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The Reaction Mechanism of Ruthenium-catalyzed Dimerization of t-Butylacetylene to *cis*-1,4-Di-t-butylbutatriene. Involvement of a Ruthenium-diacetylide Intermediate

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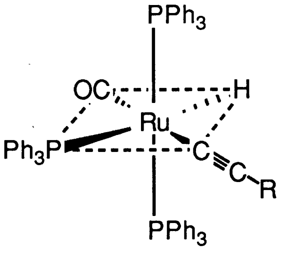
The acetylide complex $[RuH(C{\equiv}C\text{-}Bu^t)(CO)(PPh_3)_3]$ (**1**) prepared from $[Ru(H)Cl(CO)(PPh_3)_3)]$ (**2**) and $Li\text{-}C{\equiv}C\text{-}Bu^t$ has been found to be a good precursor for the catalytic dimerization of t-butylacetylene to *cis*-1,4-di-t-butyl-1,2,3-butatriene. Room temperature reaction of **1** with $HC{\equiv}CBu^t$ has afforded a new complex $[Ru(C{\equiv}CBu)_2(CO)(PPh_3)_3]$ which has been structurally characterized as possessing *cis*-diacetylide ligands. Reaction of **2** with 1,4-di-t-butylbutadiyne gave a complex with 1,4-di-t-butylbut-1-en-3-yn-2-yl ligand, $[Ru\{C(=CHBu^t)\text{-}C{\equiv}CBu^t\}Cl(CO)(PPh_3)_2]$, which decomposed at 60 °C to liberate *cis*-1,4-di-t-butylbutatriene. The reaction mechanism is discussed based on these findings.

A number of transition metal complexes have been known to catalyze dimerization of 1-alkynes to give 1-butene-3-yne skeleton,1) the formation of which can be easily explained by a conventional reaction pathway, i.e. oxidative addition of $\equiv C\text{-}H$ at metal center, insertion of further molecule of alkyne into the M-acetylide linkage, and reductive elimination of the C_4-unit with the hydride ligand. Previously one of us communicated ruthenium catalyzed dimerization of t-butylacetylene which gave unexpected product, 1,4-di-t-butylbutatriene.2) In order to understand the mechanism of this at first sight puzzling reaction, we have studied reactions of relevant ruthenium complexes. An important clue to the nature of the reaction is the *cis* stereochemistry of the 1,4-di-t-butylbutatriene formed, in spite of the fact that the thermodynamic stability of *cis*- and *trans*-1,4-disubstituted butatrienes is quite similar.3)

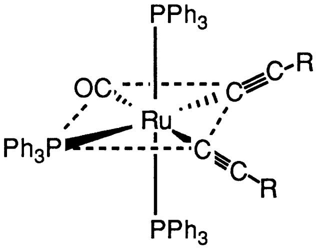
One of the precursors we have used is $[RuH_2(CO)(PPh_3)_3]$ which can form the Ru(0) species on losing the two hydride ligands. The acetylenic C-H bond is expected to add oxidatively to the Ru(0) center and indeed $[Ru(H)(C{\equiv}CBu^t)(CO)(PPh_3)_3]$ (**1**) has been isolated from the reaction of the dihydride complex with t-butylacetylene.4) Since the hydride-acetylide complex is expected to function as a good precursor for the catalytic dimerization of 1-alkyne, we prepared the hydride-acetylide complex **1** conveniently by the room temperature reaction of $[Ru(H)Cl(CO)(PPh_3)_3]$ (**2**) with $Li\text{-}C{\equiv}CBu^t$.5) Since complex **1** shows its hydride resonance in ^1H NMR as two triplets due to its coupling by *trans* phosphine and subsequently by two equivalent *cis* phosphines

(δ -8.23 in $CDCl_3$ J=87 and 26Hz), the structure illustrated below is assigned to this complex.

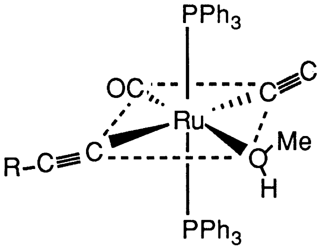


1 (R = ${}^tBu$)

Complex **1** is superior to the dihydride complex in that it can catalyze the dimerization at room temperature although the rate is slow (15 turn-over after 70 h). Concentration of this reaction mixture and addition of hexane containing excess triphenylphosphine afforded a new complex of the formula $[Ru(C{\equiv}CBu^t)_2(CO)(PPh_3)_3]$ (**3**) in 53% yield as pale yellow and moderately air-stable crystals. ${}^1H$ NMR spectrum of this complex (C_6D_6) showed ${}^tBu$ resonances at δ 0.96 and 1.28 while ${}^{31}P$ NMR ($CDCl_3$) exhibited a triplet and a doublet (J= 21.5Hz) at δ 19.34 and 29.64 in 1:2 ratio. A single-crystal X-ray analysis on **3** confirmed its solid state structure which was concomitant with the NMR spectra in solution.[6] Complex **3** showed catalytic activity almost similar to that of **1**.



