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Stereospecific protonation of coordinated alkynes

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Abstract

The reaction of $[V(\eta^5\text{-}C_5H_5)_2(\eta^2\text{-}PhCCPh)]$ with anhydrous HCl in tetrahydrofuran gives $[V(\eta^5\text{-}C_5H_5)_2Cl_2]$ together with *cis*-PhCHCHPh (ca. 85%) and *trans*-PhCHCHPh (ca. 15%). Kinetic studies indicate that the formation of *cis*-PhCHCHPh involves initial protonation of the metal followed by migration of the hydride on to the alkyne to give the *cis*-vinyl species. Subsequent further protonation gives *cis*-PhCHCHPh. *trans*-PhCHCHPh is formed by direct protonation of the coordinated alkyne to form the *trans*-vinyl species which, upon further protonation, gives the corresponding alkene.

Keywords: Vanadium; Alkynes; Vinyl; Cyclopentadienyl; Mechanism

Understanding the protonation of coordinated unsaturated hydrocarbons is fundamental both to the utilization of such reactions in synthesis [1] and to defining the non-physiological reactions of the metalloenzyme nitrogenase [2]. In particular the vanadium- or molybdenum-based nitrogenases are capable of converting acetylene into ethylene by a sequence of simple electron and proton transfer reactions. In the presence of deuterons stereospecific formation of *cis*-CHDCHD occurs [3,4]. Previously it has been proposed that this stereospecificity is a consequence of constraints imposed by the geometry of the active site of the enzyme [5]. However, we know little about the mechanism of protonation of coordinated alkynes and the stereochemistry of this process, even in simple complexes. We show below that for $[V(\eta^5\text{-}C_5H_5)_2(\eta^2\text{-}PhCCPh)]$ [6] the mechanism of protonation results in the preferential formation of the *cis*-alkene.

Upon mixing $[V(\eta^5\text{-}C_5H_5)_2(\eta^2\text{-}PhCCPh)]$ and anhydrous HCl in tetrahydrofuran (thf) there is a rapid colour change from green to blue. The metal-containing product of this reaction was identified as $[V(\eta^5\text{-}C_5H_5)_2Cl_2]$ by elemental analysis of the isolated material, and comparison of the IR and EPR spectra with those of an authentic sample (see Fig. 1) [7].

The identity of the organic product from the reaction was identified as a mixture of *cis*-and *trans*-PhCHCHPh by ^{1}H NMR spectroscopy [8]. The isomers can be distinguished from the peaks attributable to PhC*H*C*H*Ph (δ 7.23, *trans*; δ 6.62, *cis*). Quantitative analysis of the spectra shows that the predominant product is *cis*-PhCHCHPh (85 ± 5%), with the thermodynamically more stable *trans*-PhCHCHPh (15 ± 5%) present only as a minor component (Eq. (1)).

$$[V(\eta^5\text{-}C_5H_5)_2(\eta^2\text{-}PhCCPh)] + 2HCl \longrightarrow [V(\eta^5\text{-}C_5H_5)_2Cl_2] + \textit{cis}\text{-PhCHCHPh (85\%)} + \textit{trans}\text{-PhCHCHPh (15\%)} \quad (1)$$

When monitored by use of stopped-flow apparatus, the reaction between $[V(\eta^5\text{-}C_5H_5)_2(\eta^2\text{-}PhCCPh)]$ and an excess of anhydrous HCl in thf exhibits an absorbance-time trace typified by that shown in Fig. 1. At all acid concentrations the final absorbance is that of $[V(\eta^5\text{-}C_5H_5)_2Cl_2]$. At low concentrations of HCl the initial absorbance is that of $[V(\eta^5\text{-}C_5H_5)_2(\eta^2\text{-}PhCCPh)]$, but at higher concentrations of acid the initial absorbance is noticably lower (ca. 0.05 absorbance units) (vide infra). At all acid concentrations the absorbance–time traces can be fitted satisfactorily to two exponential curves, corresponding to the reaction occuring in two stages and both stages exhibiting a first

