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Preliminary communication

The stereoselective reaction of sodium cyanide with the cationic ruthenium vinylidene complex $[(\eta^5\text{-}C_5H_5)(PMe_3)_2Ru{=}C{=}C(Me)Ph]^+$

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Abstract

The reaction of sodium cyanide with $[(\eta^5\text{-}C_5H_5)(PMe_3)_2Ru{=}C{=}C(Me)Ph]PF_6$ (**1**) proceeds with high stereoselectivity ($> 95:5$) to give (Z)-$(\eta^5\text{-}C_5H_5)(PMe_3)_2Ru$–C(CN)=C(Me)Ph, which under acid conditions isomerises ($< 5:95$) to the E isomer.

The nucleophilic addition of alcohols to cationic vinylidene complexes is a very common process but little is known about the detailed mechanism or stereochemistry [1]. We describe here the stereoselective addition of cyanide to a ruthenium vinylidene cation.

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 [2], hence the orientation of the vinylidene unit in these complexes will be governed by the need to minimise steric interactions. Calculations which take into account only Van der Waals interactions indicate that the lowest energy conformation has the vinylidene unit orthogonal to the plane bisecting the P–Ru–P angle (Fig. 1) and this analysis is consistent with all known X-ray crystal structures of ruthenium vinylidene complexes [3].

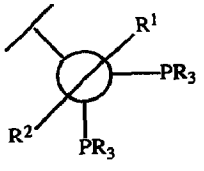

Fig. 1. Newman projection of $[\eta^5\text{-}C_5H_5)(PR_3)_2Ru{=}C{=}CR^1(R^2)]^+$ along C_β–C_α–Ru bonds.

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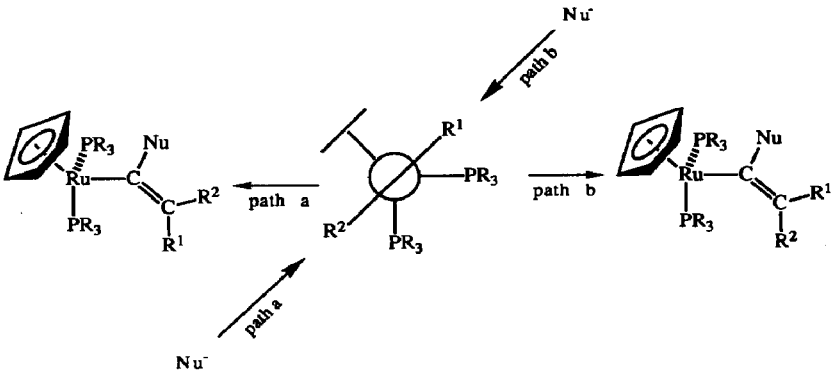
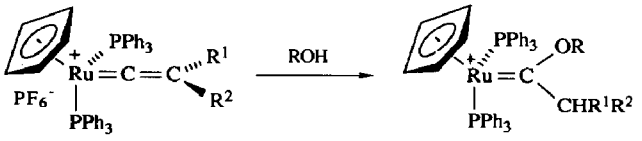


Scheme 1. Addition of a nucleophile to $[(\eta^5\text{-}C_5H_5)(PR_3)_2Ru{=}C{=}C(R^1)R^2]^+$.



Scheme 2. Reaction of alcohols with ruthenium vinylidene complexes.

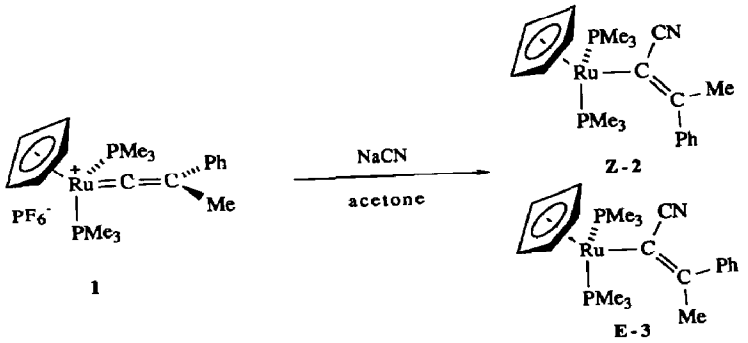
For nucleophilic addition to the α-carbon of $[(\eta^5\text{-}C_5H_5)(PR_3)_2Ru{=}C{=}C(R^1)R^2]^+$ to occur the nucleophile must approach in the plane $Ru{-}C_\alpha{-}C_\beta{-}(R^1)R^2$, that is *syn* periplanar to either R^1 or R^2 (path a or b, Scheme 1). Steric interactions with the metal auxiliary will be identical for these two pathways and therefore any preference should be determined by the relative sizes of R^1 and R^2. The size of the phosphine will of course influence the overall rate of the reaction.

