One of the alkynyl ligands in this vinylidene intermediate (**12**) will then migrate to the vinylidene α-carbon to give a complex (**13**) with a but-1-en-3-yn-2-yl ligand. Examination of a molecular model has indicated that the *cis* form of the butenynyl moiety is sterically much more favoured over the *trans* form because repulsive interaction between the bulky ^{t}Bu group and other ligands is severe in the latter. Thus, the observed *Z*-stereoselectivity in the final product, (*Z*)-**dbb**, can be traced back to this transformation step. Our next assumption is a rearrangement of the but-1-en-3-yn-2-yl ligand into the buta-1,2,3-trien-4-yl form (**14**) by a 1,3-shift of the metal. It was shown recently that RuH_4(triphos) reacts with phenylacetylene to give a complex with η^3-PhC_3CHPh ligand [30]. A similar complex has been isolated in the reaction of phenylacetylene with $FeCl_2(DMPE)_2$ [31]. In both cases migration of the alkynyl ligand to give a vinylidene has been proposed for the C–C bond formation step. However, an osmium



Scheme 4.

analog, $[Os(\eta^3\text{-}PhC_3CHPh)(PMe_3)_4]PF_6$, has been obtained by oxidative coupling of two alkynyl ligands [32]. The reported structure of these complexes may be regarded as a transient form of the isomerization from **13** to **14**.



The equilibrium between **13** and **14** is expected to lie far to the side of **13**, the enyne skeleton being thermodynamically much more stable than the butatriene form (Fig. 3). If the C4 chain lies in the basal plane, as in the model complex (**13′**) described later, there will be few steric problems in **13**. However, to allow another alkyne molecule to coordinate, the Ru–C bond has to rotate to open the coordination site in the equatorial position so that the butenynyl plane is almost perpendicular to the basal plane of the complex. Our examination of a molecular model indicates that in this ‘upright form’ of the butenynyl ligand there is severe steric repulsion between bulky tertiary phosphines in the axial positions and the C≡C–^{t}Bu moiety of the butenynyl group. Such a conformation forces the butenynyl ligand to move the ^{t}Bu group into the cone-space occupied by PPh_3. Thus coordination of an alkyne molecule to **13** appears to be sterically prohibited. In contrast, the ‘upright form’ of the butatrienyl ligand suffers from significantly smaller steric problems, since the ^{t}Bu group is bent away from the phosphine. The attacking alkyne, therefore, can coordinate only to **14** to form **15**. The butatrienyl ligand in **15** will then accept hydrogen from the coordinating alkyne to be freed as (*Z*)-**dbb**, with regeneration of the original dialkynyl intermediate **10**. The three model reactions used to support this reaction scheme are described below.

Firstly, we have found that the vinylidene complexes of the composition $RuCl_2(PPh_3)_2(C=CH^tBu)$ (**12′f**) and its Br analog are formed by simply mixing a benzene solution of $RuX_2(PPh_3)_3$ with $HC≡C^tBu$, the formation of which is described in deatail in Section 3.

The model complex for **13** was prepared by the reaction of $RuCl(CO)(PPh_3)_3H$ (**1**) with $^tBuC≡C\text{-}C≡CBu^t$ at room temperature. Facile *cis*-addition of the Ru–H to one of the triple bonds gave a good yield of complex **13′** as orange crystals, which was structurally characterized (Fig. 4). The C4 chain of the butenynyl group lies approximately on the basal plane of the complex defined by Ru, CO, and CL, the dihedral angle between Ru–CO–CL and the butenynyl planes being 12.6°. Though there is no apparent interaction between Ru and the triple bond, it is noteworthy that Ru–C1–C2 (135.4(3)°) is larger and Ru–C1–C3 (97.9(3)°) is smaller than the typical Csp^2 bonding angle. The small Ru–C1–C3 angle should facilitate the migration of Ru from C1 to C4 (vide infra). The ^1H NMR spectra of **13′** in C_6D_6 shows two t-butyl resonances at δ 1.12 and 0.94, and the vinylic proton signal at 5.10 as a triplet due to the coupling with two equivalent phosphines.

