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# Trans-stereochemistry from the insertion of alkynes into a ruthenium - carbon bond of a bridging-phenyl ligand[1]

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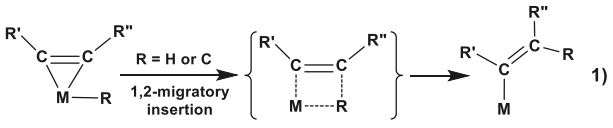
ABSTRACT

The reaction of $Ru_5(\mu_5\text{-}C)(CO)_{13}(\mu\text{-}\eta^2\text{-}Ph)[\mu\text{-}Au(NHC)]$, **1**, NHC = 1,3-bis(2,6-diisopropylphenyl-imidazol-2-ylidene) with ethyne ($C_2H_2$) yielded the new compound $Ru_5(\mu_5\text{-}C)(CO)_{13}[\mu\text{-}\eta^2\text{-}E\text{-}C(H)C(H)Ph][\mu\text{-}Au(NHC)]$, **2** in 89 % yield. Compound **2** contains a square-pyramidal cluster of five ruthenium atoms with a carbido ligand in the base of the square pyramid and a bridging $\sigma+\pi$-coordinated 2-phenylvinyl ligand, $\mu-\eta^2$-E-CHCHPh, formed by an overall trans-insertion of the $C_2H_2$ into the Ru-C bond to the bridging $\eta^2$-Ph ligand in **1**. A similar reaction of **1** with phenylacetylene ($PhC_2H$) yielded the new compound $Ru_5(\mu_5\text{-}C)(CO)_{13}[\mu\text{-}\eta^2\text{-}E\text{-}C(Ph)C(H)Ph][\mu\text{-}Au(NHC)]$, **3** in 96 % yield. Compound **3** contains a bridging $\sigma+\pi$-coordinated, $\eta^2$-1,2-diphenylvinyl ligand, $\eta^2$-E-C(Ph)C(H)Ph, formed by an overall trans-insertion of the molecule of $PhC_2H$ into the Ru-C bond of the bridging $\eta^2$-phenyl ligand in **1**. The phenyl ligand was shifted to the unsubstituted carbon atom of the $PhC_2H$ molecule.



## 1. Introduction

Insertion reactions have been one of the most useful chemical transformations for converting small unsaturated organic molecules into more complex and valuable derivatives [1,2]. Except for a few special cases [3], the 1,2-insertion of coordinated alkynes into metal – hydrogen and metal – carbon bonds generally proceeds with the formation of cis-stereochemistry in the alkenyl group which is formed, eq. (1), [4–6]. These reactions have been used in the synthesis of functionalized alkenes and polymers [7,8].




With only a few exceptions [9], cis-olefins are the standard products formed by the semi-hydrogenation of alkynes by metal catalysts involving this reaction [10,11]. Trans-olefins have been observed, but these are generally the result of subsequent facile cis/trans isomerizations that follow the formation of cis-olefin products [11].

Insertion reactions involving alkynes with hydride containing di- and polynuclear metal complexes generally provide bridging alkenyl ligands formed by cis-insertion stereochemistry [12], although there has been one report of insertion of ditolylacetylene and 2-butyne with a hydrido-dirhodium complex to yield complexes having bridging alkenyl ligands with trans-positioned R-groups [3c]. Alkyne insertions into metal – aryl bonds are very rare [6].

In recent studies we have prepared a number of transition metal – gold cluster complexes that contain bridging phenyl ligands, e.g. $Os_3(CO)_{10}(\mu\text{-}\eta^1\text{-}Ph)[\mu\text{-}Au(PPh_3)]$ [13], $Re_2(CO)_8(\mu\text{-}\eta^1\text{-}Ph)[\mu\text{-}Au(PPh_3)]$ [14], $Ru_5(\mu_5\text{-}C)(CO)_{13}(\mu\text{-}\eta^2\text{-}Ph)[\mu\text{-}Au(NHC)]$, **1**, NHC = 1,3-bis(2,6-diisopropylphenyl-imidazol-2-ylidene) [15]. In some of these cases, the phenyl ligands have adopted unusual bridging $\eta^1$- and $\eta^2$-coordination modes that result in interesting chemical and physical properties, including hindered rotation of the phenyl ligand about the metal – carbon bonds [15,16]. In earlier studies, it was shown that CO readily inserted into the metal – carbon bond of the bridging $\eta^2$-phenyl ligand in **1** to yield the carbido-pentaruthenium complex $Ru_5(\mu_5\text{-}C)(CO)_{13}[\mu\text{-}\eta^2\text{-}C(=O)Ph][\mu\text{-}Au(NHC)]$ containing a bridging benzoyl ligand, see Scheme 1.