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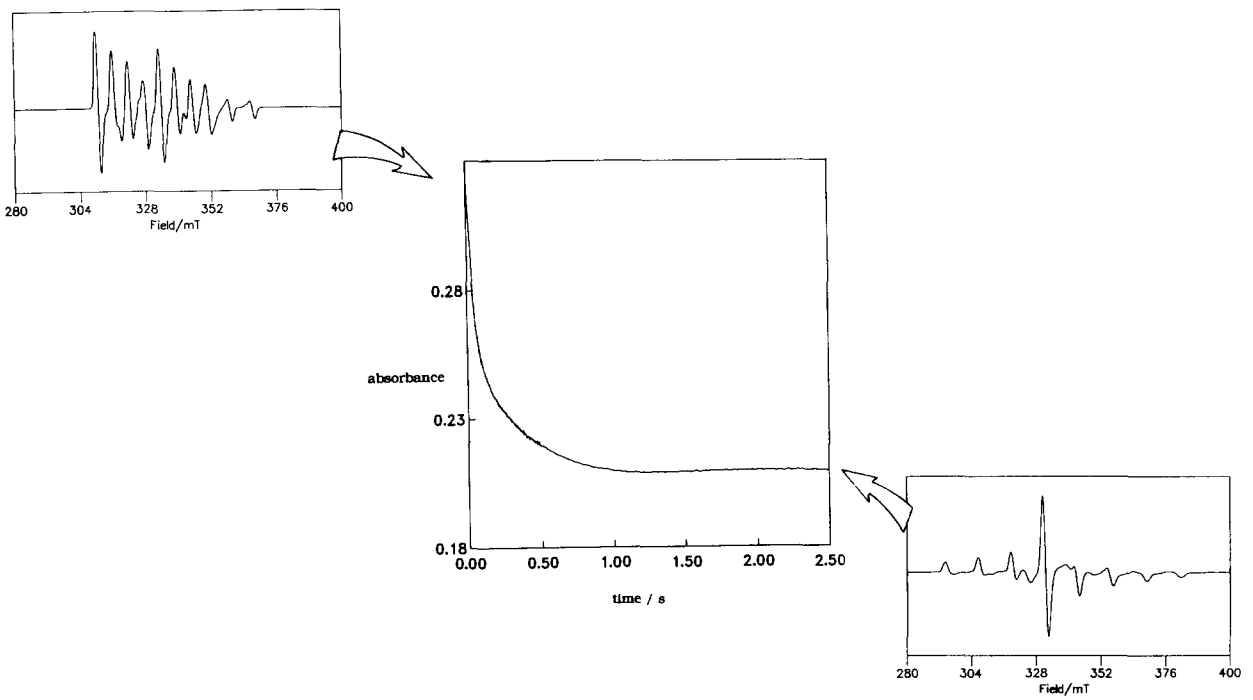
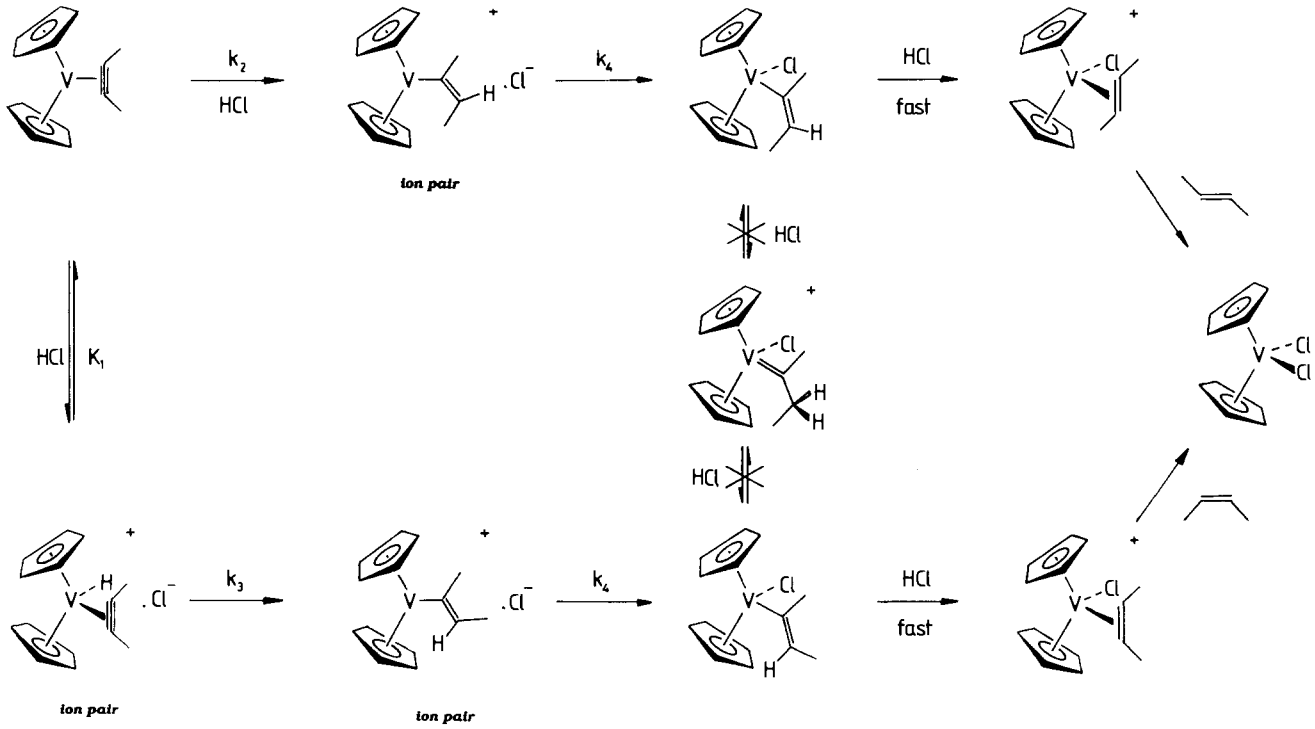


