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The stereoselective nucleophilic addition of cyanide to the cationic ruthenium complexes $[(\eta^5\text{-}C_5H_5)L_2Ru{=}C{=}C(Me)Ph]^+$ ($L_2 = (PMe_3)_2$ or $(PPh_2CH_2)_2$) *

Stephen G. Davies * and Andrew J. Smallridge
Dyson Perrins Laboratory, South Parks Road, Oxford, OX1 3QY (UK)

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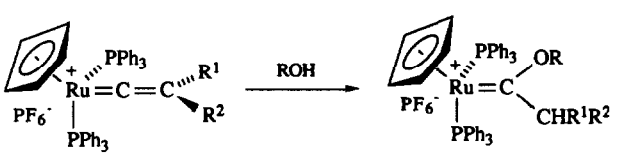
Abstract

Sodium cyanide reacts with the cationic ruthenium vinylidene complexes $[(\eta^5\text{-}C_5H_5)L_2Ru{=}C{=}C(Me)Ph]^+$ ($L_2 = (PMe_3)_2$ or $(PPh_2CH_2)_2$) to form ruthenium η^1-vinyl complexes in high yield and with a high degree of stereoselectivity. Computer modelling has been used to rationalise the selectivity obtained.

Introduction

The preparation of alkoxy carbene complexes via the nucleophilic addition of alcohols to cationic vinylidene species is a well known reaction (Scheme 1) [1], however there are very few examples of reactions using nucleophiles other than alcohols [2]. We now describe the first example of a carbon nucleophile reacting with a metal vinylidene species. Part of this work has been previously communicated [3].



Scheme 1. Preparation of ruthenium alkoxy carbenes.

* Dedicated to Professor Peter Pauson.

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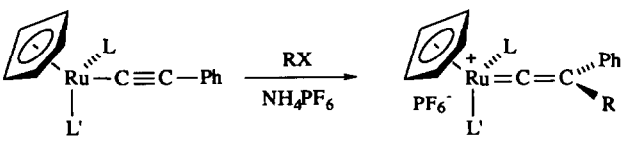
Results and discussion

Ruthenium vinylidene complexes are readily prepared by reacting an electrophile with the nucleophilic β-carbon of ruthenium acetylides. We have previously reported the preparation of disubstituted ruthenium vinylidene complexes from the reaction of an alkyl halide and a ruthenium acetylide complex in acetone or dichloromethane [4] and these results were subsequently confirmed and extended by Bruce et al. [5]. A simpler method for the preparation of this type of complex involves treating the acetylide complex with neat alkyl halide in the presence of ammonium hexafluorophosphate at room temperature for 1 h (Scheme 2).

For pseudo-octahedral systems with at least two available lone pairs of electrons, such as $[(\eta^5\text{-}C_5H_5)(PR_3)_2Ru{=}C{=}C(R^1)R^2]^+$, rotation about metal–carbon bonds with π–π interactions is stereoelectronically favourable [6]. The need to minimise steric interactions will therefore determine the orientation of the vinylidene unit. Molecular modelling calculations [7], taking into account electrostatic and van der Waals interactions, on $[(\eta^5\text{-}C_5H_5)(PMe_3)_2Ru{=}C{=}C(Me)Ph]^+$ (1) indicate that the lowest energy conformation for this complex has the vinylidene almost orthogonal to the plane bisecting the P–Ru–P angle (Fig. 1) i.e. parallel to the cyclopentadienyl ligand. This analysis is consistent with all known X-ray crystal structures of ruthenium vinylidene complexes [8]. Furthermore, it has previously been shown that there is rapid rotation of the vinylidene unit about the C_α–Ru bond in the complex



L	L'	RX	Yield (%)
PPh_3	PPh_3	MeI	83
PPh_3	PMe_3	MeI	84
PMe_3	PMe_3	MeI	72
dppe		MeI	91
PMe_3	PMe_3	BnBr	79

Scheme 2. Preparation of ruthenium vinylidene complexes.