In a continuation of this work, we have now investigated the reactions of the pentaruthenium complex **1** with the alkynes $C_2H_2$ and $HC_2Ph$ which have been found yield the new alkenyl complexes $Ru_5(\mu_5\text{-}C)(CO)_{13}[\mu\text{-}\eta^2\text{-}E\text{-}C(H)C(H)Ph)][\mu\text{-}Au(NHC)]$, **2** and $Ru_5(\mu_5\text{-}C)(CO)_{13}[\mu\text{-}\eta^2\text{-}E\text{-}C(Ph)C(H)Ph][\mu\text{-}Au(NHC)]$, **3** by insertion of the alkyne into the metal – carbon $\sigma$-bond of the phenyl ligand

[1] Dedicated to Professor Pradeep Mathur on the occasion of his 65th birthday.

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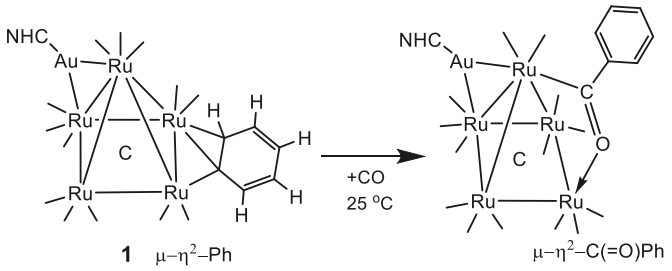



**Scheme 1**

**Scheme 1.** A schematic showing the insertion coupling of CO to the bridging $\eta^2$-phenyl ligand of compound **1** to from the compound $Ru_5(\mu_5\text{-}C)(CO)_{13}[\mu\text{-}\eta^2\text{-}C(=O)Ph][\mu\text{-}Au(NHC)]$ [15]. CO ligands are shown only as lines to the Ru atoms.

in **1**. The synthesis, structures and bonding of these new complexes are described in this report.

## 2. Experimental section

### 2.1. General data

All reactions were performed under nitrogen atmosphere. Reagent grade solvents were dried by standard procedures and were freshly distilled prior to use. Infrared spectra were recorded on a Thermo Scientific Nicolet IS10. $^1$H NMR spectra were recorded on a Varian Mercury 300 spectrometer operating at 300.1 MHz. Mass spectrometric (MS) measurements were performed by a direct-exposure probe by using electron impact (EI) ionization on a VG 70S instrument. Ethyne gas ($HC_2H$) (industrial grade) was purchased from Praxair and was used without further purification. Phenylacetylene ($PhC_2H$) was purchased from Sigma-Aldrich and was used without further purification. $Ru_5(\mu_5\text{-}C)(CO)_{13}(\mu\text{-}\eta^2\text{-}Ph)[\mu\text{-}Au(NHC)]$, **1**, NHC = 1,3-bis(2,6- diisopropylphenyl-imidazol-2-ylidene) was prepared according to previously reported procedure [15]. Product separations were performed by TLC in the air on Analtech 0.25 mm and 0.50 mm silica gel 60 Å F254 glass plates.