Fig. 1. Centre—Typical stopped-flow absorbance–time curve for the reaction of $[V(\eta^5\text{-}C_5H_5)_2(\eta^2\text{-}PhCCPh)]$ (0.25 mmol dm^{-3}) with anhydrous HCl (10.0 mmol dm^{-3}) in thf at 25.0°C, measured at $\lambda = 420$ nm. Left—EPR spectrum of $[V(\eta^5\text{-}C_5H_5)_2(\eta^2\text{-}PhCCPh)]$in thf. Right—EPR spectrum of the product of the reaction between $[V(\eta^5\text{-}C_5H_5)_2(\eta^2\text{-}PhCCPh)]$ and anhydrous HCl in thf. This spectrum is essentially identical to that of an authentic sample of $[V(\eta^5\text{-}C_5H_5)_2Cl_2]$.

order dependence on the concentration of the complex [9].

The rate of the first stage exhibits a complicated dependence on the concentration of HCl. At low concentrations of acid, the rate of the reaction exhibits a first order dependence on the concentration of HCl, while at high concentrations of acid it is independent of that concentration. Analysis of these data by the



Scheme 1.

usual "double reciprocal plot" [10] gives the rate law shown in Eq. (2).

$$-d[V(\eta^5\text{-}C_5H_5)_2(\eta^2\text{-PhCCPh})]/dt = \frac{(6.2 \pm 0.3) \times 10^3[HCl]}{\{1 + (156 \pm 10)[HCl]\}} \times [V(\eta^5\text{-}C_5H_5)_2(\eta^2\text{-PhCCPh})] \quad (2)$$

The slow stage occurs at a rate that is independent of the concentration of HCl, $k_{obs} = (1.0 \pm 0.2)\ s^{-1}$.

The complexity of Eq. (2), and the absence of a primary isotope effect in studies with DCl argues against simple, direct photon transfer to the coordinated alkyne, but rather is consistent with the pathways shown in Scheme 1.

The *cis*- and *trans*-PhCHCHPh produced in the reaction are formed by protonation of the alkyne at the face bound to the metal and that remote from the metal, respectively. The kinetics associated with the faster phase are consistent with both of these processes. Rapid protonation of $[V(\eta^5\text{-}C_5H_5)_2(\eta^2\text{-PhCCPh})]$ at the metal gives $[V(\eta^5\text{-}C_5H_5)_2H(\eta^2\text{-PhCCPh})]^+$, within the dead-time of the stopped-flow apparatus (2 ms). As mentioned earlier, the initial absorbance of the stopped-flow trace depends on the concentration of HCl, and this reflects the protonation equilibrium. The intermediate, $[V(\eta^5\text{-}C_5H_5)_2H(\eta^2\text{-PhCCPh})]^+$ then undergoes an intramolecular migration of the hydride ligand on to the metal-bound face of the alkyne ligand to form the *cis*-vinyl species. In addition, a *trans*-vinyl species is formed in another pathway involving direct protonation of $[V(\eta^5\text{-}C_5H_5)_2(\eta^2\text{-PhCCPh})]$ at the alkyne face remote from the metal. Consideration of Scheme 1. gives the rate law shown in Eq. (3), with $(k_2 + k_3K_1) = (6.2 \pm 0.3) \times 10^3$ $dm^3\ mol^{-1}\ s^{-1}$ and $K_1 = 156 \pm 10\ dm^3\ mol^{-1}$.