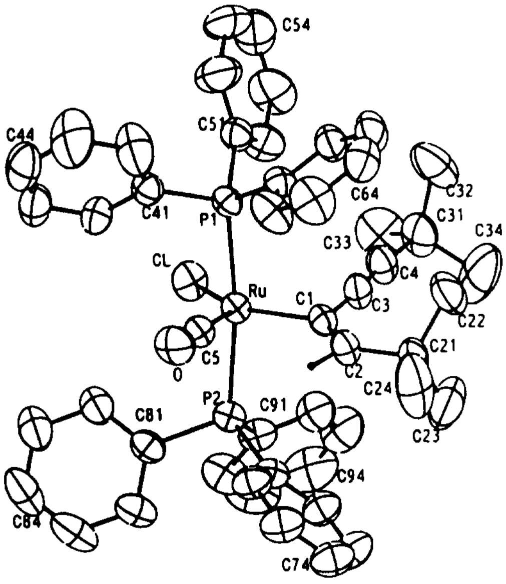
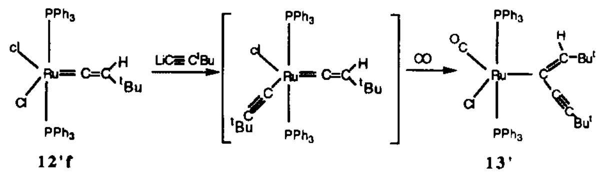
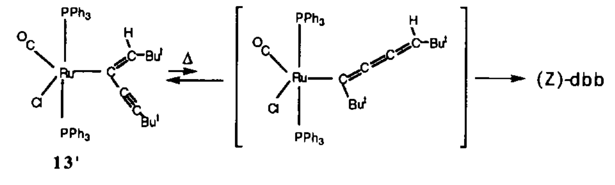


Fig. 4. Molecular structure of **13′**.

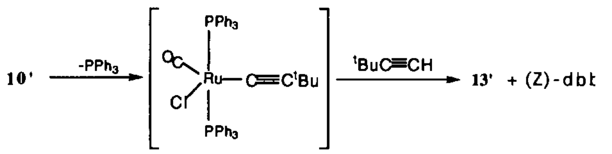
The vinylidene complex **12′f** in THF was treated with 0.8 equiv. of $Li\text{-}C≡C^tBu$ at −50°C for 1 h and then a 4 molar excess of CO was bubbled through the solution at the same temperature. The reaction mixture was allowed to warm to room temperature and work-up by column chromatography of the resulting orange-brown solution then afforded crystals of **13′** in 27% yield based on **12′f**. Intramolecular migration of methyl group to a carbene ligand has been reported for $[Br(PMe_3)_2(Ir=CH_2)CH_3]^+$, and there have been several reports of carbon–carbon bond formation of this type [33]. The methyl–methylene coupling at the Ir center to give ethyl ligand occurs readily, in contrast to the difficulty of forming carbon–carbon bond by reductive elimination of the related dimethyl complex.



When a solution of **13′** was monitored by NMR spectroscopy at 50°C, slow decomposition was indicated by decrease of the peaks due to **13′**. At the same time new singlets at δ 1.09 and 5.54 appeared in a 9/1 intensity ratio and grew as the decomposition of **13′** proceeded. These peaks were due to (*Z*)-**dbb**, and its presence in the solution was further confirmed by GLC and GC/MS spectroscopy. The half-life of **13′** was ca. 70 h. The change was very clean and no other peak could be detected in the ^{1}H NMR spectra. The butatrienyl ligand which rearranged from butenynyl form in **13′** abstracted hydrogen, presumably from triphenylphosphine, to be liberated as (*Z*)-**dbb**.



When a benzene solution of **9** was shaken with an equimolar amount of aqueous hydrogen chloride, a new colorless crystalline complex, RuCl(CO)$(PPh_3)_3$(C≡C^{t}Bu) (**10′**), was obtained. This complex may release one of the triphenylphosphines in solution, as in the case of **9**, giving a coordinatively unsaturated intermediate which may be regarded as a monoalkynyl version of **10**. When a C_6D_6 solution of **10′** is kept at 60°C in the presence of an excess of t-butylacetylene for 12 h, the original ^{t}Bu resonance of **10′** at δ 1.08 disappears and new peaks due to complex **13′** along with smaller peaks due to (*Z*)-**dbb** (**13′**/**dbb** = ca. 3) emerge. The conversion is rather clean, and side reactions are virtually negligible as judged by ^{1}H NMR spectroscopy.