### 2.2. Reaction of $Ru_5(\mu_5\text{-}C)(CO)_{13}(\mu\text{-}\eta^2\text{-}Ph)[\mu\text{-}Au(NHC)]$, 1 with $C_2H_2$

10.0 mg (0.0065 mmol) of **1** was dissolved in 20 mL of hexane and transferred in three-neck flask. $C_2H_2$ gas at 1 atm pressure was purged through the solution for 0.5 h at 25 °C. The progress of the reaction was followed by IR spectroscopy. The solvent was then removed in vacuo, and 9.0 mg of $Ru_5(\mu_5\text{-}C)(CO)_{13}[\mu\text{-}\eta^2\text{-}E\text{-}C(H)C(H)Ph][\mu\text{-}Au(NHC)]$, **2** (yield 89%) was isolated by TLC by using a 6/3 of hexane/methylene chloride solvent mixture. The product **2** was recrystallized from a hexane/methylene chloride solvent mixture. Spectral data for **2**: IR $\nu$CO (cm$^{-1}$ in hexane): 2072(m), 2039(vs), 2027(s), 2017(s), 2008(s), 1990(w), 1979(w), 1957(vw), 1937(vw). $^1$H NMR ($CD_2Cl_2$, in ppm): $\delta$ = 10.90 (d, 12 Hz, 1H, CH=CH), 7.46 (t, 8 Hz, 2H, para CH–$(CH)_2$), 7.21-7.37 (m, 9H, meta H ($C_6H_5$)), 7.14 (s, 2H, N$(CH)_2$), 5.28 (d, 12 Hz, 1H, CH=CH), 2.78 (sept, 7 Hz, 4H, CH–$(CH_3)_2$), 1.37 (d, 6 Hz, 12H, CH$(CH_3)_2$), 1.14 (d, 6.9 Hz, 12H, CH$(CH_3)_2$). EI$^+$/MS: m/z 1572 (M$^+$).

### 2.3. Reaction of 1 with $PhC_2H$

12.8 mg (0.0083 mmol) of **1** was dissolved in toluene-$d_8$ solvent in a NMR tube. 10.0 $\mu$L (0.9105 mmol) of phenylacetylene, $PhC_2H$, was added to the solution. The reaction mixture was heated in a constant temperature oil bath at 80 °C for 45 min. The progress of the reaction was followed by $^1$H NMR spectroscopy. The solvent was removed in vacuo and 13.2 mg of $Ru_5(\mu_5\text{-}C)(CO)_{13}[\mu\text{-}\eta^2\text{-}E\text{-}C(Ph)C(H)Ph][\mu\text{-}Au(NHC)]$, **3** (96% yield) was isolated by TLC by using a 2/1 of hexane/methylene chloride solvent mixture for elution. The product was then crystallized from an octane/methylene chloride solvent mixture. Spectral data for **3**: IR $\nu$CO (cm$^{-1}$ in hexane): 2071(m), 2040(vs), 2028(s), 2018(s), 2009(s), 1992(vw), 1987(vw), 1977(vw), 1969(vw), 1959(vw), 1940(vw). $^1$H NMR ($CD_2Cl_2$, in ppm): 7.45–6.84 (m, 16H, ($C_6H_5$), 7.14 (s, 2H, N$(CH)_2$), 5.26 (s, 1H, PhC=CH), 2.79 (sept, 7.2 Hz, 4H, CH$(CH_3)_2$), 1.37 (d, 5.7 Hz, 12H, CH$(CH_3)_2$), 1.14 (d, 6.9 Hz, 12H, CH$(CH_3)_2$).

### 2.4. Crystallographic analyses

Single crystals of compound **2** suitable for X-ray diffraction analyses were obtained by slow evaporation of solvent from solutions of the pure compounds in a hexane/methylene chloride solvent mixture at room temperature. Single crystals of compound **3** suitable for X-ray diffraction analyses were obtained by slow evaporation of solvent from a solution of the pure compound in octane/methylene chloride solvent at room temperature. Crystals for compounds **2** and **3** were glued onto the end of a thin glass fiber. X-ray diffraction intensity data for compound **2** was measured by using a Bruker SMART APEX CCD-based diffractometer by using Mo K$\alpha$ radiation ($\lambda$ = 0.71073 Å). The raw data frames were integrated with the SAINT+ program by using a narrow frame integration algorithm. Corrections for Lorentz and polarization effects were also applied with SAINT+ [17]. An empirical absorption correction based on the multiple measurements of equivalent reflections was applied by using the program SADABS in each analysis [18].