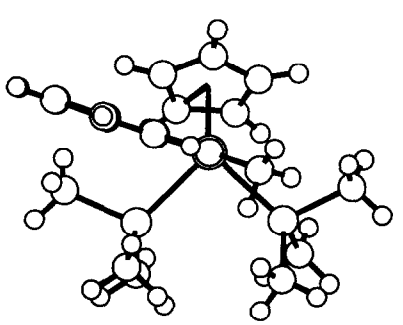
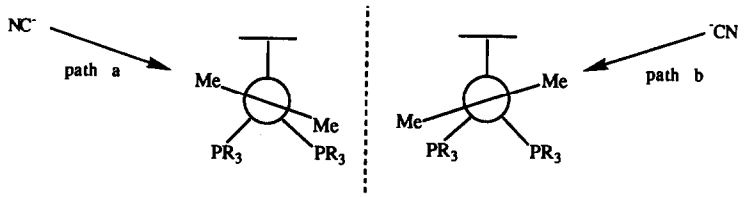


Fig. 1. Computer generated Newman projection of the lowest energy structure for $[(\eta^5\text{-}C_5H_5)(PMe_3)_2Ru{=}C{=}C(Me)Ph]^+$ (1) along C_β–C_α–Ru bonds.

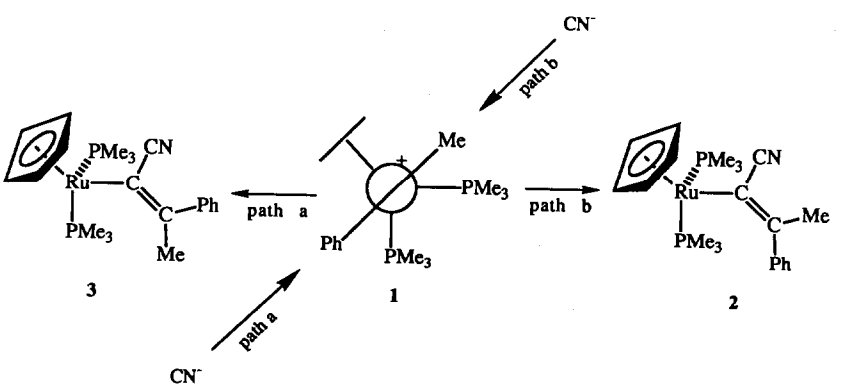


Scheme 3.

$[(\eta^5\text{-}C_5H_5)(PPh_2CH_2)_2Ru{=}C{=}C(H)Ph]^+$ [9]. Calculations have shown that rotation of the vinylidene unit in $[(\eta^5\text{-}C_5H_5)(PMe_3)_2Ru{=}C{=}C(Me)Ph]^+$ (**1**) is also a sterically feasibly process.

For complexes of the type $[(\eta^5\text{-}C_5H_5)(PR_3)_2Ru{=}C{=}C(R^1)R^2]^+$ to undergo nucleophilic attack the nucleophile must approach the α-carbon in the plane $Ru{-}C_\alpha{-}C_\beta{-}(R^1)(R^2)$, that is *syn* periplanar to either the R^1 or R^2 group. In a symmetrical complex such as $[(\eta^5\text{-}C_5H_5)(PR_3)_2Ru{=}C{=}CMe_2]^+$ there is no steric preference for approach past one methyl group over the other as the vinylidene will rotate to minimise the steric interactions between the incoming nucleophile and the $[(\eta^5\text{-}C_5H_5)(PR_3)_2Ru]$ auxiliary (degenerate paths a or b, Scheme 3). Calculations, using cyanide as the nucleophile, indicate that for both pathways steric interactions are minimised when the nucleophile bisects the Cp–Ru–P angle.

In the case of complexes with two different substituents on the vinylidene unit such as $[(\eta^5\text{-}C_5H_5)(PMe_3)_2Ru{=}C{=}C(Me)Ph]^+$ (**1**) the pathways are sterically identical in terms of the symmetrical $[(\eta^5\text{-}C_5H_5)(PMe_3)_2Ru]$ auxiliary (Path a or b, Scheme 4) and therefore any preference will be determined by the relative sizes of the substituents (Ph and Me). Calculations, using cyanide as the nucleophile, again indicate that for both pathways steric interactions are minimised when the nucleophile bisects the Cp–Ru–P angle, however, assuming that the phenyl group remains in conjugation with the double bond, there is a large difference in energy for the two approach paths in favour of path b where the nucleophile approaches past the smaller (methyl) substituent. Allowing the phenyl group to come out of conjugation lowers this calculated energy difference but there is still about a 10 Kcal mol^{-1} energy difference favouring approach past the smaller methyl group.



