Regio- and Stereocontrolled Dimerization of *tert*-Butylacetylene to (*Z*)-1,4-Di-*tert*-butylbutatriene by Ruthenium Catalysis. Reaction Mechanism Involving Alkynyl–Vinylidene Coupling and Rearrangement of the Metal-Bound C4 Unit

Yasuo Wakatsuki,*,† Hiroshi Yamazaki,† Nami Kumegawa,‡ Toshiaki Satoh,‡ and James Y. Satoh‡

Contribution from the Institute of Physical and Chemical Research, Wako-shi, Saitama 351-01, Japan, and Department of Chemistry, College of Science, Rikkyo University, Nishi-Ikebukuro, Toshima-ku, Tokyo 171, Japan. *Received June 17, 1991*

Abstract: Ruthenium complexes, Ru(cod)(cot) (cod = 1,5-cyclooctadiene, cot = cyclooctatriene) and $Ru(CO)(PPh_3)_3(H)_2$ (**1**), catalyze the dimerization of *tert*-butylacetylene to (*Z*)-1,4-di-*tert*-butylbutatriene ((*Z*)-dbb). In the case of the Ru(cod)(cot) catalyst, the addition of bulky tertiary phosphines is an essential factor to effect good selectivity to dbb, the byproducts being isomers of 1,3-enynes. From the reaction of **1** with *tert*-butylacetylene, $Ru(CO)(PPh_3)_3(H)(C{\equiv}C^tBu)$ was isolated, which reacted further with $HC{\equiv}C^tBu$ to give $Ru(CO)(PPh_3)_3(C{\equiv}C^tBu)_2$ (**3**). The halogen analogue of this complex, $RuX_2(PPh_3)_3$, reacted with $HC{\equiv}C^tBu$ to give vinylidene complexes $RuX_2(PPh_3)_2(C{=}CH^tBu)$ (**11a**, X = Cl; **11b**, X = Br). Reaction of **11a** with a calculated amount of $LiC{\equiv}C^tBu$ followed by bubbling of CO yielded $RuCl(CO)(PPh_3)_2\{C(C{\equiv}C^tBu){=}CH^tBu\}$ (**12**), where the $C{\equiv}C^tBu$ group and ^tBu are mutually cis to each other with respect to the double bond of the C4 unit. Complex **12** in benzene decomposed at 50 °C releasing the C4 chain as (*Z*)-dbb. From these reactions, the mechanism for the catalytic production of (*Z*)-dbb has been derived. The X-ray structure of **12** is reported.

The regio- and stereoselective dimerization of terminal acetylenes by transition metal catalysts provides a highly attractive route to C4 units with unsaturation, which are useful for further structural elaboration. Recent developments in this field include regioselective head-to-tail coupling by Ti or Pd catalysts giving 2,4-disubstituted (branched) enynes,[1] and head-to-head dimerization of ethynylsilanes by Pd or Rh complexes to produce exclusively (*E*)-1,4-disubstituted enynes.[2] We have found a completely different type of dimerization of *tert*-butylacetylene, which is catalyzed by ruthenium complexes to give (*Z*)-1,4-di-*tert*-butylbutatriene (abbreviated (*Z*)-dbb) in good yield and excellent stereoselectivity. Though a similar reaction takes place with (trimethylsilyl)acetylene,[3] in this paper we focus on the dimerization of *tert*-butylacetylene since the mechanism of this remarkable reaction can be best investigated by the reaction of $HC{\equiv}C^tBu$ with $Ru(CO)(PPh_3)_3(H)_2$, one of the catalysts employed, or complexes derived from it.

The dimerization leading to 2,4- and (*E*)-1,4-disubstituted enynes can easily be explained by a series of conventional reaction steps: oxidative addition of ≡CH, insertion of C≡C of the second alkyne molecule, and then reductive elimination.[4] On the other hand, besides the strict cis stereoselectivity of the two substituents, the formation of the butatriene backbone in our dimerization appeared puzzling at first since the butatriene skeleton is thermodynamically much less stable than the enyne form according to ab initio MO calculations (Figure 1). In this paper we report the full details of our study on the catalytic dimerization of *tert*-butylacetylene to (*Z*)-dbb. On the basis of model reactions a catalytic cycle is proposed, which includes several important key steps, i.e. ruthenium η^2-alkyne to ruthenium vinylidene rearrangement, alkynyl–vinylidene coupling, and isomerization of the resulting butenynyl moiety to the butatrienyl form. Part of this work has already been reported.[5]

Results and Discussion

Ruthenium complexes capable of generating zero-valent ruthenium species catalyze the dimerization of *tert*-butylacetylene to butatriene under appropriate conditions. Some Ru(II) species which are related to intermediates present in the catalytic cycle also have catalytic ability. We have studied the $Ru(cod)(cot)/PR_3$ (cod = 1,5-cyclooctadiene, cot = cyclooctatriene) system in order to examine the effect of tertiary phosphines. The other class of ruthenium complexes examined was $Ru(CO)(PPh_3)_3(H)_2$ (**1**) and its derivatives, which have been found to be useful both for synthesis of the butatriene and for mechanistic studies.

(1) Dimerization of $HC{\equiv}C^tBu$ by Ru(cod)(cot)/PR_3. The complex Ru(cod)(cot) alone has little ability to effect dimerization, but the addition of phosphines markedly increases its catalytic activity. A mixture of resulting dimers consists mainly of (*Z*)-dbb, but enynes are also present. Figure 2 shows the yield of the dimers vs the amount of phosphines added when the reaction is carried out at 100 °C in benzene. At least 3 mol of phosphine is required per mole of Ru. Of the tertiary phosphines examined, the catalytic activity increases in the order: $P(OPh)_3 < PPh_3 < P^iPr_3 < P^nBu_3$. It appears that basic phosphines are preferred in view of the catalytic activity. As for the selectivity to the butatriene, which is plotted in Figure 3, the efficiency increases in the order: $P(OPh)_3 < P^nBu_3 < PPh_3 < P^iPr_3$. Under the conditions described in Figure 3 with the addition of 3 mol of P^iPr_3, the distribution of dimers was as follows: branched enyne 15%, (*E*)-enyne 3%, (*Z*)-enyne 6%, (*E*)-dbb 3%, and (*Z*)-dbb 73%. Addition of 3 mol of $P(OPh)_3$ resulted in the following distribution: branched enyne 49%, (*E*)-enyne 0.5%, (*Z*)-enyne 6.5%, (*E*)-dbb 13%, and (*Z*)-dbb 31%. The above order of phosphines coincides with that of their cone angle values, suggesting that a crowded environment around the metal center is favored for the selective formation of (*Z*)-dbb.