X-ray intensity data for compound **3** was measured by using a Bruker D8 QUEST diffractometer equipped with a PHOTON-100 CMOS area detector and an Incoatec microfocus source (Mo K$\alpha$ radiation, $\lambda$ = 0.71073 Å) [19]. Both structures were solved by a combination of direct Methods and difference Fourier syntheses, and refined by full-matrix least-squares refinement on F$^2$ by using the SHELXTL software package [20]. Compound **2** crystallized in the monoclinic crystal system. The space group *P*2/n was identified for compound **2** based on systematic absences observed in the intensity data. Compound **3** crystallized in the orthorhombic crystal system. The space group *P*bca was identified for compound **3** based on systematic absences observed in the intensity data. Crystal data, data collection parameters, and results for the structural analyses are listed in Table 1. See Supporting Information for further information.

## 3. Results and discussion

The reaction of **1** with ethyne ($C_2H_2$) in hexane solvent at 25 °C for 30 min yielded the new compound $Ru_5(\mu_5\text{-}C)(CO)_{13}[\mu\text{-}\eta^2\text{-}E\text{-}C(H)C(H)Ph][\mu\text{-}Au(NHC)]$, **2** in 89 % yield. Compound **2** was characterized by a combination of IR, $^1$H NMR, mass spectrometry, and single-crystal X-ray diffraction analyses. Crystals of **2** contain two structurally similar molecules of the complex in the asymmetric crystal unit. An ORTEP diagram of the molecular structure of one of these molecules of **2** is shown in Fig. 1.

Compound **2** is structurally very similar to the structure of **1** [15] containing a square pyramidal cluster of five ruthenium atoms with a carbido ligand in the base of the square pyramid and thirteen linear terminal carbonyl ligands distributed about the cluster as shown in Fig. 1. An Au(NHC) group bridges the apical–basal Ru(1)–Ru(2) bond of the cluster. The Ru–Au bond distances in **2**, Ru1–Au1 = 2.7848(7) Å, Ru2–Au1 = 2.8282(7) Å, are similar to those in its parent cluster 1, Ru - Au = 2.7906(4) Å and 2.8338(4) Å, respectively. The most interesting ligand in **2** is a $\sigma+\pi$-coordinated 2-phenylvinyl ligand, $\mu\text{–}\eta^2$-E-CHCHPh, which was formed by insertion of $C_2H_2$ into the Ru-C bond of an $\mu\text{-}\eta^2$-Ph ligand in **1**. The alkenyl carbon atoms, C(2) and C(3), are $\pi$-coordinated to Ru(3) and Ru3–C2 = 2.205(8) Å, Ru3–C3 = 2.315(9)

**Table 1**
Crystal data, data collection parameters for compounds **2** and **3**.

| Compound | **2** | **3** |
|---|---|---|
| Empirical formula | $Ru_5AuO_{13}N_2C_{49}H_{43}$ | $Ru_5AuO_{13}N_2C_{55}H_{47}$ |
| Formula weight | 1570.17 | 1646.28 |
| Crystal system | Monoclinic | Orthorhombic |
| Lattice parameters | | |
| *a* (Å) | 33.0470(9) | 19.6303(7) |
| *b* (Å) | 10.6332(3) | 34.9241(12) |
| *c* (Å) | 33.3022(9) | 36.2726(13) |
| $\alpha$ (deg) | 90.00 | 90.00 |
| $\beta$ (deg) | 109.248(1) | 90.00 |
| $\gamma$ (deg) | 90.00 | 90.00 |
| V (Å$^3$) | 11048.1(5) | 24867.4(15) |
| Space group | *P*2/n | *P*bca |
| Z value | 8 | 16 |
| $\rho_{calc}$ (g/cm$^3$) | 1.888 | 1.850 |
| $\mu$ (Mo K$\alpha$) (mm$^{-1}$) | 4.037 | 2.406 |
| Temperature (K) | 294(2) | 100(2) |
| 2Θmax (°) | 50.06 | 60.20 |
| No. Obs. (I > 2$\sigma$(I)) | 19541 | 9265 |
| No. Parameters | 1293 | 433 |
| Goodness of fit (GOF) | 1.030 | 1.029 |
| Max. shift in cycle | 0.003 | 0.006 |
| Residuals*: R1; wR2 | 0.0404; 0.0908 | 0.0239, 0.0413 |
| Absorption Correction, Max/min | Multi-scan 1.00/0.749 | Multi-scan 0.5969/0.3924 |
| Largest peak in Final Diff. Map (e$^-$/Å$^3$) | 1.275 | 0.857 |