$$-d[V(\eta^5\text{-}C_5H_5)_2(\eta^2\text{-PhCCPh})]/dt = \frac{(k_2 + k_3K_1)[HCl]}{(1 + K_1[HCl])} \times [V(\eta^5\text{-}C_5H_5)_2(\eta^2\text{-PhCCPh})] \quad (3)$$

Provided the carbon–carbon double bond of the vinyl ligand is retained throughout the remainder of the reaction the stereochemistry of the alkenes formed by protonation of alkyne complexes is defined by the first protonation: that is the *cis*-vinyl complex gives the *cis*-alkene and the *trans*-vinyl complex gives the *trans*-alkene. Previous studies on vinyl complexes [11] have shown that if protonation occurs at the carbon atom remote from the metal then mixtures of *cis*- and *trans*-alkenes are produced because free rotation about the carbon–carbon single bond in an alkylidene intermediate effectively equilibrates the isomeric vinyl species. Protonation of the remote carbon atom of a vinyl species involves formal oxidation of the metal by two units. This is not possible in the vanadium system studied here since the vinyl complex is a vanadium(IV) species. Consequently protonation of $[V(\eta^5\text{-}C_5H_5)_2(CPhCHPh)]^+$ can occur only at the carbon atom bound to the metal.

The second stage observed by use of the stopped-flow spectrophotometer corresponds to the formation of alkenes from the vinyl species. The kinetics for the second stage are too simple to give detailed information about this process. However, the kinetics are consistent with rate-limiting attack of solvent, or an ion-paired chloride ion, on the vinyl complexes, $k_4 = (1.0 \pm 0.2)\ s^{-1}$. The binding of solvent or chloride to the metal renders the vinyl ligand sufficiently basic to be protonated giving the corresponding alkene.

Since there is no pathway that allows equilibration of the isomeric vinyl species, the alkene product distribution reflects the rates of formation of these vinyl intermediates, as described in Eq. (4).

$$\frac{[cis\text{-PhCHCHPh}]}{[cis\text{-PhCHCHPh}] + [trans\text{-PhCHCHPh}]} = \frac{k_3K_1}{k_3K_1 + k_2} = 0.85 \quad (4)$$

Using the value of the elementary rate and equilibrium constants derived in Eq. (3) the values, $k_3 = 33.8 \pm 1.0\ s^{-1}$ and $k_2 = (9.3 \pm 0.3) \times 10^2\ dm^3\ mol^{-1}\ s^{-1}$ can be calculated.

This study shows how protonation of a coordinated alkyne results in the preferential formation of *cis*-PhCHCHPh because of initial, rapid protonation of the metal followed by migration of the hydride ligand to the alkyne. Slower direct protonation of the alkyne results in *trans*-PhCHCHPh. The preferential formation of the *cis*-alkene by protonation of an alkyne at such a symmetrical site as "$V(\eta^5\text{-}C_5H_5)_2$" indicates that the nitrogenases are perhaps exhibiting nothing more than the normal stereochemical behaviour associated with the protonation of coordinated alkynes.

References and notes

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[7] The EPR spectra of the reaction product and $[V(\eta^5\text{-}C_5H_5)_2Cl_2]$ were superimposable apart from a number of weak features in

the product that could be identified with ca. 2% of residual starting material.

[8] The procedure used to identify the organic products was as follows. To a solution of $[V(\eta^5\text{-}C_5H_5)_2(\eta^2\text{-}PhCCPh)]$ (0.34 g, 0.95 mmol) in thf (10 cm^3) was added anhydrous HCl (5 molar equivalents, generated from $SiMe_3Cl$ and MeOH). The solvent was removed in vacuo at room temperature and the residue extracted into hexane (30 cm^3). After filtration to remove most of the $[V(\eta^5\text{-}C_5H_5)_2Cl_2]$ the hexane was removed in vacuo. The residue was dissolved in CD_2Cl_2 and the solution filtered through Celite into a 5 mm NMR tube.
Studies on mixtures of *cis*- and *trans*-PhCHCHPh showed that both isomers are readily soluble in hexane or CD_2Cl_2 under the conditions used in the extraction procedure.

[9] The first order dependence on the concentration of complex for both stages was confirmed by studies with [HCl] = 20 mmol dm^{-3} and $[V(\eta^5\text{-}C_5H_5)_2(\eta^2\text{-}PhCCPh)]$ = 1.0–0.1 mmol dm^{-3}. Over this range of complex concentration the values of k_{obs} for both phases does not vary; $k_{obs}(\text{fast}) = 26.2 \pm 1.0\ s^{-1}$, $k_{obs}(\text{slow}) = 1.1 \pm 0.2\ s^{-1}$.

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