(2) Dimerization of $HC{\equiv}C^tBu$ by $Ru(CO)(PPh_3)_3(H)_2$ (1) and Its Derivatives. In the presence of a catalytic amount of the dihydride complex **1**, *tert*-butylacetylene dimerizes at 50–100 °C in benzene to give (*Z*)-dbb in 85–90% selectivity, with 25–50 catalytic turnovers per Ru atom. An alkynyl complex Ru-

† The Institute of Physical and Chemical Research.
‡ Rikkyo University.

(1) (a) Akita, M.; Yasuda, H.; Nakamura, A. *Bull. Chem. Jpn.* **1984**, *57*, 480. (b) Trost, B. M.; Chan, C.; Ruhter, G. *J. Am. Chem. Soc.* **1987**, *109*, 3486.

(2) (a) Ishikawa, M.; Ohshita, J.; Minato, A. *J. Organomet. Chem.* **1988**, *346*, C58. (b) Ohshita, J.; Furumori, K.; Matsuguchi, A.; Ishikawa, M. *J. Org. Chem.* **1990**, *55*, 3277.

(3) Under similar reaction conditions, other alkyl- and aryl-substituted 1-alkynes generally gave a mixture of isomeric enynes.

(4) Kovalev, I. P.; Yevdakov, K. V.; Strelenko, Yu. A.; Vinogradov, M. G.; Nikishin, G. I. *J. Organomet. Chem.* **1990**, *386*, 139.

(5) (a) Yamazaki, H. *J. Chem. Soc., Chem. Commun.* **1976**, 841. (b) Wakatsuki, Y.; Satoh, T.; Yamazaki, H. *Chem. Lett.* **1989**, 1585.

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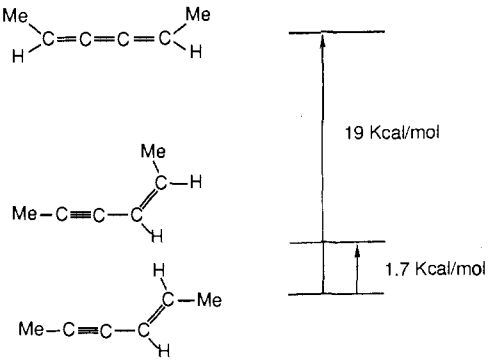


Figure 1. Relative energies of the three isomers. Geometries and energies were calculated by the ab initio LCAO-MO-SCF method with a DZV basis set.[23]

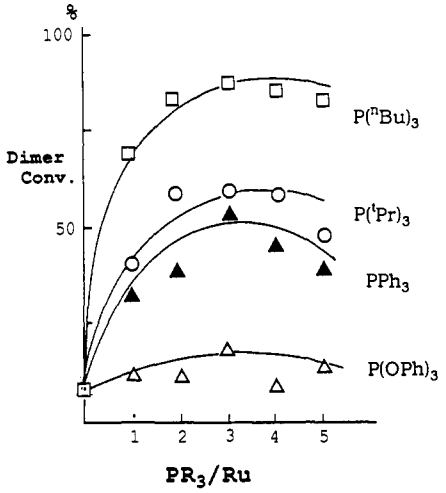


Figure 2. Effect of added tertiary phosphines on the dimer yield: Ru(cod)(cot) catalyst in benzene, 100 °C, 18 h.

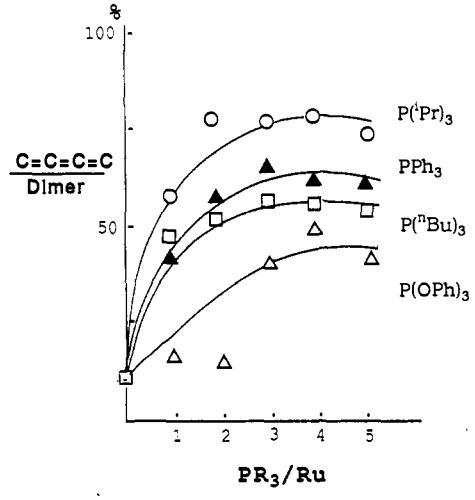
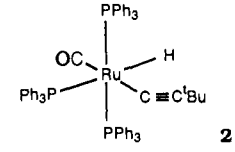


Figure 3. Effect of added tertiary phosphines on the butatriene/total dimer ratio: Ru(cod)(cot) catalyst in benzene, 100 °C, 18 h.

$(CO)(PPh_3)_3(H)(C{\equiv}C^tBu)$ (**2**), which can easily be prepared by the reaction of $Ru(CO)(PPh_3)_3(H)Cl$ with $LiC{\equiv}C^tBu$, also works as a precursor of the active species for the same dimerization. As in the case of the Ru(cod)(cot) system, the effect of added tertiary phosphines was examined with this catalyst system. The best result was obtained when a 3 molar excess of P^iPr_3 was added, similar to the results observed for the Ru(cod)(cot)/PR_3 system. Addition of a 6 molar excess of P^iPr_3 gave essentially the same result as the case of the 3 molar excess. The reaction stops after 48 h at 50 °C to give (*Z*)-dbb in 96% selectivity with ca. 90 catalytic turnovers per Ru. The catalytic turnover increases at higher reaction temperatures, but selectivity to the butatriene decreases.

(3) Reaction Mechanism. The reaction mechanism was studied using the precursor **1** and related model complexes.

(3-1) Generation of Active Species. The first clue to the mechanism was isolation of a hydride alkynyl complex (**2**) from the catalytic reaction mixture. Thus when the catalytic reaction using **1** was stopped at an early stage and the reaction mixture was worked up using column chromatography, complex **2** was isolated in ca. 20% yield. The two hydride ligands of **1** presumably were consumed to hydrogenate 1 molecule of $HC{\equiv}C^tBu$ to $H_2C{=}CH^tBu$, and then the oxidative addition of the $\equiv$CH bond of a second alkyne molecule to the Ru(0) center took place.[6] The ^1H NMR spectrum shows the hydride resonance at δ −8.23 as two triplets (J = 87 and 26 Hz) due to its coupling by trans phosphine and subsequently by two equivalent cis phosphines. The ^{31}P NMR spectrum is also consistent with the structure illustrated below since the two equivalent phosphine ligands have a doublet peak, J = 17.1 Hz (44.6 ppm), while the other phosphine (20.8 ppm) shows a triplet resonance of the same coupling constant.