*R1 = $\Sigma_{hkl}(||F_{obs}|-|F_{calc}||)/\Sigma_{hkl}|F_{obs}|$; wR2 = $[\Sigma_{hkl}w(|F_{obs}|-|F_{calc}|)^2/\Sigma_{hkl}wF^2_{obs}]^{1/2}$; w = $1/\sigma^2(F_{obs})$; GOF = $[\Sigma_{hkl}w(|F_{obs}|-|F_{calc}|)^2/(n_{data} - n_{vari})]^{1/2}$.

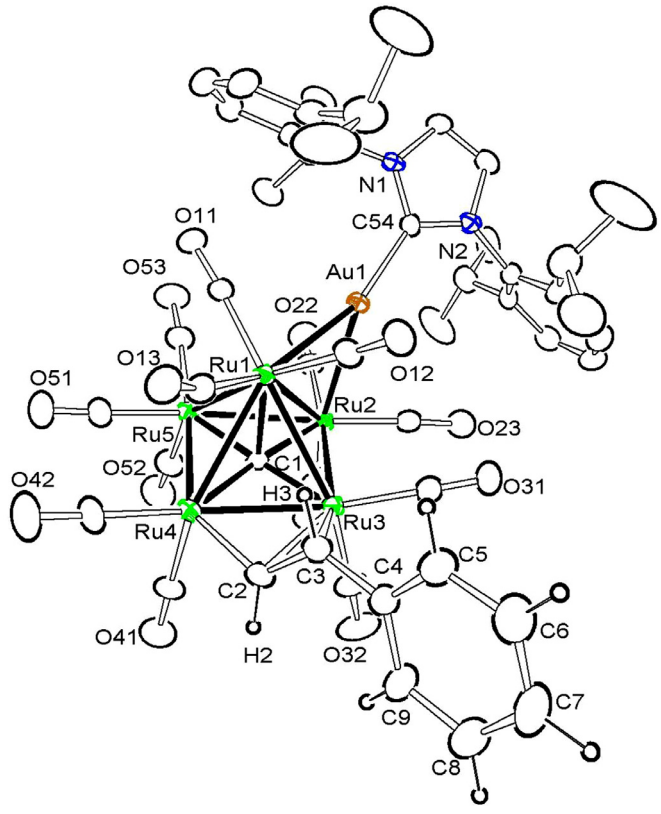


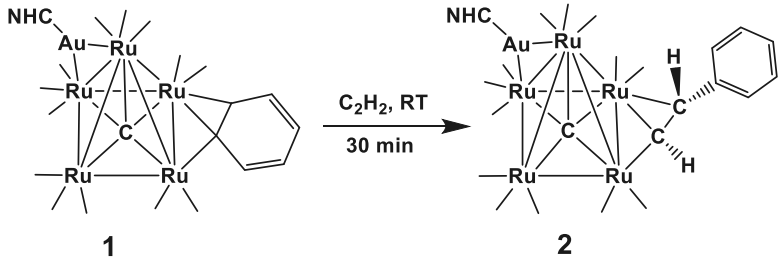

**Fig. 1.** ORTEP diagram of the molecular structure of one of two similar, independent molecules in the crystallographic asymmetric unit cell of $Ru_5(\mu_5\text{-}C)(CO)_{13}[\mu\text{-}\eta^2\text{-E-C(H)C(H)Ph}][\mu\text{-Au(NHC)}]$, **2** showing 15% thermal ellipsoid probability. The hydrogen atoms on the carbene ligand are omitted for clarity. Selected interatomic distances in (Å) for molecule 1 in the crystal are as follows: Ru1-Au1 =2.7848 (7), Ru2-Au1 = 2.8282 (7), Ru1-Ru2 = 2.9511 (9), Ru1-Ru5 = 2.8240(10), Ru1-Ru3 = 2.8303(9), Ru1-Ru4 = 2.8988(9), Ru2-Ru3 = 2.8688 (10), Ru2-Ru5 = 2.8943(10), Ru3-Ru4 = 2.6828 (9), Ru4-Ru5 = 2.8893(9), Au1-C54 = 2.014(7), Ru4-C2 = 2.053 (9), Ru3-C3 = 2.315 (9), Ru3-C2 = 2.205 (8), C2-C3 = 1.390 (12), C3-C4 = 1.482 (12).

Å. Atom C(2) is also $\sigma$-bonded to Ru(4), Ru4–C2 = 2.053(9) Å. There is an E-stereochemistry at the coordinated double bond C2 – C3 due to its $\sigma$-coordination to Ru4. The C2 – C3 bond distance is 1.390(12) Å. The alkenyl hydrogen atoms in **2** have a trans-relationship and appear as two deshielded doublets at $\delta$ = 10.90 and 5.28 with a large coupling constant, $^3J_{H\text{-}H}$ = 12 Hz in the $^1$H NMR spectrum. The $\mu-\eta^2$-CHCHPh ligand in **2** is unusual because the two alkenyl hydrogen atoms have a trans-stereochemistry, see Scheme 2 and Fig. 1.