The presence of the t-butyl substituent in the acetylene in the dimerization reaction above is clearly not attractive from the viewpoint of organic synthesis. During the course of our study of dimerization of trimethylsilylacetylene to butatriene, we found that the activity and selectivity of ruthenium-catalyzed dimerization of HC≡CR are very dependent on the substituent R. Ru(CO)$H_2(PPh_3)_3$, which is one of the most active catalysts for the dimerization of HC≡CBu^t, is not active for the selective dimerization of HC≡CSiMe$_3$. However, when a benzene solution of HC≡CSiMe$_3$ and a catalytic amount of Ru(cod)(cot)/P(Bu^n)$_3$ (1/3 ratio, cod = 1,5-cyclooctadiene, cot = cyclooctatriene) was simply kept for 3 days at room temperature under argon and then fractionally distilled, a single dimerization product was obtained in 87% yield [34]. This dimer was not, however, the expected butatriene but instead (*Z*)-Me$_3$SiCH = CHC≡CSiMe$_3$. No *E*-isomer was detected. This result was troublesome at first sight; the selective formation of *Z*-enyne appeared to be reasonably accounted for in terms of Scheme 4, but with release of the product from intermediate **13** by acceptance of hydrogen from HC≡CSiMe$_3$ with regeneration of the intermediate **10**. Such a dimerization has been reported by Bianchini and co-workers, who used a tetrapod phosphine complex [Ru–P$(CH_2CH_2PPh_2)_3$-(C≡CSiMe$_3$)]$^+$ as catalyst, and essentially the same reaction route was suggested [35]. In our case, however, this path contradicts the assumption made in the case of the dimerization of HC≡C^{t}Bu that in an intermediate **13** there is no space for interaction with acetylene and therefore no possibility of generating the *Z*-enyne.

Detailed investigation of the extent of conversion of this reaction with time clearly showed that a different route was operating: the initial product of the catalytic dimerization was indeed the expected butatriene, which was gradually isomerized to the *Z*-enyne during 30 h at room temperature. Analysis by GLC showed that the butatriene initially formed contained *Z*- and *E*-forms in ca. 85/15 ratio. The isomerization of the *E*-butatriene to *Z*-enyne was much slower than that of the *Z*-butatriene, and probably proceeded via initial isomerization to the *Z*-butatriene. The possibility that a little of the (*Z*)-Me$_3$SiCH = CHC≡CSiMe$_3$ was formed directly from intermediate **13** and HC≡CSiMe$_3$ could not be ruled out.

No isomerization of butatriene to enyne was observed when triarylphosphines were employed. Thus, a hexane solution of HC≡CSiMe$_3$ in the presence of a catalytic amount of Ru(cod)(cot)/PPh$_3$ (1/6 ratio) gave a 92% yield of dimer which consisted of (*Z*)-Me$_3$SiCH = CHC≡CSiMe$_3$ (5%), (*E*)-Me$_3$SiCH = C = C = CHSiMe$_3$ (19%), and (*Z*)-Me$_3$SiCH = C = C = CH-SiMe$_3$ (76%).

3. Terminal alkyne to vinylidene isomerization on ruthenium(II)

The electronic character and reactivity of organic compounds change, often dramatically, when they interact with transition metals. Since this effect is very relevant in many catalyzed processes, clarification or understanding of this basic problem is an important topic for organometallic chemists. The relative stabilities of acetylene and its isomeric vinylidene form provides a good and simple example: free vinylidene, :C = CH$_2$, has been the subject of a number of theoretical and physicochemical studies [36] and is considered nowadays to be ca. 44–47 kcal mol^{-1} less stable than acetylene, HC≡CH [36–38]. In contrast, 1-alkyne to vinylidene tautomerization in the coordination sphere of a transition metal has proved to be a useful entry into vinylidene complexes, apparently with vinylidene being the more stable form in many transition metal complexes [39].

In respect of the mechanism of the conversion of coordinated 1-alkynes into metal-bound vinylidenes, Antonova and coworkers have suggested that oxidative addition of the alkyne to give an alkynyl(hydrido)metal intermediate and subsequent 1,3-shift of the hydride from metal to the β-carbon of alkynyl might give the vinylidene complex [40]. However, the extended Hückel calculations on $Mn(C_5H_5)(CO)_2(C_2H_2)$ suggest that concerted intramolecular 1,3-hydrogen shift of the alkynyl(hydrido)metal complex would have a very high activation energy and direct 1,2-hydrogen shift from the α- to β-carbon might be plausible [41]. A series of studies by Werner and co-workers has provided experimental information to assist assessment of which of these pathways is more likely. They showed that square-planar η^2-alkyne complexes *trans*-$[MCl(RC{\equiv}CH)(P^iPr_3)_2]$ (M = Rh, Ir) rearrange to square-pyramidal alkynyl(hydrido) complexes $MCl(P^iPr_3)_2(H)(C{\equiv}CR)$, which on warming isomerize further to the vinylidene complexes *trans*-$[MCl(C=CHR)(P^iPr_3)_2]$ [42]. In a possible modification of Antonova's mechanism, the possibility of intermolecular hydrogen shift between two alkynyl(hydrido)metal molecules has been pointed out. More recently, Bianchini and coworkers have carried out kinetic studies on the rearrangement of a cationic alkynyl(hydrido)cobalt to its vinylidene form, and suggested that it proceeds via a dissociative (non-concerted) intramolecular 1,3-proton shift [43].