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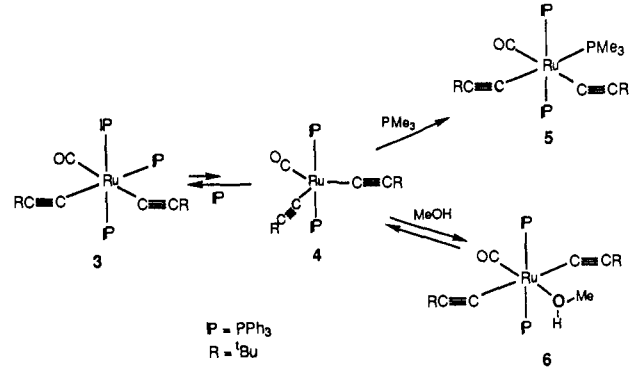
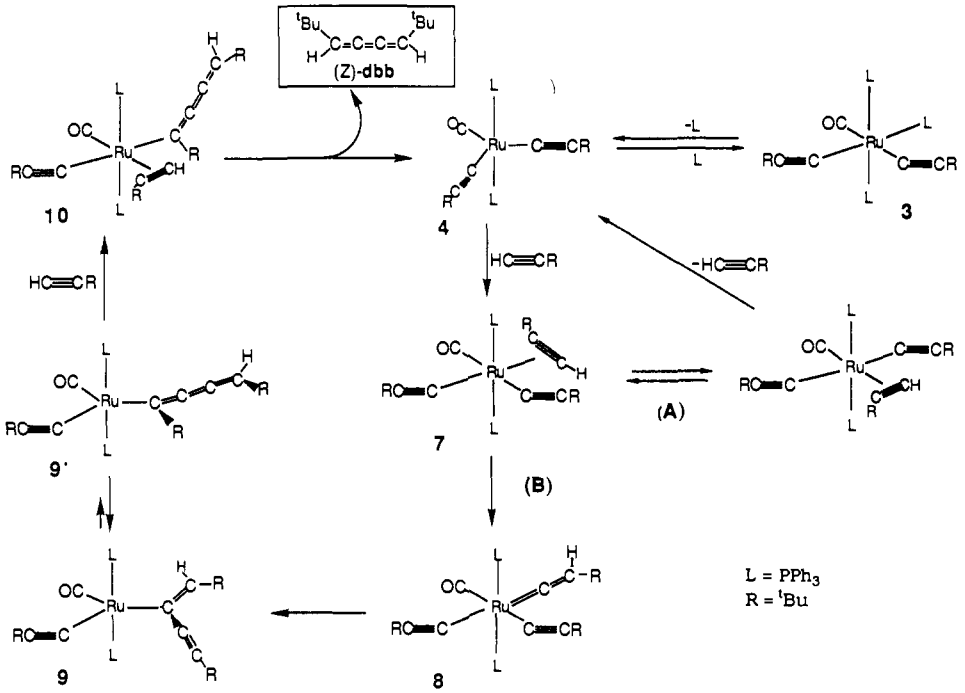
Hydride alkynyl complexes like **2** are active species often proposed in the dimerization of terminal alkynes to give head-to-tail or (*E*)-enyne type dimers. However, when an excess of $HC{\equiv}C^tBu$ is added to a benzene solution of **2** at room temperature, a slow dimerization of (*Z*)-dbb (15 turnovers in 70 h) begins after a few hours of induction. Concentration of this reaction mixture after 24 h and addition of hexane afforded a colorless crystalline complex of the formula $Ru(CO)(PPh_3)_3(C_2{}^tBu)_2$ (**3**) in 60–70% yield. A single-crystal X-ray analysis on **3** confirmed its solid-state structure,[5b] which is consistent with the NMR spectra in solution: the ^1H NMR spectrum (C_6D_6) showed ^tBu resonances at δ 0.96 and 1.28, and the ^{31}P NMR spectrum ($CDCl_3$) showed a triplet peak and a doublet peak at δ 19.34 and 29.64 (J = 21.5 Hz) in a 1:2 ratio. Complex **3** catalyzes the dimerization of $^tBuC{\equiv}CH$ to (*Z*)-dbb at room temperature. Since the equatorial triphenylphosphine ligand is found to be easily replaced by trimethylphosphine at room temperature to give complex **5**, it is likely that the equatorial triphenylphosphine in complex **3** dissociates in solution to give a five-coordinate species (**4**).



The concentration of **4** must be very low since its presence was not detected by ^1H or ^{31}P NMR spectroscopy. When **3** was recrystallized from benzene/methanol solution, a new colorless complex (**6**) was isolated in 52% yield. An X-ray structure analysis revealed this to be a methanol complex with two trans $C{\equiv}C^tBu$ units.[4b] Addition of triphenylphosphine to this complex in benzene instantaneously regenerated the original **3** with two cis $C{\equiv}C^tBu$ ligands. The interchange between complexes with cis and trans $C{\equiv}C^tBu$ ligands must proceed via **4**. We assume intermediate **4** is the active species involved in the catalytic cycle for the production of (*Z*)-dbb.

(6) The presence of $H_2C{=}CH^tBu$ in the reaction mixture was confirmed by GC/MS spectroscopy.

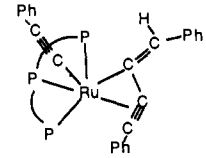
Scheme I



(3-2) Alkynyl Exchange Reaction of 3. On reacting complex **3** with $HC{\equiv}CSiMe_3$ or $HC{\equiv}CPh$ at room temperature, facile alkynyl exchange was observed to give $Ru(CO)(PPh_3)_3(C{\equiv}CR)_2$ (R = $SiMe_3$, Ph). The reaction is instantaneous when a several molar excess of $HC{\equiv}CR$ is added to a C_6D_6 solution of **3** as monitored by ^1H NMR spectroscopy, but the same reaction takes about 1 day in the presence of 10 molar excess PPh_3. Even under these conditions, the mixed dialkynyl complex, $Ru(CO)(PPh_3)_3(C{\equiv}C^tBu)(C{\equiv}CR)$, could not be detected. The first step of the reaction must be the displacement of triphenylphosphine by alkyne at the coordination site trans to one of the alkynyl ligands, which is followed by a hydrogen transfer of the coordinated alkyne to the neighboring alkynyl carbon. Whether this transfer proceeds via a discrete hydride trialkynyl Ru(IV) species or via a metal-assisted hydrogen shift between η^2-alkyne and alkynyl ligands is not clear yet.[7] The important point to note here is that the hydrogen transfer from a (coordinated) terminal alkyne is very easy in this intermediate complex.

(3-3) Proposed Reaction Mechanism. Starting from intermediate **4**, the reaction sequence illustrated in Scheme I may be proposed for the catalytic and stereoselective (*Z*)-dbb formation. Coordination of an alkyne molecule to **4** will give **7**, which is the common intermediate for both the alkynyl exchange (route A) by interligand hydrogen-transfer and the isomerization to a vinylidene complex (route B) by an intraligand hydrogen transfer. The rearrangement of a η^2-coordinated alkyne to a vinylidene is a well-documented process.[8] One of the alkynyl ligands in this vinylidene intermediate (**8**) will first migrate to the vinylidene α-carbon to give a complex (**9**) with a but-1-en-3-yn-2-yl ligand. Our molecular model study has indicated that the cis form of the butenynyl moiety is sterically much more favored than the trans form because repulsive interaction between the bulky ^{t}Bu group and other ligands is severe in the trans form. Therefore, the observed *Z*-stereoselectivity in the final product, (*Z*)-dbb, can be traced back to this transformation step.