There are a number of reports of polynuclear metal carbonyl cluster complexes containing similar bridging $\sigma+\pi$-coordinated 2-phenylvinyl ligands [21], but all have been synthesized by reactions of phenylacetylene, PhC≡CH, with hydride-containing polynuclear metal complexes by insertion of the alkyne into an M – H bond to yield 2-phenylvinyl ligands having an overall cis-insertion stereochemistry of the vinyl hydrogen atoms. The $\mu-\eta^2$-CHCHPh ligand in **2** serves formally as a three-electron neutral donor to the $Ru_5$ cluster, and the Au(NHC) group formally donates only one electron. Overall the $Ru_5$ cluster contains a total of 74 valence electrons, which is exactly the number required for a square-pyramidal cluster of five metal atoms [22].

The reaction of **1** with mono-phenylacetylene ($PhC_2H$), in toluene-$d_8$ solvent at 80 °C for 45 min yielded the new compound **3** in 96 % yield. Compound **3** was also characterized by a combination of IR, $^1$H NMR, and single-crystal X-ray diffraction analyses. Crystals of **3** contain two structurally similar molecules of the complex in the asymmetric crystal unit. An ORTEP diagram of the molecular structure of one of these molecules of **3** is shown in Fig. 2.

Compound **3** is very similar to **2** containing of a square pyramidal $Ru_5C$ cluster as shown in Fig. 2, and an Au(NHC) group bridging the apical–basal Ru(1a)–Ru(2a) bond of the cluster. The Ru–Au bond distances in **3**, Ru1a–Au1a = 2.7701(2) Å, Ru2a–Au1a = 2.8463(2) Å, are very similar to those distances in **1** and **2**. Compound **3** contains a $\sigma+\pi$-coordinated, $\eta^2$-1,2-diphenylvinyl ligand, $\eta^2$-E-C(Ph)C(H)Ph, bridging the Ru3 – Ru4 edge of the $Ru_5$ cluster. Compound **3** was formed by the insertion of $PhC_2H$ into the Ru-C bond of the $\mu-\eta^2$-Ph ligand in compound **1**, Ru3a–




**Scheme 2.** A schematic of the formation of **2** by a formal trans-insertion of $C_2H_2$ into the Ru – C bonds to the bridging phenyl ligand of **1**. The CO ligands are represented only as lines from the Ru atoms.

