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Preliminary communication

MECHANISTIC ASPECTS OF (C=C) ISOMERIZATION IN VINYLIC RHODIUM(III) COMPLEXES

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Summary

Observations concerning the (C=C) isomerization of several vinylic Rh^{III} complexes suggest an intramolecular pathway; isomerization occurs at a rate which is affected by the backbonding ability of the metal and the π-acidity of the vinylic ligand in the complex.

Transition metal hydrides in general react with non-terminal acetylenes to give (C=C) *cis* vinylic metal complexes; however, the reaction of certain hydrides with some acetylenes has been noted to produce only (C=C) *trans* products [1-4]. A reasonable suggestion to account for the (C=C) *trans* products observed involves (C=C) *cis*-M—H β-addition to coordinated acetylene followed by (C=C) isomerization. Accordingly, we prepared a series of (C=C) *cis*-vinylic rhodium(III) complexes and found that several of them do isomerize to their (C=C) *trans* counterparts. These compounds represent the first examples wherein isolable (C=C) *cis*-vinylic complexes have been shown to be the precursors of (C=C) *trans* products.

We noted [5] that rapid pyrolysis of crystalline Ia-*cis* at 110° gave 98% *cis* organic product II. We now find that if Ia-*cis* is stirred in benzene at room temperature for several (up to 24) hours and the Rh^{III} material is isolated, dried and rapidly pyrolyzed, substantial amounts of *trans* compound III are also formed. The ratio of II to III depends on the length of time that Ia was stirred in solution. Since Ia-*cis* gives *cis* organic product only, this result implies that Ia-*cis* must isomerize slowly, in solution, to a (C=C) *trans* vinylic species. The rate of this (C=C) isomerization is independent of the concentration of Rh^{III} species and is also unaffected by added acid (dil. HCl), base (pyridine) or a free radical inhibitor (hydroquinone). These observations suggest that (C=C) isomerization is an intramolecular process.

(C=C) isomerization apparently occurs via five coordinate intermediate IV

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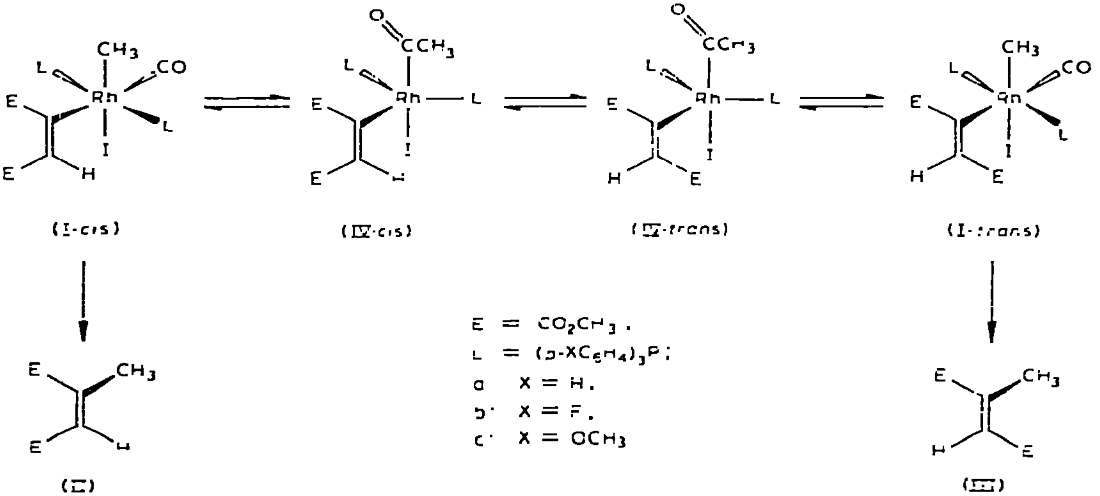
(reaction 1). Infrared analysis* shows that Ia is almost entirely converted to IVa on a time scale much shorter than that required for observation of (C=C) *trans* products from reductive elimination. Pyrolysis of freshly prepared isolable IVa-*cis* yields only the alkyl substituted olefin II**; that of IVa which has been stirred in solution for several hours gives a mixture of II and III. That the gross composition of IVa does not change during this time is evidenced by the superimposition of the IR spectra of aliquots of Rh^{III} materials obtained during the isomerization process. Similar observations were made in studies involving Ib and Ic.