Our next assumption is a rearrangement of the but-1-en-3-yn-2-yl ligand into the buta-1,2,3-trien-4-yl from (**9'**) by a 1,3-shift of the metal. It has been shown recently that RuH_4(triphos) reacts with phenylacetylene to give a complex with an η^3-PhC_3CHPh ligand.[9] A similar complex has been isolated in the reaction of phenylacetylene with $FeCl_2(DMPE)_2$.[10] In both cases migration of the alkynyl ligand to vinylidene has been considered for the C–C bond-formation step. However, an osmium analogue, $[Os(\eta^3\text{-}PhC_3CHPh)(PMe_3)_4]PF_6$, has been obtained by oxidative coupling of two alkynyl ligands.[11] The reported structure of these complexes may be regarded as a transient form of the isomerization from **9** to **9'**.



The equilibrium between **9** and **9'** is expected to lie far to the **9** side, the enyne skeleton being thermodynamically much more stable than the butatriene form (Figure 1). If the C4 chain lies in the basal plane as in the model complex (**12**) described later, there will be few steric problems in **9**. However, in order for another alkyne molecule to coordinate, the Ru–C bond has to rotate to open the coordination site in the equatorial position so that the butenynyl plane is almost perpendicular to the basal plane of the complex. Our molecular model study indicates that this "upright form" of the butenynyl ligand causes severe steric repulsion between the bulky tertiary phosphines of the axial positions and the $C{\equiv}C^tBu$ moiety of the butenynyl group. As shown in Figure 4a, such a conformation forces the butenynyl ligand to move the ^{t}Bu group into the cone space occupied by PPh_3. Thus coordination of an alkyne molecule to **9** appears to be sterically prohibited. In contrast, the "upright form" of the butatrienyl ligand suffers from significantly fewer steric problems, as shown in Figure 4b, since the ^{t}Bu group is bent away from the phosphine. The attacking alkyne, therefore, can manage to coordinate only to **9'**, forming **10**. The butatrienyl ligand in **10** will then accept hydrogen from the coordinating alkyne to be freed as (*Z*)-dbb, with regeneration of the original dialkynyl intermediate **4**. The

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(8) (a) Bruce, M. I.; Swincer, A. G. *Adv. Organomet. Chem.* **1983**, *22*, 59. (b) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197.
(9) (a) Jia, G.; Rheingold, A. L.; Meek, D. W. *Organometallics* **1989**, *8*, 1378. (b) Jia, G.; Meek, D. W. *Organometallics* **1991**, *10*, 1444.
(10) Field, L. D.; George, A. V.; Hambley, T. W. *Inorg. Chem.* **1990**, *29*, 4565.
(11) Gotzig, J.; Werner, O. H. *J. Organomet. Chem.* **1985**, *287*, 247.

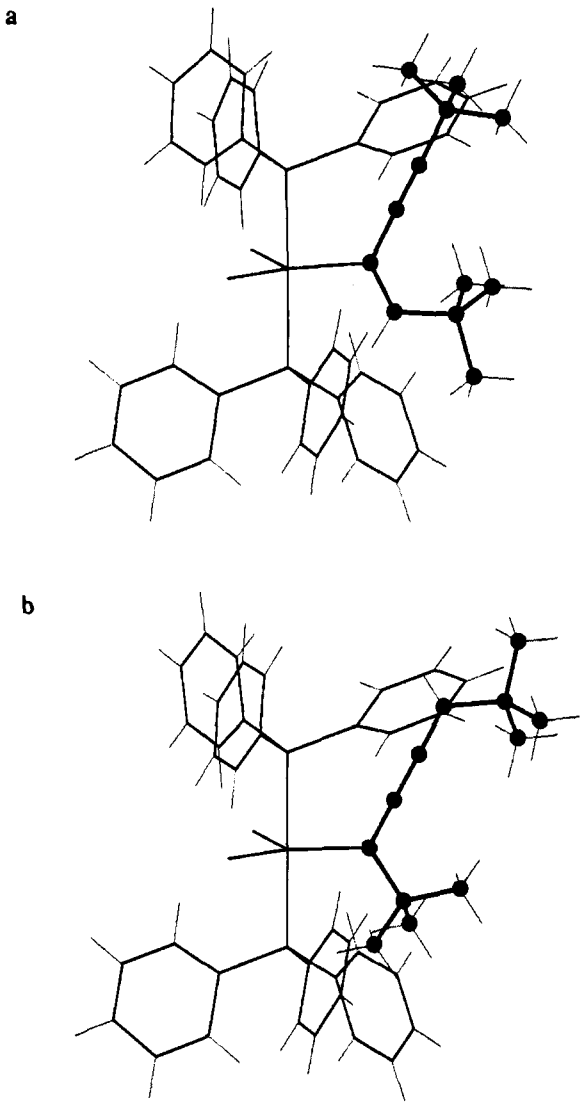


Figure 4. Steric interference between triphenylphosphine and the "upright form" of the C4 unit: (a) butenynyl and (b) butatrienyl ligands, with α,ω-di-*tert*-butyl groups. The geometry in a was taken from the X-ray structure of **12** and the Ru–C bond was rotated. In b, the Ru–C bond lengths were the same as in a, and the calculated C=C bond lengths for free Me(H)C_4(H)Me (Figure 1) were applied.

four model reactions to support this reaction scheme are described in the following sections.

Two other mechanisms are conceivable. One is intra- and intermolecular coupling of two vinylidene units.[12] It is, however, difficult to explain the specific *Z* stereochemistry of the product by this mechanism, the thermodynamical stability of (*Z*)- and (*E*)-1,4-disubstituted butatriene being much the same. The other mechanism is the formation of a C4 unit by coupling of the two alkynyl groups in **4** or in **7**. The diyne thus formed may insert into a RuH species to form an intermediate of the type **9**. This route is also unlikely since (i) thermal decomposition of complex **3** at 70 °C with or without free alkynes did not give diyne but liberated *tert*-butylacetylene as confirmed by NMR spectroscopy, (ii) di-*tert*-butylbutadiyne added to the catalytic dimerization system was not consumed at all, and (iii) no diyne was detected in the catalytic reaction. The model complex (**13**) described below has further shown that the Ru(II) complex with one alkynyl and one chloride ligands, where the formation of the diyne is much less likely, can also give a stoichiometric amount of (*Z*)-dbb on heating (60 °C) with *tert*-butylacetylene.