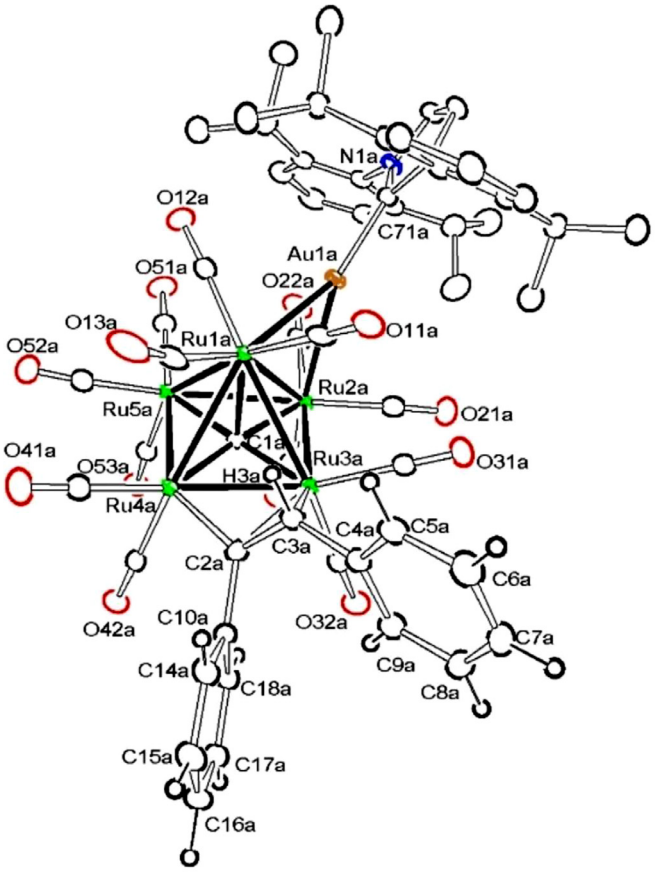



**Fig. 2.** ORTEP diagram of the molecular structure of one of two similar, independent molecules in the crystallographic asymmetric unit cell of $Ru_5(\mu_5\text{-}C)(CO)_{13}[\mu\text{-}\eta^2\text{-}E\text{-}C(Ph)C(H)Ph][\mu\text{-}Au(NHC)]$, **3** showing 40% thermal ellipsoid probability. The hydrogen atoms on the carbene ligand are omitted for clarity. Selected interatomic distances in (Å) for molecule "a" are as follows: Ru1a-Au1a =2.7701(2), Ru2a-Au1a = 2.8463(2), Ru1a-Ru2a = 2.9175(3), Ru2a-Ru3a = 2.8574(3), Ru1a-Ru3a = 2.8748(3), Ru1a-Ru4a = 2.9317(3), Ru1a-Ru5a = 2.7969(3) Ru2a-Ru5a = 2.8878(3), Ru4a-Ru5a = 2.9186(3), Ru3a-Ru4a = 2.6859(3), Ru4a-C2a = 2.083(2), Ru3a-C3a = 2.262(2), Ru3a-C2a = 2.246(2), Au1a-C71a = 2.050(2), C2a-C3a = 1.421(3), C3a-C4a = 1.490 (3), C2a-C10a = 1.493(3); torsion angle Ph-C2a-C3a-Ph = 17.1(4)°.

C2a = 2.246(2) Å, Ru3a–C3a = 2.262(2) Å. Atom C2a remains $\sigma$-coordinated to Ru4a, Ru4a–C2a = 2.083(2) Å. Most interestingly, the phenyl groups on the C(Ph)C(H)Ph ligand exhibit a pseudo-cis-stereochemistry at the C – C double bond. The C(Ph)C(H)Ph ligand is not completely planar. The Ph-C2a-C3a-Ph torsion angle is 17.1(4)°.

The single hydrogen atom on the coordinated double bond of the alkenyl ligand in **3** exhibits a deshielded, singlet resonance in the $^1$H NMR spectrum at 5.26 ppm. Assuming that the PhCC(H)Ph ligand donates three electrons and the Au(NHC) group donates one electron to the cluster, the $Ru_5$ cluster of **3** then contains a total of 74 cluster valence electrons, which is exactly the number required for a square-pyramidal cluster of five metal atoms [22].