Scheme 4. Nucleophilic addition of cyanide to $[(\eta^5\text{-}C_5H_5)(PMe_3)_2Ru{=}C{=}C(Me)Ph]^+$ (**1**).

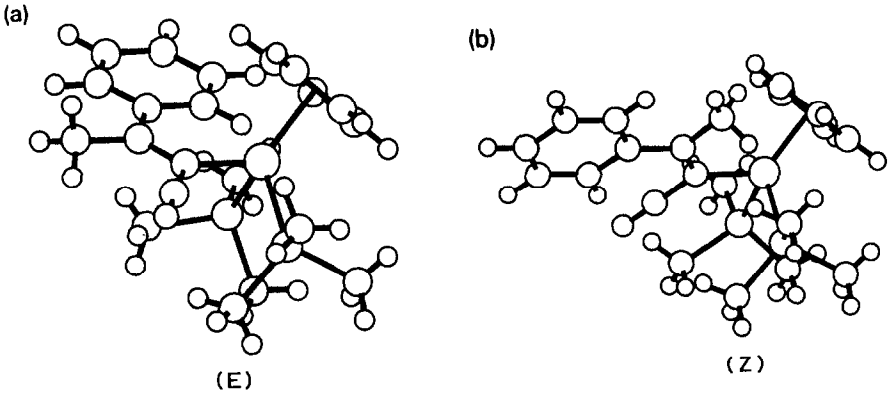


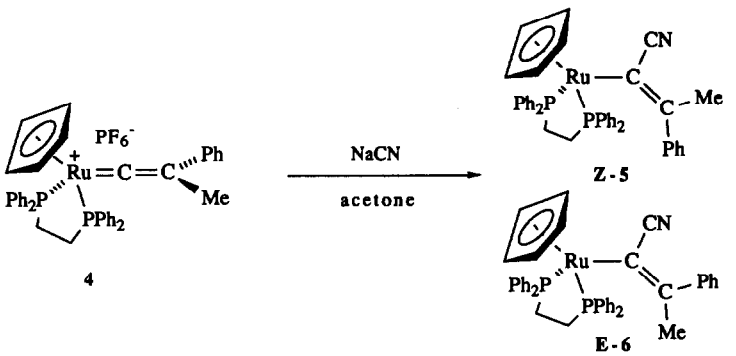
Fig. 2. Calculated most stable conformations of the *E* and *Z* forms of $(\eta^5\text{-}C_5H_5)(PMe_3)_2Ru\text{-}C(CN)=C(Me)Ph$.

Heating an acetone solution of sodium cyanide and **1** at reflux for 4 h under an inert atmosphere produces an almost quantitative yield (95%) of the η^1-vinyl complexes **2** and **3** in a ratio of > 95 : 5. The isomer ratio was determined using ^1H NMR spectroscopy on the reaction mixture in benzene-d^6 as equilibration of the complexes occurs in chlorinated solvents (CH_2Cl_2 and $CHCl_3$). Monitoring a deuteriochloroform solution of **2** : **3** (95 : 5) using ^1H NMR spectroscopy indicated that almost complete isomerisation (**2** : **3**, 5 : 95) had occured after 24 h. Both isomers **2** and **3** retain their stereochemical integrity in deuteriobenzene over a period of days. Working up the reaction in benzene gave **2** as the major product whilst **3** was obtained after work up in dichloromethane.

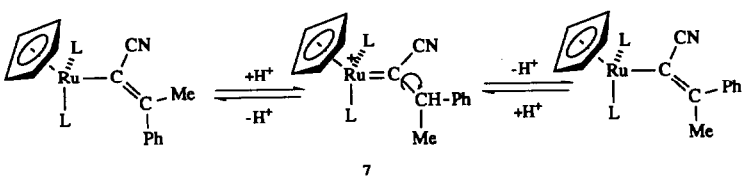
An equimolar solution of the two isomers, **2** and **3**, in benzene-d^6 was prepared and subjected to standard NOE techniques in order to determine their relative structures. Irradiation of the methyl singlet of complex **3** produced enhancement of the cyclopentadienyl (15%), trimethyl phosphine (15%) and *o*-phenyl (8%) hydrogen signals whilst no such enhancements of the cyclopentadienyl or trimethyl phosphine signals were observed when the methyl singlet of complex **2** was irradiated; only the *o*-phenyl hydrogen signal being enhanced (5%) in the latter case. This confirms the prediction that complex **2** has the methyl group *trans* to the ruthenium (Fig. 2a) while in **3** the methyl is *cis* to the ruthenium and hence in close proximity to the cyclopentadienyl and trimethylphosphine groups as is clearly seen in Fig. 2b.