(3-4) Model Reaction for 7 to 8. Several examples of the conversion of coordinated terminal alkynes to vinylidene ligands

(12) Schubert, U.; Grönen, J. *Organometallics* **1987**, *6*, 2458.

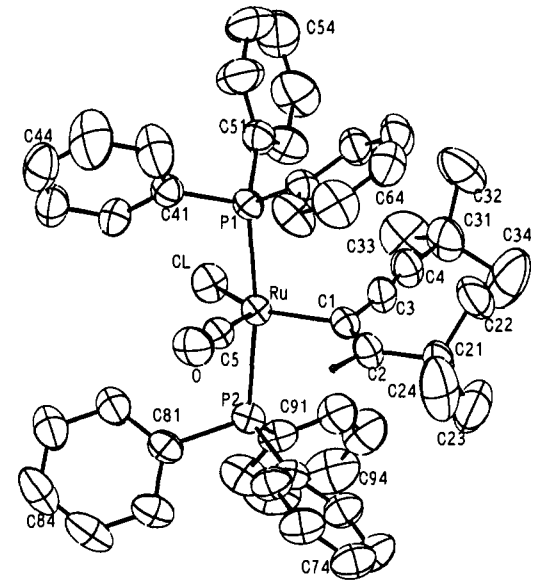
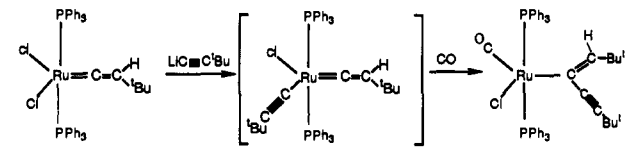


Figure 5. Molecular structure for **12** with atomic numbering scheme.

have been described in the literature.[8] In the case of ruthenium, the rearrangement of $[Ru(\eta^5\text{-}C_5H_5)(PMe_3)_2(\eta^2\text{-}MeC{\equiv}CH)]^+$ to $[Ru(\eta^5\text{-}C_5H_5)(PMe_3)_2(C{=}CHMe)]^+$ has been reported recently.[13] On studying a neutral Ru(II) system which is similar to our reaction, we found that the vinylidene complex of the composition $RuX_2(PPh_3)_2(C{=}CH^tBu)$ (**11a**, X = Cl; **11b**, X = Br) was formed by simply mixing a benzene solution of $RuX_2(PPh_3)_3$ with $HC{\equiv}C^tBu$ at room temperature. After 12–24 h the complex was isolated by concentration and addition of hexane. These complexes showed IR bands at 1630 cm^{-1} in the characteristic $\nu_{C=C}$ stretching region for vinylidene ligands.[8] The structure of **11b** was confirmed by X-ray crystallography.[14]

(3-5) Model Reaction for 8 to 9. The model complex for **9** was prepared by the reaction of $RuCl(CO)(PPh_3)_3H$ with $^tBuC{\equiv}CC{\equiv}CBu^t$ at room temperature. Facile cis addition of the RuH to one of the triple bonds gives a good yield of complex **12** as orange crystals, which has been structurally characterized as shown in Figure 5. The C4 chain of the butenynyl group lies approximately on the basal plane of the complex defined by Ru, CO, and Cl, the dihedral angle between Ru–CO–Cl and the butenynyl planes being 12.6°. Though there is no apparent interaction between Ru and the triple bond, it is noteworthy that Ru–C1–C2 (135.4 (3)°) is larger and Ru–C1–C3 (97.9 (3)°) is smaller than the typical C sp^2 bonding angle. The small Ru–C1–C3 angle should facilitate the migration of Ru from C1 to C4 described in the following section. The ^1H NMR spectrum of **12** in C_6D_6 shows two *tert*-butyl resonances at δ 1.12 and 0.94 and the vinylic proton at 5.10 as a triplet due to the coupling with two equivalent phosphines.

The vinylidene complex **11a** in THF was reacted with 0.8 equiv of $LiC{\equiv}C^tBu$ at −50 °C for 1 h and then a 4 molar excess of CO was bubbled through the solution at the same temperature. After the reaction mixture was allowed to warm to room temperature, workup by column chromatography of the resulting orange-brown solution afforded crystals of **12** in 27% yield based on **11a**.

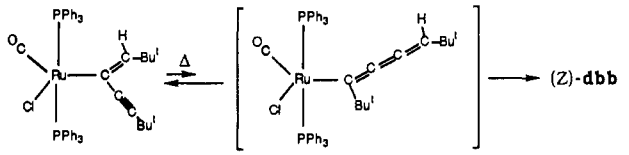


Intramolecular migration of a methyl group to a carbene ligand has been reported for $[Br(PMe_3)_2(Ir{=}CH_2)CH_3]^+$,[15] and several

(13) Bullock, R. M. *J. Chem. Soc., Chem. Commun.* **1989**, 165.
(14) Wakatsuki, Y.; Kumegawa, N.; Yamazaki, H. Unpublished results.
(15) Thorn, D. L.; Tulip, T. H. *J. Am. Chem. Soc.* **1981**, *103*, 5984.

papers have established carbon–carbon bond formation of this type.[16] The methyl–methylene coupling on the Ir center to give an ethyl ligand occurs readily, in contrast to the difficulty in forming carbon–carbon bonds by reductive elimination of the related dimethyl complex.[15] The vinyl–vinylidene coupling somewhat related to our system has been reported recently for a cationic Ir(II) complex.[17]

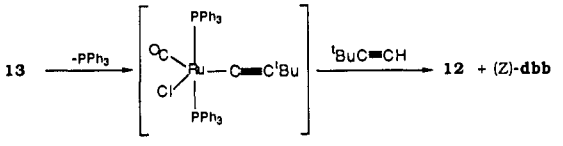
(3-6) Model Reaction for 9 to 9′. On heating an NMR sample of **12** at 50 °C, slow decomposition was noted as monitored by the decrease of the peaks due to **12**. At the same time, new singlet peaks at δ 1.09 and 5.54 in a 9:1 intensity ratio emerged and grew as the decomposition of **12** proceeded. These peaks were due to (*Z*)-dbb, and its presence in the solution was further confirmed by GLC and GC/MS spectroscopy. The half-life time of **12** was ca. 70 h. The change was very clean and no other peak could be detected in the ^{1}H NMR spectra. The butatrienyl ligand, which rearranged from the butenynyl form in **12**, abstracted hydrogen, presumably from triphenylphosphine, to be liberated as (*Z*)-dbb.



12

(3-7) Model Reaction for 3 (4) to 9. When a benzene solution of **3** was shaken with an equimolar amount of aqueous hydrogen chloride, a new colorless crystalline complex, RuCl(CO)-$(PPh_3)_3$(C≡C^{t}Bu) (**13**), was obtained. This complex may dissociate one of the triphenylphosphines in solution, as in the case of **3**, giving a coordinatively unsaturated intermediate which may be regarded as a monoalkynyl version of **4**.