Obviously, many possibilities exist once acetylene interacts with transition metal complexes. In view of the diversity of configurations around the central metal, this problem is a challenge to theorists. Ab initio MO calculations on the acetylene–vinylidene rearrangement under the influence of a non-transition metal atom have been reported [44], but to our knowledge there has been no ab initio study for the process involving transition metal complexes. As a model for the key step in our catalytic dimerization described in Section 2, we have found that the readily available ruthenium complexes $RuX_2(PPh_3)_3$ (X = Cl or Br) react readily with t-butylacetylene to give stable vinylidene complexes.

$$RuX_2(PPh_3)_3 + HC{\equiv}C^tBu$$
$$\longrightarrow RuX_2(PPh_3)_2(C=CH^tBu) + PPh_3$$

12′f

Since this reaction seemed rather simple and suitable for the mechanistic investigations, we decided to examine it in detail both experimentally and through ab initio calculations. NMR specrocopy and X-ray structural analysis were used to determine the orientation of ligands around the central metal, while calculations were used successfully to throw light on transition states and unstable key forms of the C2 unit under such circumstances [45].

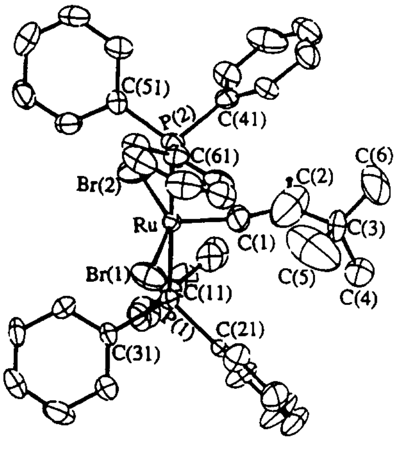
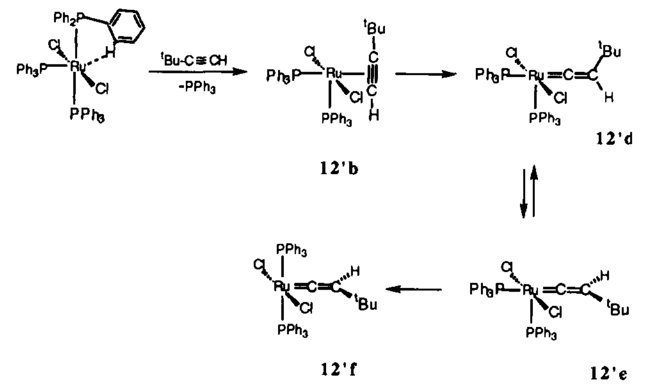


Fig. 5. Molecular structure of **12′f** (Br analog).

3.1. Reactions of $RuX_2(PPh_3)_3$ with $HC{\equiv}C^tBu$

The complexes $RuX_2(PPh_3)_3$ (X = Cl, Br) react with an excess of $HC{\equiv}C^tBu$ in benzene during over 24 h at room temperature to give the vinylidene complex $RuCl_2(PPh_3)_2(C=CH^tBu)$ (**12′f**) or its Br analog. An X-ray structural analysis of the bromo derivative (Fig. 5) showed that the molecule has a trigonal bipyramidal structure with two phosphines at axial positions but is markedly deformed toward square pyramidal with the vinylidene Cα in an apical position, the Br–Ru–Br angle being 145.6(1)°. Though calculations on five-coordinate d^6 metal complexes favour the square-pyramidal over the trigonal-bipyramidal structure, the energy difference is small. A large deviation of the Br–Ru–Br angle from linearity, with deformation toward the trigonal bipyramid, is likely when there is steric repulsion between the Brs and the vinylidene moiety. The M–C–C angles in vinylidene complexes often deviate from linearity, but the value of 161(2)° in the present structure is one of the largest observed [39b]. This is probably due to severe steric repulsion between the phenyl rings of PPh_3 with the bulky ^tBu group at Cβ.