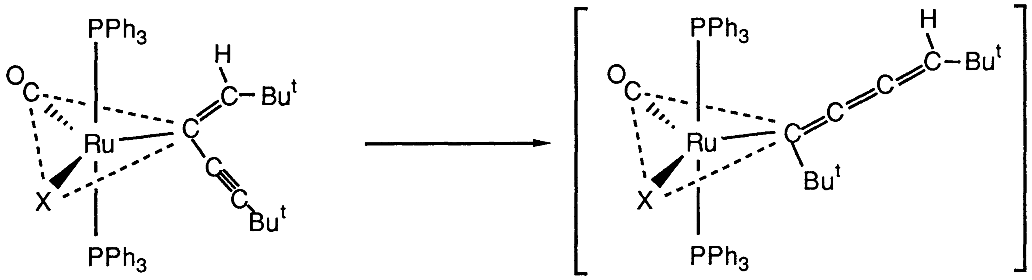
3



3'

When **3** was recrystallized from benzene/methanol solution, a complex of the composition $[Ru(C_2Bu^t)_2(CO)(PPh_3)_2(MeOH)]$ (**3'**) was isolated. ${}^1H$ NMR spectra (C_6D_6) indicated that the two acetylide ligands were magnetically equivalent exhibiting a single resonance of ${}^tBu$ at δ 1.103. The X-ray crystallographic analysis of **3'** confirmed the *trans* orientation of the two acetylide ligands as shown above.[7] The Ru--O(H)Me bond is long (2.218(7) Å) suggesting that MeOH molecule is weakly bound. Easy dissociation of methanol in solution was evidenced by ${}^1H$ NMR spectra measured with a small amount of added free methanol. Only one CH_3O peak appeared but at varying chemical shifts of δ 2.64 to 3.12 depending upon the amount of free MeOH added, indicating rapid exchange between free and coordinated MeOH molecules. Addition of triphenylphosphine to a solution of **3'** instantaneously reproduced the parent complex **3**. Seemingly, bulkiness of the entering ligand is the controlling factor if the two acetylide ligands take *cis* or *trans* arrangement. These observations imply that **3** in solution dissociates PPh_3 *trans* to the acetylide ligand forming a trigonal bipyramidal intermediate. Formation of related diacetylide complex of 5-coordinated ruthenium, $[Ru(C{\equiv}CPh)_2(CO)(PPr^i_3)_2]$, from the reaction of $[RuH(\eta^2\text{-}H_2BH_2)(CO)(PPr^i_3)_2]$ with $PhC{\equiv}CH$ has been reported recently where *trans* orientation of the two $-C{\equiv}CPh$ ligands in square pyramid arrangement of the complex has been suggest ed.[8)] Since isolated **3** and **3'** are stable and do not show any tendency to release butatriene unit, attack of the third alkyne molecule on the 5-coordinated intermediate appears to be necessary. As a model complex for a product of such reactions, complex **4a** was prepared by treating **2** with 1,4-di-t-butylbutadiyne.

Complex **4a** is a trigonal bipyramidal complex with but-1-en-3-yn-2-yl ligand which was formed by *cis* addition of the Ru-H to one of the C≡C triple bonds, as confirmed by an X-ray diffraction study.[9)] A C_6D_6 solution of **4a** was heated to 60°C and monitored by ^1H NMR spectroscopy.

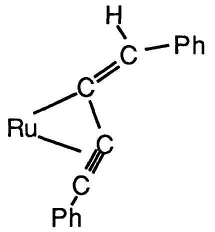


(1)

4a (X = Cl)
4b (X = C_2Bu^t)

Interestingly, peaks due to *cis*-1,4-di-t-butyl-buta-triene, δ 1.086 (C_4H_9) and 5.534 (H), emerged and increased as slow decomposition proceeded. The liberation of free butatriene was also checked by GLC analysis. We propose the isomerization of the organic moiety as shown in equation *(1)*, where the butatrienyl ligand would further abstract hydrogen, probably from triphenylphosphine, to liberate the butatriene. However, in the actual catalytic cycle where the probable intermediate is **4b**, hydrogen should be supplied by attacking 1-alkyne reproducing the 5-coordinated complex with diacetylide ligands after liberation of the butatriene.