When a C_6D_6 solution of **13** is heated to 60 °C in the presence of excess *tert*-butylacetylene for 12 h, the original ^{t}Bu resonance of **13** at δ 1.08 disappears while new peaks due to complex **12** along with smaller peaks due to (*Z*)-dbb (**12**/dbb = ca. 3) emerge. The change is rather clean, and side reactions are virtually negligible as judged by ^{1}H NMR spectroscopy.



Conclusion

tert-Butylacetylene undergoes stereoselective dimerization to (*Z*)-1,4-di-*tert*-butylbutatriene by ruthenium complex catalysts. The reaction sequence in the catalytic cycle (Scheme I) was elucidated by a series of model reactions: formation of the bis(alkynyl) complex, isomerization of the η^2-alkyne to the vinylidene ligand, migration of the alkynyl to the vinylidene carbon, and finally, rearrangement of the butenynyl moiety to the butatrienyl form. While some of these elemental reaction steps have precedents in coordination chemistry, the present system is unique in that all of these reactions are linked to form a catalytic cycle.

Experimental Section

IR spectra were obtained with a Shimadzu IR-27G spectrometer using the KBr pellet method. NMR spectra were recorded on a JEOL JNM-GX-400 or GX-500 spectrometer using $SiMe_4$ (^{1}H and ^{13}C) or H_3PO_4 (^{31}P) as the internal standard. For column chromatography, WAKO-GEL KCG-30 was used. Ru(cod)(cot),[18] $Ru(CO)(PPh_3)_3(H)_2$, and $RuCl(CO)(PPh_3)_3H$[19] were prepared according to the literature. All reactions were carried out under an atmosphere of argon. GC analyses were performed on a Hewlett-Packard 5890 with a 30 m × 0.32 mm DB1 column using *n*-dodecane as the internal standard.

Catalytic Dimerization by Ru(cod)(cot)/Pt(^{i}Pr$_3$)$_3$. A mixture of Ru(cod)(cot) (35 mg, 0.11 mmol), P(^{i}Pr$_3$)$_3$ (53 mg, 0.33 mmol), and HC≡C^{t}Bu (1 mL) in benzene (3 mL) was sealed in an ampule and heated at 100 °C. After 20 h, the reaction mixture was subjected to GC analysis.

Catalytic Dimerization by Ru(CO)(PPh$_3$)$_3$H$_2$ (1). *tert*-Butylacetylene (4.1 g, 50 mmol) and **1** (367 mg, 0.4 mmol) were dissolved in benzene (10 mL) and heated to 100 °C in a sealed ampule. After 10 h, the mixture was fractionally distilled. The 1,4-di-*tert*-butylbutatriene[20] distilled out at 80–85 °C (20 mmHg), which had an isomer ratio (*Z*):(*E*) = 9:1, and was confirmed by elemental analysis and GC/MS and NMR spectroscopies. Yield = 2.1 g (51%).

Preparation of Ru(CO)(PPh$_3$)$_3$(H)(C≡C^{t}Bu) (2). To a solution of Li^{n}Bu (1.9 mmol) in dry Et_2O (1.5 mL) was added HC≡C^{t}Bu (0.12 mL, ca. 0.95 mmol) with stirring at 0 °C. Addition of an extra equivalent of Li^{n}Bu was preferred in order to prevent a facile reaction between free HC≡C^{t}Bu and $RuCl(CO)(PPh_3)_3H$ giving the vinyl complex. After 20 min, the mixture was added to a suspension of $RuCl(CO)(PPh_3)_3H$ (300 mg, 0.31 mmol) in dry THF (20 mL) at 0 °C. The mixture was stirred for 1 h at 0 °C and an additional 2 h at room temperature. After the solvent was evaporated under reduced pressure, the residue was dissolved in a minimum amount of CH_2Cl_2. The solution was column chromatographed (2 × 17 cm), and the *n*-hexane/benzene (2:1) eluate was concentrated under reduced pressure. Dilution with *n*-hexane gave colorless crystals of **2** (161 mg, 52% yield): mp 76–79 °C dec; ^{1}H NMR ($CDCl_3$) δ 0.56 (C_4H_9, s), −8.23 (RuH, dt, $J(P_{tr}H)$ = 87 Hz, $J(P_{cis}H)$ = 26 Hz); ^{31}P NMR ($CDCl_3$) δ 44.6 (P_{ax}, d, $J(P_{tr}P_{cis})$ = 17 Hz), 20.8 (P_{eq}, t); IR 1996 (ν(RuH), ν(C≡C)), 1923 (ν(CO)) cm^{-1}. Anal. Calcd for $C_{61}H_{55}OP_3Ru$: C, 73.41; H, 5.55. Found: C, 73.10; H, 5.54. Other alkynyl complexes can be prepared by a similar procedure. Ru(CO)-$(PPh_3)_3$(H)(C≡CPh): mp 133–134 °C dec; ^{1}H NMR ($CDCl_3$) δ −8.13 (RuH, dt, $J(P_{tr}H)$ = 85 Hz, $J(P_{cis}H)$ = 25 Hz); IR 2012 (ν(C≡C)), 1993 (ν(RuH)), 1923 (ν(CO)) cm^{-1}. Anal. Calcd for $C_{69}H_{56}OP_3Ru$: C, 75.60; H, 5.24. Found: C, 75.56; H, 5.23. $Ru(CO)(PPh_3)_3(H)(C{\equiv}CSiMe_3)\cdot{}^1/_2(CH_2Cl_2)$: mp 134–135 °C dec; ^{1}H NMR ($CDCl_3$) δ −0.42 (SiMe, s), −8.22 (RuH, dt, $J(P_{tr}H)$ = 83 Hz, $J(P_{cis}H)$ = 26 Hz); IR 2003 (ν(C≡C)), 1995 (ν(RuH)), 1936 (ν(CO)) cm^{-1}. Anal. Calcd for $C_{60.5}H_{56}ClOP_3RuSi$: C, 68.77; H, 5.34. Found: C, 68.85; H, 5.34.