When the reaction of $RuCl_2(PPh_3)_3$ with $HC{\equiv}C^tBu$ was stopped at an early stage, e.g. after 15 min, by evaporating off the excess alkyne and the solvent, a fine red-brown powder was obtained. It showed an IR band at 1638 cm^{-1}, the typical $\nu_{(C=C)}$ region for a vinylidene ligand, but no bands at all at 1700–2000 cm^{-1}, the region for η^2-coordinated alkyne or σ-alkynyl. The ^1H NMR spectrum in C_6D_6 showed the ^tBu resonance at δ 0.91 (broad s) and a proton resonance at 2.41 (broad t,



Scheme 5.

J = ca. 4 Hz). When the NMR sample was kept at room temperature, the intensities of these peaks gradually decreased while the peaks due to **12'f** at 0.79 (s, ^{t}Bu) and 3.87 (t, J = 4.4 Hz, = CH) increased. The change was complete within 30 h. The ^{31}P NMR of the initial brown-red powder in C_6D_6 revealed that it was a mixture of almost equal amounts of two isomers, each of which contained two non-equivalent phosphines: the spectrum exhibited two AB-type quartets centered at δ 46.5 (J = 38 Hz) and 34.4 (J = 25 Hz) in almost equal intensities. A small amount (ca. 5%) of a singlet at δ 27.2 due to **12'f** was also observed, besides a singlet for the free PPh_3 generated. When the NMR sample was allowed to stand at room temperature, the two quartets decreased as the singlet of **12'f** at 27.2 increased at a rate almost equal to that observed for the change in the ^{1}H NMR spectra. From these spectral data, we conclude that the initially formed brown-red powder consists of two isomers, **12'd** and **12'e**, depicted in Scheme 5. The ^{1}H NMR absorption of the t-butyl and vinylidene protons of the two isomers must have coincided, since they are remote enough from the central metal and the peaks are broad. Efforts to detect η^2-alkyne complex **12'b** were unsuccessful: shorter reaction times resulted in a lower yield of the vinylidene complex and more unchanged starting material.

The reaction route we propose is illustrated in Scheme 5, and is fully consistent with the known structure of the starting $RuCl_2(PPh_3)_3$. An X-ray structural analysis of $RuCl_2(PPh_3)_3$ has shown that it has slightly distorted square pyramidal configuration [46]. Though we have been unable to detect an η^2-alkyne complex, it is reasonable to assume that coordination of the alkyne through the triple bond is involved in the present reaction sequence, since the alkyne π-complex is a thermodynamically stable species but is less stable than the final vinylidene complex (vide infra). The bulky alkyne attacking this site will displace one of the neighbouring triphenylphosphines to form an η^2-CC alkyne complex **12'b** with *cis*-bis(phosphines) which quickly isomerizes to the vinylidene complex **12'd** with the same metal configuration and the t-butyl group occupying the least crowded position. Our ab initio MO calculations on $RuCl_2(PH_3)_2(C=CH_2)$ suggest that a rotational isomer **12'e** is electronically favourable (vide infra). But the bulky t-butyl group present in the reactant should favour **12'd** over **12'e** in view of steric effects, thus equalizing the total energies of the two isomers to give a 1-to-1 mixture. Complex **12'e** will slowly isomerize to the final product **12'f**, which has been shown by calculations to be the most stable form, as described in the next section.

3.2. Molecular orbital calculations on the intramolecular rearrangement of $RuCl_2(PH_3)_2(HC\equiv CH)$ to $RuCl_2(PH_3)_2(C=CH_2)$

We decided to use ab initio molecular orbital calculations to see whether there is a reasonable path for the concerted intramolecular rearrangement of the π-coordinated acetylene complex to the vinylidene ruthenium complex. Throughout the calculations, geometries of the stationary points were optimized at the MP2 (electron correlation by second-order Møller–Plesset perturbation) level using [2s2p2d]/(3s3p4d) and the 8 valence electron effective core potential of Hay and Wadt for the metal [45]. To refine the energetics of these optimized structures the MP2 energies were re-calculated using the 16 valence electron effective core potential for Ru, which takes explicitly into account the outmost core orbitals, with [3s3p2d]/(5s5p4d) basis functions.