Assuming that the phenyl group on C3a is the one that was originally on the Ru atoms in **1**, this would imply that the insertion of the PhC≡CH molecule into the Ru – C $\sigma$-bond of the phenyl ligand proceeded with transfer of the phenyl ligand to the unsubstituted carbon atom of the PhC≡CH molecule with an overall trans-insertion stereochemistry, i. e. the phenyl group on C2a and the H atom on C3a are trans to one another. The C2a – C3a bond length in **3**, 1.421(3) Å, is slightly longer than the corresponding C – C bond length (1.390(12) Å) in **2**, see above.

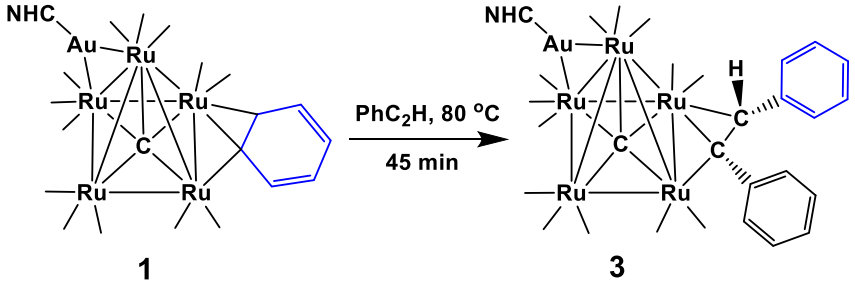
There are many examples of $\sigma+\pi$-coordinated, bridging C(Ph)C(H)Ph ligands in the literature [22,23,24]. All of these were synthesized by the addition and insertion of diphenylacetylene into a metal – hydrogen bond in polynuclear metal complexes. All of these exhibit a cis-stereochemistry of the two phenyl rings, like those in **3**, and were presumably formed by cis-insertion into the M-H bonds. Two exceptions are for the compounds $Rh_2[P(O\text{-}i\text{-}C_3H_7)_3]_4[\mu\text{-}\eta^2\text{-}C(Tol)C(H)Tol](\mu\text{-}H)$, **4** and $Rh_2[P(O\text{-}i\text{-}C_3H_7)_3]_4[\mu\text{-}\eta^2\text{-}C(Me)C(H)Me](\mu\text{-}H)$, **5** that were obtained by reactions of the hydride complex $\{Rh[P(O\text{-}i\text{-}C_3H_7)_3]_2(\mu\text{-}H)]\}_2$ with di(p-tolyl)acetylene, TolC≡CTol, and 2-butyne, MeC≡CMe, respectively, and were reported by Muetterties and others in 1983 [3c]. Compound **4** contains trans-oriented tolyl groups on its bridging C(Tol)C(H)Tol ligand. The bridging $\eta^2$-C(Tol)C(H)Tol ligand in **4** clearly contains trans-oriented tolyl rings. The mechanism of the formation of **4** was not established in this work and it cannot be ruled out that the mechanism may have involved an unobserved cis-insertion step that was followed by an unobserved cis-trans isomerization of the alkenyl ligand via a transient intermediate [25].

Similarly, it cannot be ruled out at this time that the formations of **2** and **3** may have mechanistically involved cis-alkyne insertion steps involving the phenyl ligand in **1** which were then followed by cis-trans isomerizations of incipient alkenyl ligands in unobserved intermediates.

## 4. Conclusions

The insertion of the alkynes, HC≡CH and HC≡CPh, into the Ru - C bond of the bridging phenyl ligand of the complex **1** yielded the complexes **2** and **3** containing bridging 2-phenylvinyl and bridging 1,2-diphenylvinyl ligands respectively, by C – C bond formation. Most notably, the overall stereochemistry of both alkenyl ligands is formally a result of an overall trans-insertion coupling of the alkyne to the bridging phenyl ligand of **1**. However, the mechanism of the formation of these vinyl ligands is not yet established. It is possible that both reactions proceed via cis-insertions of the alkynes via unobserved intermediate(s) that subsequently isomerize to the observed products **2** and **3**.

Scheme. 3




**Scheme 3.** A schematic of the formation of **3** by a formal trans-insertion of $PhC_2H$ into the Ru – C bonds of the bridging phenyl ligand of **1**. The CO ligands are represented only as lines from the Ru atoms.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Acknowledgements

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## Supplementary materials

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