Preparation of Ru(CO)(PPh$_3$)$_3$(C≡C^{t}Bu)$_2$ (3). To a solution of **2** (500 mg, 0.5 mmol) in benzene (100 mL) was added HC≡C^{t}Bu (0.5 mL, ca. 4 mmol). The mixture was stirred for 4 days at room temperature and concentrated under reduced pressure to ca. 5 mL. The solution of PPh_3 (530 mg, 2.02 mmol) in hexane (13 mL) was added slowly to give pale yellow crystal of $Ru(CO)(PPh_3)_3(C{\equiv}C^tBu)_2\cdot 2(C_6H_6)$ (321 mg, 52% yield): mp 130–133 °C dec; ^{1}H NMR (C_6D_6) δ 1.28 (^{t}Bu, s), 0.96 (^{t}Bu, s); ^{31}P NMR ($CDCl_3$) δ 29.64 (P_{ax}, d, $J(P_{ax}P_{eq})$ = 21.5 Hz), 19.34 (P_{eq}, t); IR 2090 (ν(C≡C)), 1959 (ν(CO)) cm^{-1}. Anal. Calcd for $C_{79}H_{75}OP_3Ru$: C, 76.87; H, 6.12. Found: C, 76.67; H, 6.10.

Exchange of PPh$_3$ in 3 with PMe$_3$. A solution of PMe_3 (0.32 mmol) in toluene (1 mL) was added to a solution of **3** (100 mg, 0.08 mmol) in benzene (20 mL) at room temperature. After the mixture was allowed to stand overnight, it was concentrated under a reduced pressure. Dilution with *n*-hexane gave colorless crystals of $Ru(CO)(PPh_3)_2(PMe_3)(C{\equiv}C^tBu)_2\cdot(C_6H_6)$ (**5**) (32 mg, 44% yield): mp 141–142 °C dec; ^{1}H NMR (C_6D_6) δ 1.36 (^{t}Bu, s), 0.98 (^{t}Bu, s), 0.96 (Me, d, J(PH) = 7.6 Hz); IR 2080 (ν(C≡C)), 1966 (ν(CO)) cm^{-1}. Anal. Calcd for $C_{58}H_{63}OP_3Ru$: C, 71.81; H, 6.55. Found: C, 71.88; H, 6.71.

Exchange of PPh$_3$ in 3 with MeOH. Complex **3** (100 mg) was dissolved in benzene (20 mL) and the volume of the solution was reduced

Table I. Crystallographic Data for **12**

$C_{49}H_{49}ClOP_2Ru$	V = 2194 Å^3
fw = 852.4	Z = 2
cryst class: triclinic	λ = 0.7107 Å
space group: $P\bar{1}$	ρ_c = 1.291 g cm^{-3}
a = 12.326 (5) Å	μ(Mo Kα) = 5.16 cm^{-1}
b = 16.120 (5) Å	cryst size: 0.9 × 0.8 × 0.7 mm
c = 11.774 (3) Å	
α = 95.66 (3)°	R = 0.045
β = 101.64 (3)°	R_w = 0.048
γ = 73.41 (3)°	

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Table II. Atomic Coordinates for **12** with Estimated Standard Deviations in Parentheses[a]

atom	x	y	z	atom	x	y	z
Ru	12522 (2)	25620 (2)	22419 (2)	C54	−2896 (6)	5017 (3)	4155 (5)
Cl	1307 (1)	4029 (1)	2888 (1)	C55	−1757 (5)	4662 (3)	4508 (5)
P1	−809 (1)	2950 (1)	1848 (1)	C56	−1136 (4)	4051 (3)	3799 (4)
P2	3272 (1)	2244 (1)	2351 (1)	C61	−1429 (3)	2045 (2)	1809 (3)
O	1105 (3)	1738 (2)	−99 (2)	C62	−1995 (4)	1949 (3)	2673 (3)
C1	1381 (3)	1432 (2)	2949 (3)	C63	−2411 (4)	1231 (3)	2645 (4)
C2	1583 (3)	601 (2)	2578 (3)	C64	−2267 (4)	607 (3)	1776 (4)
C3	1224 (3)	1772 (2)	4083 (3)	C65	−1690 (5)	684 (3)	923 (5)
C4	1069 (4)	2147 (2)	5001 (3)	C66	−1265 (4)	1396 (3)	941 (4)
C5	1168 (3)	2046 (2)	810 (3)	C71	4050 (3)	1098 (2)	2231 (3)
C21	1725 (4)	−197 (2)	3254 (3)	C72	3812 (3)	630 (3)	1194 (4)
C22	704 (5)	−92 (3)	3857 (5)	C73	4364 (4)	−237 (3)	1058 (4)
C23	2833 (5)	−332 (4)	4196 (6)	C74	5163 (4)	−661 (3)	1949 (4)
C24	1834 (7)	−988 (3)	2410 (5)	C75	5407 (4)	−213 (3)	2980 (4)
C31	920 (5)	2494 (3)	6197 (4)	C76	4856 (4)	663 (3)	3122 (4)
C32	−370 (6)	2620 (4)	6281 (5)	C81	3651 (3)	2690 (2)	1161 (3)
C33	1198 (6)	3379 (4)	6429 (5)	C82	4696 (4)	2312 (3)	784 (4)
C34	1717 (8)	1811 (5)	7036 (5)	C83	4961 (4)	2657 (3)	−125 (5)
C41	−1343 (3)	3395 (2)	404 (3)	C84	4218 (5)	3371 (4)	−652 (5)
C42	−771 (4)	3913 (2)	39 (3)	C85	3185 (5)	3749 (4)	−294 (5)
C43	−1170 (4)	4309 (3)	−1011 (4)	C86	2905 (4)	3410 (3)	609 (4)
C44	−2142 (5)	4199 (4)	−1701 (4)	C91	4099 (3)	2620 (2)	3669 (3)
C45	−2727 (6)	3704 (5)	−1355 (5)	C92	3897 (4)	2457 (3)	4729 (4)
C46	−2327 (5)	3287 (4)	−305 (4)	C93	4582 (5)	2652 (4)	5754 (4)
C51	−1656 (3)	3782 (2)	2739 (3)	C94	5447 (5)	3011 (4)	5711 (5)
C52	−2820 (4)	4146 (4)	2374 (5)	C95	5633 (5)	3201 (4)	4678 (5)
C53	−3440 (5)	4768 (4)	3094 (6)	C96	4967 (4)	3003 (3)	3647 (4)

[a] Parameters are multiplied by 10^5 for Ru and 10^4 for others.

to ca. one-half. Methanol (20 mL) was added slowly and the mixture was allowed to stand overnight. Pale yellow crystals of **6** with a crystal solvent of 1 molecule of methanol and 0.5 molecule of benzene, $[Ru(CO)(PPh_3)_2(C{\equiv}C^tBu)_2(CH_3OH)]\cdot(CH_3OH)\cdot{}^1/_2(C_6H_6)$, precipitated (43 mg, 54% yield): mp 100-103 °C dec; ^{1}H NMR (toluene-d_8) δ 2.68 (OCH_3, br s), 1.05 (^{t}Bu, s); IR 1925 (ν(CO)) cm^{-1}. Anal. Calcd for $C_{54}H_{59}O_3P_2Ru$: C, 71.31; H, 6.45. Found: C, 70.57; H, 6.47.