Through calculations on the complexes we examined the rearrangement of the free C_2H_2 unit. Many theoretical studies have already focused on the isomerization of free vinylidene (:C = CH_2) to acetylene (HC≡CH) [36], the reverse of the process we are considering here. Petersson et al. have recently provided a comparison at the various levels of ab initio theory for this isomerization reaction, including HF, MP2, and CCSD (coupled cluster single and double excitations) methods with STO-3G, 6-31G**, and 6-311 + G** basis sets [36c]. The calculated geometries for vinylidene, acetylene, and the transition state were found to be fairly insensitive to the level of theory in spite of the flat potential surface between the vinylidene and the transition state. In contrast, the height of the calculated barrier was very sensitive to the level of theory: only a sophisticated method, the quadratic configuration interaction (QCI) calculations with large basis sets, could reproduce the experimentally observed values of the reaction barrier (2 kcal mol^{-1}) and the energy of isomerization (-47.4 ± 4.0 kcal mol^{-1} [37], -44.4 ± 0.3 kcal mol^{-1} [38]). The results of MP2/6-31G* calculations were found to be qualitatively satisfactory (barrier 1.07, isomerization energy -48.7 kcal mol^{-1}). It appears, therefore, reasonable from the point of view of economy to optimize

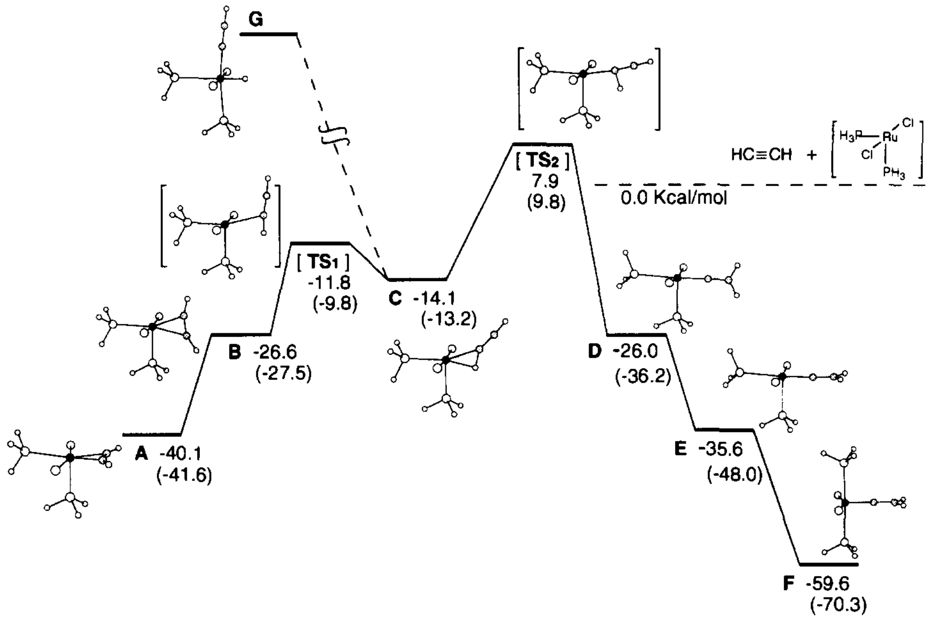


Fig. 6.

the geometry by the MP2 method. The geometries and energies of free acetylene, vinylidene, and the transition state were calculated by this method and with the basis sets we have employed. The difference of 51.7 kcal mol^{-1} between the vinylidene and the more stable acetylene form, and the difference of 0.1 kcal mol^{-1} between the vinylidene form and transition state deviate by a few kcal mol^{-1} from the experimental values but are qualitatively, if not quantitatively, satisfactory.

Performing calculations on the system involving the C_2H_2 unit and the $Ru(PH_3)_2Cl_2$ moiety, we identified in total six complexes, **A**–**F**, and two transition states, **[TS1]** and **[TS2]**, whose relative energies are summarized in Fig. 6; the optimized structures are shown in Fig. 7 only for the key intermediate **C** and the two transition states. In the geometry optimizations, C2v symmetry was assumed for the final product **F**, and Cs symmetry for others.

Complexes **A** and **B** are rotational isomers of the η^2-CC acetylene complex with *cis*-bis(phosphine) and *trans* dichloride. Isomer **B** is less stable than **A** by 13.5 kcal mol^{-1} and is likely to be the transition state for this rotation. We could not find an acetylene complex with *trans*-bis(phosphine) and *trans*-dichloride probably for steric reasons. On the vinylidene complex side, however, such a conformation gives the most stable form **F**. As described in Section 3.1, the primary vinylidene product must contain two non-equivalent phosphines. Of the three different square pyramidal geometries for the vinylidene complexes which have nonequivalent *cis* phosphines, forms **D** and **E** (*cis*-phosphines and *trans* chlorides) are found to be energetically favourable (the other two have *cis* phosphines and *cis* chlorides). The rotational isomer **D**, rotation around the metal–carbon bond by 90°, was calculated to be 9.6 kcal mol^{-1} higher in energy than **E**. Similarly, the rotational isomer of **F** was calculated to be more unstable than **F** by 11.4 kcal mol^{-1}, but it is omitted from Fig. 6 for simplicity. These less stable rotatory