(I-*cis*) (IV-*cis*) (IV-*trans*) (I-*trans*)

(II) (III)

E = CO_2CH_3,
L = $(p\text{-}XC_6H_4)_3P$;
a X = H,
b X = F,
c X = OCH_3

(1)

The formation of (C=C) *trans* product from various types of metal hydrides and electron-deficient acetylenes [e.g., $HIr(CO)L_3$ and NCC≡CCN (L = PPh_3) [2]; $(\eta^5\text{-}C_5H_5)_2MoH_2$ and $CF_3C{\equiv}CCF_3$] [3] indicates that the basic isomerization pathway does not depend uniquely on a certain metal or vinylic substituent. We suggest that the Rh^{III} complexes discussed herein undergo (C=C) isomerization by a dipolar mechanism, via V*** (reaction 2), similar to the one proposed [1] with regard to a Ru^{II} complex. The ease of (C=C) isomerization by this route would be a function of both the π-donor ability of the metal atom (in turn related to the nature of the other ligands in the complex) and the π-acidity of the vinylic ligand; indeed, we find that, for the series of complexes IVa-IVc, the rate of (C=C) isomerization (at room temperature) increases with increasing donor

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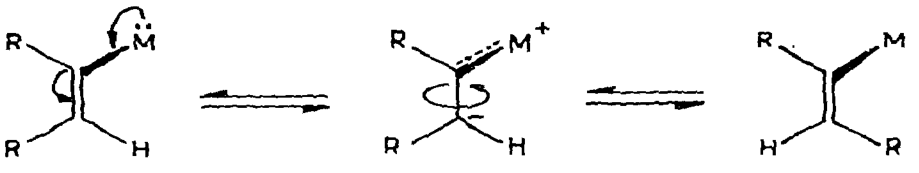
*Because of the very low solubility of I and IV, it was impossible to obtain meaningful NMR data for them. For Ia-*cis*, ν(CO) 2023 cm^{-1}, IVa-*cis*, ν(CO) 1680 cm^{-1}. No ν(C=C) was discernible due to interference from PPh_3 bands. An analogous isomerization to a five-coordinate acyl complex has been observed [6].

**Reductive elimination must occur, therefore, from the six-coordinate Rh^{III} species I. Indeed, carbonylation of a solution of Ia yields the acetyl-substituted olefin only.

***This dipolar species is just the extreme representation for weakening of the C—C π bond order in the vinylic substituent by metal to organic ligand backbonding. This weakening should also be paralleled in lowered ν(CO) of carbonyl ligands in these complexes.

It has not been possible to determine the rate of (C=C) isomerization meaningfully as a function of solvent polarity. Complexes IVa-IVd are insoluble in aliphatic hydrocarbons and undergo rapid reductive elimination when dissolved in coordinating solvents.



(2)

(IV-*cis*) (V) (IV-*trans*)

a–c: M = $L_2Rh(COCH_3)I$; R = CO_2CH_3 ;
a: L = $(p\text{-}XC_6H_4)_3P$, X = H ;
b: L = $(p\text{-}XC_6H_4)_3P$, X = F ;
c: L = $(p\text{-}XC_6H_4)_3P$, X = OCH_3 ;
d: M = $L_2Rh(COCH_3)I$, R = CF_3 , L = PPh_3 ;
e: M = Cp_2MoH , R = CF_3

ability of the $(p\text{-}XC_6H_4)_3P$ ligands (in reactions 1 and 2, $X = F < H < OCH_3$)* Delocalization of electron density to the oxygen atom of the β-ester group in Va-Vc would enhance the π-acidity of this ligand relative to the non-conjugated vinylic ligands (Vd or Ve)**. The greater π-donor ability of Mo^{IV} in IVe compared with Rh^{III} in IVa-IVd can be inferred by comparison of ν(CO) in analogous carbonyl complexes***. Thus, reaction of $(\eta^5\text{-}C_5H_5)_2MoH_2$ with $CF_3C{\equiv}CCF_3$ ultimately yields (C=C) *trans* material below room temperature [3], but IVd undergoes no detectable (C=C) isomerization☆ below the temperature (120°) at which it reductively eliminates *cis*-1,1,1,4,4,4-hexafluoro-2-methyl-2-butene [8]. Consideration of these trends should prove to be of use in predicting the occurrence of (C=C) *trans* vinylic complexes as products in new reactions involving π-acidic acetylenes and transition metal hydrides with strong backbonding ability.

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*This was determined by measuring initial rates of appearance for III produced by pyrolysis of Rh^{III} containing materials. Relative rates for (C=C) isomerization, where, for I, X = F, H, OCH_3 are 0.51/1.00/1.30 and parallel ν(CO) for Ib, Ia and Ic (2050, 2023 and 2020 cm^{-1}, respectively). These relative rates are comparable to those observed for oxidative addition to Rh^{I} complexes containing these ligands [6].

**Enhancement of π-acidity by conjugation can also be envisioned where R = CN, a substituent which leads to (C=C) *trans* product [2].

***One such comparison involves $[(\eta^5\text{-}C_5H_5)_2MoH(CO)]^+PF_6^-$ (ν(CO) 2030 cm^{-1}) [7] and $[L_2Rh(CO)(CH_3)Cl]^+SbCl_6^-$ (ν(CO) 2125 cm^{-1}).

☆It is interesting to note that insertion of $RC{\equiv}CR$ into a $Pt^{II}{-}CH_3$ bond produces *trans*-vinylic product when R = CO_2CH_3 but *cis* product when R = CF_3 [9]. Mechanistic considerations in this work may indeed parallel those described herein.

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