The rate of reaction of alcohols with $[(\eta^5\text{-}C_5H_5)(PR_3)_2Ru{=}C{=}C(R^1)R^2]^+$ is influenced both by the size of the substituents on the vinylidene and the size of the phosphine ligands (Scheme 2). The unsubstituted vinylidene complex (R^1,R^2 = H) reacts rapidly with methanol at room temperature [4], monosubstituted vinylidene complexes (R^1 = H, $R^2 \neq$ H) slowly react with methanol at reflux whilst no reaction is observed with disubstituted vinylidenes (R^1,$R^2 \neq$ H) [5]. Bruce et al. have also shown that there is an inverse relationship between the relative reaction rates of $[(\eta^5\text{-}C_5H_5)(PPh_3)LRu{=}C{=}CHPh]^+$ with methanol and the cone angle of the phosphine ligand [6].

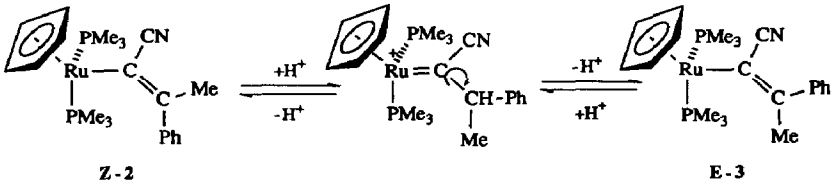
An acetone solution of **1** and NaCN was heated under reflux for 4 hours to give a high yield (95%) of the η^1-vinyl complexes **2** and **3** in a ratio of > 95 : 5 (determined by ^{1}H NMR spectroscopy in C_6D_6 *) (Scheme 3). Monitoring a deuteriochloroform solution of **2** : **3** (> 95 : 5) by ^{1}H NMR spectroscopy over 24 hours demonstrated equilibration to **2** : **3** (< 5 : 95). No isomerisation was observed in deuteriobenzene over a similar period.

The relative structure of the two isomers was assigned using standard nOe techniques on an equimolar solution of the two complexes in benzene-d_6. Irradiation of the methyl singlet of complex **3** gave enhancement of both the cyclopenta-

* All new compounds gave satisfactory elemental and spectroscopic analysis.



Scheme 3. Nucleophilic attack of cyanide on $[(\eta^5\text{-}C_5H_5)(PMe_3)_2Ru{=}C{=}C(Me)Ph]^+$.



Scheme 4. Acid-catalysed isomerisation of $(\eta^5\text{-}C_5H_5)(PMe_3)_2Ru{-}C(CN){=}C(Me)Ph$.

dienyl and trimethyl phosphine signals whilst no such enhancements were observed when the methyl peak of complex **2** was irradiated. This establishes that in complex **2** the methyl group is *trans* to the ruthenium and in complex **3** the methyl group is *cis* to the ruthenium and hence close to the cyclopentadienyl and trimethyl phosphine groups.

These results are consistent with the following mechanism. Addition of cyanide to the α-carbon *syn* to the smaller methyl group on the β-carbon of the vinylidene, i.e. *anti* to the relatively larger phenyl group. Since the ruthenium moiety is very much larger than the cyanide group this must generate the thermodynamically less stable *Z* isomer **2**. In the presence of acid (DCl is a ubiquitous impurity in $CDCl_3$ [7]), catalytic isomerisation to the thermodynamically more stable *E* isomer occurs via protonation–deprotonation at the β-carbon (Scheme 4).

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