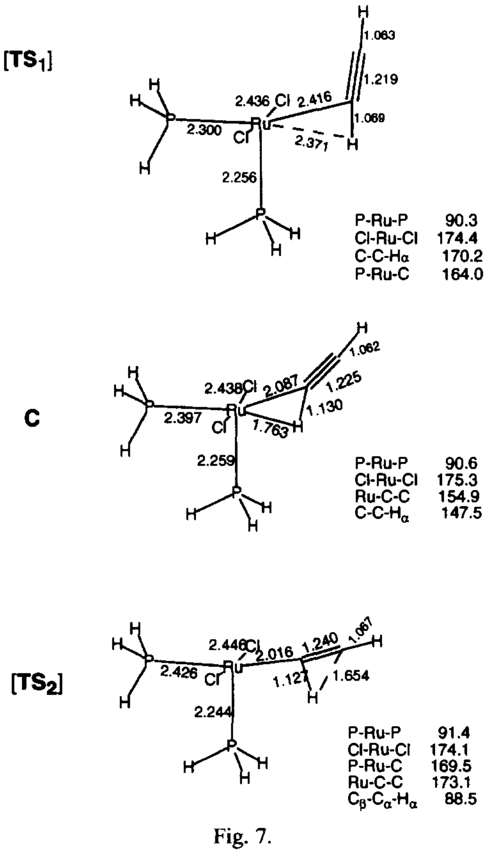
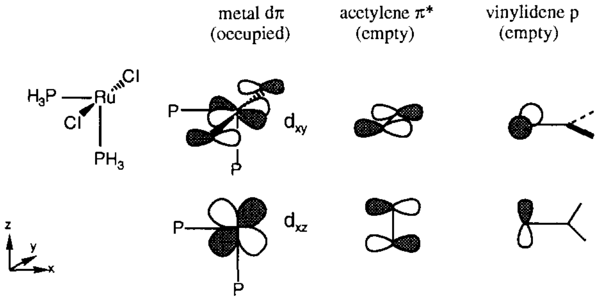


Fig. 7.

isomers are probably the transition states for the vinylidene rotation around the metal–carbon bond.

The higher stability of the η^2-alkyne complex **A** than of its isomer **B**, as well as the higher stability of the vinylidene **E** than of the rotational isomer **D**, may be attributed to the efficiency of back-donation from the metal dπ orbitals. The importance of back-bonding in low valent transition metal alkene (dπ–π^*) and vinylidene (dπ–empty p) [47] complexes has been established. Calculations on the $RuCl_2(PH_3)_2$ fragment, which has *trans*-dichloride and *cis*-bis(phosphine) ligands, have shown that the d_{xy} orbital lies at a much higher energy level than d_{xz}. The energy difference amounts to 0.09 au, and this can be traced back to an antibonding interaction of d_{xy} with the p orbitals of Cl, as illustrated below. The dπ orbital with higher orbital energy (d_{xy}) can more efficiently back-donate its electrons to the empty π^* orbital of the incoming alkyne or to the empty p orbital of the vinylidene ligand.



With monosubstituted acetylenes, especially when account is taken of the presence of bulky t-butyl group in our model reaction (Scheme 5), the acetylene complex **A** should be far less stable than is indicated by the energy level expected from Fig. 6 owing to steric repulsion between the substituent and chloride. We may reasonably assume that the acetylene complex **B** is much more important, since the substituent has most empty space available when it is attached to the upper carbon. The crucial hydrogen migration should occur on the way from **B** to **D** and the migrating hydrogen must be that at the lower carbon in **B**.

The transition state for the hydrogen migration step (**[TS2]**) has been found to be that in which the C_2H_2 moiety adopts a structure similar to that calculated for the transition state of free C_2H_2, but it is situated a little more towards the alkyne side in the complex; the Cα–$H_{\mathrm{migrating}}$ distances of the free and complexed transition state are 1.175 and 1.127, and those of Cβ–$H_{\mathrm{migrating}}$ are 1.417 and 1.654 Å, respectively. The transition state for the complex is located early, reflecting the much smaller energy of isomerization. It is apparent that, in the coordination sphere of the transition metal, the vinylidene lone pair can be stabilized by coordination to the metal. The large endothermic transformation from free acetylene to vinylidene is now thermoneutral in the complexed form **B** → **D**. The lowering of the transition-state energy in the complex by ca. 17 kcal mol^{-1} relative to that in the free C_2H_2 can also be attributed to coordination of the lone pair electrons.