Very recently, it was shown that [RuH_4(triphos)] reacted with phenylacetylene to give a complex with η^3-PhC_3CHPh ligand, which was formed probably by end-to-end coupling of two phenylacetylene fragments.[10)] The coordination mode of the η^3-PhC_3CHPh moiety has been structurally analyzed and may be regarded as a transient form of the isomerization *(1)*.



It is not clear how the attack of 1-alkyne on the diacetylide intermediate **3** can produce a complex **4b**. The most probable route at first seems to be reductive coupling of the two acetylide ligands and insertion of the resulting diyne into Ru-H bond, which in turn will be formed by oxidative addition of the attacking 1-alkyne. However, this "diyne route" appears to be unlikely since (1) no 1,4-di-t-butylbutadiyne was detected in the catalytic reaction; (2) when the catalytic dimerization reaction was carried out in the presence of free 1,4-di-t-butylbutadiyne, the diyne was not consumed at all; (3) the hydride-acetylide complex **1** did not react with 1,4-

di-t-butylbutadiyne at 50 °C; (4) thermal decomposition of **3** did not yield the diyne but merely liberated ^{t}BuC≡CH; (5) formation of the diyne from **3** was also not observed by addition of 1,2-disubstituted alkynes such as diphenylacetylene. Although we have no direct evidence, a probable alternative could be replacement of a phosphine in **3** by another molecule of 1-alkyne, which undergoes η^2-alkyne → η^1-vinylidene rearrangement to give $[Ru(C{=}CHBu^t)(C{\equiv}CBu^t)_2(CO)(PPh_3)_2]$, followed by migration of the neighbouring acetylide group onto the vinylidene carbon. Steric repulsion between bulky ^{t}Bu group and other ligands should favour *cis* arrangement of the 1,4-di-t-butylbut-1-en-3-yn-2-yl moiety as in **4a**.

References

1) M. Akita, H. Yasuda, and A. Nakamura, Bull. Chem Soc. Jpn., 57, 480 (1984) and references therein.
2) H. Yamazaki, J. Chem. Soc., Chem. Commun., 1976, 841. The 1,4-di-t-butylbutatiene obtained in this reaction was originally assigned to *trans* isomer but recent detailed analysis on IR [3] and NMR (M. Tigchelaar, H. Kleijn, C.J. Elsevier, J. Meijer, and P. Vermeer, Tetrahedron Lett., 22, 2237 (1981)) proved this to be the *cis* isomer.
3) W.R. Roth and H-D. Exner, Chem. Ber., 109, 1158 (1976).
4) H. Yamazaki and K. Aoki, J. Organomet. Chem., 122, C54 (1976).
5) The complex gave satisfactory elemental analysis. Other acetylide complexes can be prepared similarly by using Li-C≡CR (R= ^{n}Bu, Me, CO_2Me, Ph, $SiMe_3$).
6) The unit cell of **3** contained 3 molecules of benzene. Formula $C_{85}H_{81}OP_3Ru$; space group $P\bar{1}$, a=13.430(4), b=23.327(4), c=13.188(6) Å, α=104.33(3), β=119.29(3), γ=74.58(2)°, V=3439(2) Å^3, Z=2, $D_{calcd}=1.266 g\cdot cm^{-1}$, R=0.059 for 7723 independent reflections.
7) The unit cell of **3'** contained one molecule of methanol and 0.5 molecule of benzene. Formula $C_{54}H_{59}O_3P_2Ru$; space group $P2_1/c$, a=20.744(4), b=13.230(5), c=19.003(3) Å, β=103.55(2)°, V=5070(2) Å^3, Z=4, $D_{calcd}=1.203 g\cdot cm^{-1}$, R=0.068 for 5002 independent reflections.
8) H. Werner, U. Meyer, M.A. Esteruelas, E. Sola, and L.A. Oro, J. Organomet. Chem., 366, 187 (1989).
9) Formula $C_{49}H_{49}ClOPRu$; space group $P\bar{1}$, a=12.326(5), b=16.120(5), c=11.774(3) Å, α=95.66(3), β=101.64(3), γ=73.41(3)°, V=2194(3) Å^3, Z=2, $D_{calcd}=1.289 g\cdot cm^{-1}$, R=0.086 for 5296 independent reflections.
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