The ruthenium vinylidene complex **4** containing the bulkier diphosphine ligand 1,2-bis(diphenylphosphino)ethane reacts considerably more slowly than **1** with sodium cyanide (Scheme 5). Heating this complex in acetone for 24 h resulted in the formation of the expected η^1-vinyl complexes (**5** and **6**) in excellent yield although with reduced selectivity (70 : 30) compared to the trimethyl phosphine complex **1**. While the isomers are prone to isomerisation in chlorinated solvents it is a much slower process than in the first example and monitoring a deuteriochloroform solution of **5** and **6** (70 : 30) using ^1H NMR spectroscopy over a period of 4 days demonstrated equilibration to 5 : 6 (15 : 85).

Calculations indicate that in both cases the *E* isomers (**3** and **6**), with the smaller methyl group cis to the bulky ruthenium moiety, have a much lower energy (ca 40 Kcal mol^{-1}) than the corresponding *Z* isomers (**2** and **5**) and the isomerisation of



Scheme 5. Nucleophilic addition of cyanide to $[(\eta^5\text{-}C_5H_5)(PPh_2CH_2)_2Ru{=}C{=}C(Me)Ph]^+$ (4).



Scheme 6. Acid catalysed rearrangement of ruthenium η^1-vinyl complexes.

the thermodynamically less stable isomer can be rationalised in the following manner. In the presence of a catalytic amount of acid (DCl is a ubiquitous impurity in $CDCl_3$ [10]) protonation can occur at the β-carbon, rotation about the C_α–C_β bond followed by deprotonation results in the formation of the other isomer (Scheme 6). Calculations indicate that rotation about the C_α–C_β bond in the carbene **7** is a much more facile process for the complex containing the smaller trimethyl phosphine ligands than the complex with the 1,2-bis(diphenylphosphino)-ethane and this could explain the slower rate of isomerisation of complex **5**.

Conclusion

We have demonstrated that the cationic ruthenium vinylidene complexes **1** and **4** undergo nucleophilic attack by sodium cyanide and that the stereoselectivity observed is controlled by the steric bulk of the vinylidene substituents.

Experimental

General

The ruthenium acetylide complexes were prepared from the appropriate ruthenium chloride and acetylide using a literature procedure [11]. ^{1}H NMR spectra were recorded at 200 MHz on a Varian Gemini 200 instrument. ^{31}P NMR were recorded on a Bruker AM 250 (62.90 MHz) in benzene-d_6. The NOE experiments were recorded on a Bruker AM 500 (500 MHz) in benzene-d_6.

Molecular modelling calculations

All molecular modelling calculations were conducted using the CHEMX modelling package on a VAXstation 3520. The initial geometry of complex **1** was derived from the crystal structure [12] of $[(\eta^5\text{-}C_5H_5)(PMe_3)_2Ru{=}C{=}CHMe]^+$ by replacing the proton with a phenyl group. Rotational conformers were then generated by revolving the vinylidene unit about the Ru–C_α bond. The summation of electrostatic and Van der Waals energy of each generated conformer was minimised by independent rotations about all single bonds (not to hydrogen) within the molecule. An atom centred point charge distribution was calculated for the complex by the programme, with the charge on ruthenium set to plus one. For the calculations for the docking experiments the cyanide was constrained to approach C_α in the plane Ph–C_α–C_β–Ru or Me–C_α–C_β–Ru and orthogonal to the C_α–C_β–Ru bond.

$[(\eta^5\text{-}C_5H_5)(PPh_3)_2Ru{=}C{=}C(Me)Ph]PF_6$

Ruthenium (η^5-cyclopentadienyl)(bistriphenylphosphine)phenyl acetylide (220 mg, 0.27 mmol) and ammonium hexafluorophosphate (100 mg, 0.61 mmol) were stirred in methyl iodide (2 ml) for 1 h at 20 °C. After removal of the methyl iodide, dichloromethane was added and the solution filtered. Removal of the dichloromethane gave the pure vinylidene complex. Yield 217 mg, 83%. M.p. 207–210 °C (dec.), Ref. [11] 205–210 °C (dec.). ^{1}H NMR ($CDCl_3$): δ 1.94 (s, 3H, Me); 5.18 (s, 5H, Cp); 6.8–7.5 (m, 36H, Ar).