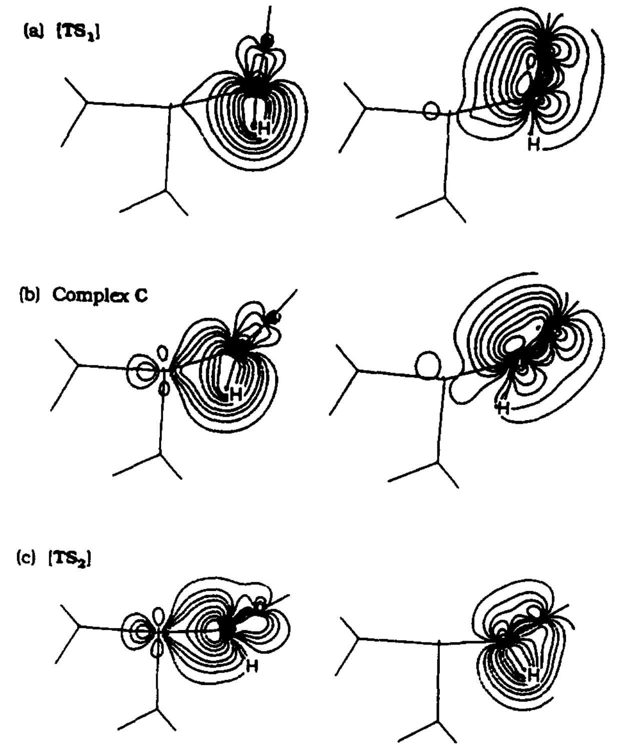
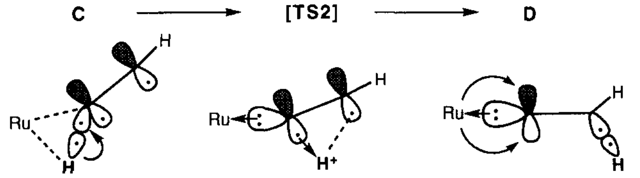


Fig. 8. Localized molecular orbitals in the plane of P–Ru–CH–CH for intermediate C and the two transition states: left, C–H_α → lone pair; right, (C–C)θ.

Careful inspection of the path from **B** to **[TS2]** revealed further the presence of a η^2-CH complex **C** and a small barrier **[TS1]** between **B** and **C** (Fig. 6). The rearrangement of **B** to **C** involves a slippage of the η^2-CC acetylene complex to the η^2-CH complex. In the transition state **[TS1]** for this slippage, metal interacts dominantly with only Cα, and this interaction is very weak: the geometry of C_2H_2 moiety is deformed only slightly from that of free acetylene and the Ru–Cα distance is as long as 2.4 Å (Fig. 7).

Parts (a)–(c) of Fig. 8 show a comparison of the shapes of CH σ- and CC π-orbitals in the complexes **[TS1]**, **C**, and **[TS2]**. These MO contour diagrams clearly demonstrate that the Cα–Hα σ-bond turns into the lone pair orbital along the reaction coordinate while the in-plane CC π-orbital changes into the newly formed Cβ–Hα σ-bond on going from **[TS1]** to **[TS2]**. The p orbital at Cα, which was a part of the in-plane π-orbital, is left empty as the Cβ–H σ-bond is being formed, and it should end up as the "empty p" of vinylidene available to accept back-donation from the metal.

It may be inferred that the migrating hydrogen behaves as a naked proton rather than a hydride. The migrating hydrogen leaves behind the lone pair electrons which was originally used for the Cα–H σ-bond, while it accepts electrons from those of the in-plane CC π-orbital, to form the new Cβ–H σ-bond. This view is in contrast to the concept proposed by Petersson et al. [36c] and Sakai et al. [44] for the free vinylidene → acetylene isomerization in which the lone pair of vinylidene is assumed to be correlated with a π-orbital of acetylene and the migrating hydrogen has hydride character. We conclude that the major role of Ru(II) in this rearrangement reaction is to interact first with the C–H σ-bond first and then promote its conversion to the lone pair orbital by accepting lone-pair electrons into a vacant metal d orbital.



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