$[(\eta^5\text{-}C_5H_5)(PPh_3)(PMe_3)Ru{=}C{=}C(Me)Ph]PF_6$

Yield 84%. M.p. 232–234 °C. Anal. Found: C, 55.02; H, 4.96. $C_{35}H_{37}F_6P_3Ru$ calc.: C, 54.90; H, 4.87%. ^{1}H NMR (acetone-d_6): δ 1.17 (d, J = 10.3Hz, 9H, PMe_3); 1.93 (s, 3H, Me); 5.56 (s, 5H, Cp); 7.0–7.6 (m, 20H, Ar).

$[(\eta^5\text{-}C_5H_5)(PMe_3)_2Ru{=}C{=}C(Me)Ph]PF_6$

Yield 72%. M.p. 194–196 °C (dec), Ref. [12] 195 °C (dec). ^{1}H NMR (acetone-d^6): δ 1.67 (m, 18H, PMe_3); 2.20 (s, 3H, Me); 5.81 (s, 5H, Cp); 7.1–7.4 (m, 5H, Ph).

$[(\eta^5\text{-}C_5H_5)(PPh_2CH_2)_2Ru{=}C{=}C(Me)Ph]PF_6$

Yield 91%. M.p. 200 °C (dec). Ref. [5] 200–202 °C (dec). ^{1}H NMR (CD_2Cl_2): δ 1.55 (s, 3H, Me); 2.8–3.1 (m, 4H, CH_2CH_2); 5.57 (s, 5H, Cp); 6.9–7.4 (m, 25H, Ar).

$[(\eta^5\text{-}C_5H_5)(PMe_3)_2Ru{=}C{=}C(CH_2Ph)Ph]PF_6$

Yield 79%. M.p. 207–209 °C. Anal. Found: C, 65.28; H, 4.60. $C_{56}H_{47}F_6P_3Ru$ calc.: C, 65.43; H, 4.61%. ^{1}H NMR ($CDCl_3$): δ 1.66 (m, 18H, PMe_3); 3.96 (s, 2H, CH_2); 5.85 (s, 5H, Cp); 7.0–7.4 (m, 10H, Ar).

Reaction of sodium cyanide with 1

An acetone solution of **1** (150 mg, 0.26 mmol) and sodium cyanide (60 mg, 1.5 mmol) was heated at reflux for 4 h. After removal of the acetone under reduced pressure benzene was added and the solution filtered. Removal of the benzene gave a mixture of the two isomers **2** and **3**. Yield 115 mg, 95%. M.p. 110–111 °C. Anal. Found: C, 54.89; H, 7.04; N, 3.02. $C_{21}H_{31}NP_2Ru$ calc.: C, 54.77; H, 6.78; N, 3.04%. ^{1}H NMR (benzene-d_6) for **2**: δ 1.03 (m, 18H, PMe_3); 2.65 (s, 3H, Me); 4.14 (s, 5H,

Cp); 7.0–7.4 (m, 5H, Ph). For **3**: δ 1.14 (m, 18H, PMe_3); 2.11 (s, 3H, Me); 4.28 (s, 5H, Cp); 7.0–7.4 (m, 5H, Ph). ^{31}P NMR (benzene-d_6) for **2**: δ 5.69 (s). For **3**: δ 6.62 (s).

Reaction of sodium cyanide with ***4****.*

Yield 96%. M.p. 122–123°C. Anal. Found: C, 69.62; H, 5.05; N, 1.91. $C_{41}H_{37}NP_2Ru$ calc.: C, 69.67; H, 5.28; N, 1.98%. ^1H NMR (benzene-d_6) for **5**: δ 1.52 (s, 3H, Me); 3.98 (s, 5H, Cp); 6.8–7.8 (m, 25H, Ph). For **6**: δ 2.35 (s, 3H, Me); 4.55 (s, 5H, Cp); 6.8–7.8 (m, 25H, Ph). ^{31}P NMR (benzene-d_6) for **5**: δ 84.28 (s). For **6**: δ 92.30 (s).

Acknowledgements

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