Exchange of Alkynyl Ligands in 3 with Free Alkyne. To a solution of **3** (100 mg, 0.08 mmol) in benzene (20 mL) was added (trimethylsilyl)acetylene (0.2 mL). After 1 h at room temperature, the solution was concentrated to ca. 2 mL to give crude brown crystals. Recrystallization from benzene containing 10 wt % of triphenylphosphine gave yellow crystals (56 mg, 53% yield) of $Ru(CO)(PPh_3)_3(C{\equiv}CSiMe_3)_2\cdot{}^1/_4(C_6H_6)$: mp 54-57 °C dec; ^{1}H NMR (C_6D_6) δ 0.24 ($SiCH_3$, s), −0.03 ($SiCH_3$, s); IR 2010, 2020 (ν(C≡C)), 1964 (ν(CO)) cm^{-1}. Anal. Calcd for $C_{80}H_{78}OP_3RuSi_2$: C, 73.59; H, 6.02. Found: C, 73.58; H, 5.96. A similar reaction of **3** with phenylacetylene gave yellow crystals (51% yield) of $Ru(CO)(PPh_3)_3(C{\equiv}CPh)_2\cdot{}^3/_2(C_6H_6)$: mp 142-144 °C dec; IR 2075 (ν(C≡C)), 1965 (ν(CO)) cm^{-1}. Anal. Calcd for $C_{80}H_{64}OP_3Ru$: C, 77.78; H, 5.22. Found: C, 77.79; H, 5.31.

Preparation of Vinylidene Complexes (11a, 11b). To a stirred solution of $RuCl_2(PPh_3)_3$ (794 mg, 0.83 mmol) in benzene (45 mL) was added a large excess of *tert*-butylacetylene (1 mL). The color of the solution turned from yellow-brown to red-brown. After 24 h at room temperature, the mixture was filtered when undissolved solid remained, and the solvent was evaporated from the filtrate. Crystallization of the residue from dichloromethane/*n*-hexane gave dark brown crystals of $RuCl_2(PPh_3)_2(C{=}CH^tBu)$ (**11a**) (397 mg, 62% yield): mp 161-162 °C dec; ^{1}H NMR (C_6D_6) δ 3.87 (=CH, t, J(PH) = 4.4 Hz), 0.79 (^{t}Bu, s); ^{31}P NMR (C_6D_6 δ 27.24 (s); IR 1630 (ν(C=C)) cm^{-1}. Anal. Calcd for $C_{42}H_{40}Cl_2P_2Ru$: C, 64.78; H, 5.18. Found: C, 64.73; H, 5.16. A similar reaction of $RuBr_2(PPh_3)_3$ completed in 12 h to give dark green crystals of $RuBr_2(PPh_3)_2(C{=}CH^tBu)$ (**11b**) (51% yield): mp 159-161 °C dec; ^{1}H NMR (C_6D_6, in the presence of a small amount of PPh_3) δ 3.55 (=CH, t, J(PH) = 4.3 Hz), 0.78 (^{t}Bu, s); ^{31}P NMR (C_6D_6) δ 29.93 (s); IR 1630 (ν(C=C)) cm^{-1}. Anal. Calcd for $C_{42}H_{40}Br_2P_2Ru$: C, 58.14; H, 4.65. Found: C, 58.25; H, 4.63.

Preparation of $RuCl(CO)(PPh_3)_2(C(C{\equiv}C^tBu){=}CH^tBu)$ (12). A mixture of $RuCl(CO)(PPh_3)_3H$ (343 mg, 0.36 mmol) and 1,4-di-*tert*-butylbuta-1,3-diyne (246 mg, 1.5 mmol) in THF (140 mL) was stirred at room temperature. After 16 h, the solvent was evaporated under reduced pressure and the residue was chromatographed. An orange band eluted with benzene/dichloromethane (1:1) was collected. Evaporation of the solvent and recrystallization of the residue from dichloromethane/*n*-hexane gave orange crystals of $RuCl(CO)(PPh_3)_2(C(C{\equiv}C^tBu){=}CH^tBu)$ (**12**) (152 mg, 50% yield): mp 178-179 °C dec; ^{1}H NMR (C_6D_6) δ (5.10 (=CH, t, J(PH) = 1.9 Hz), 1.12 (^{t}Bu, s), 0.94 (^{t}Bu, s); IR 1905 (ν(CO)) cm^{-1}. Anal. Calcd for $C_{49}H_{49}ClOP_2Ru$: C, 69.04; H, 5.79. Found: C, 69.19; H, 5.79.

Table III. Selected Interatomic Distances (Å) and Angles (deg)

	Distances		
Ru–Cl	2.427 (1)	Ru–P1	2.395 (1)
Ru–P2	2.373 (1)	Ru–C5	1.802 (4)
Ru–C1	2.109 (4)	C1–C2	1.336 (5)
C1–C3	1.422 (5)	C3–C4	1.207 (6)
Ru···C3	1.631 (4)	Ru···C4	3.444 (4)
	Angles		
P1–Ru–P2	171.51 (4)	C1–Ru–C1	138.1 (1)
C1–Ru–C5	130.6 (1)	C1–Ru–C5	90.8 (2)
Ru–C1–C2	135.4 (3)	Ru–C1–C3	97.9 (3)
C2–C1–C3	126.7 (4)	C1–C3–C4	173.0 (4)

Preparation of $RuCl(CO)(PPh_3)_3(C{\equiv}C^tBu)$ (13). Complex **3** (101 mg, 0.36 mmol) was dissolved in benzene (20 mL) and an aqueous solution (10 mL) containing an equimolar amount of hydrogen chloride was added. The mixture was shaken for 6 h at room temperature. The organic layer was separated and dried over anhydrous magnesium sulfate. On evaporation of the solvent under reduced pressure, colorless fine crystals of **13** were obtained, which were recrystallized from dichloromethane/*n*-hexane (10 mg, 11% yield): mp 140-142 °C dec; ^{1}H NMR (C_6D_6) δ 1.08 (^{t}Bu, s); IR 2040 (ν(C≡C)), 1948 (ν(CO)) cm^{-1}. Anal. Calcd for $C_{61}H_{54}ClOP_3Ru$: C, 69.20; H, 5.33. Found: C, 70.96; H, 5.27.

X-ray Crystal Structure Determination of 12. Crystal data are summarized in Table I. X-ray measurements were carried out with a Nonius CAD4 four-circle diffractometer equipped with a graphite monochromator using ω–2θ scans. An absorption correction was not made because deviations of F_o for axial reflections at χ = 90° were within ±5%. A total of 13 017 unique reflections in the range $\pm h,\pm k,+l$ and $2° < 2\theta < 55°$ were measured, of which 9053 independent reflections having $I > 3\sigma(I)$ were used in subsequent analysis.

The structure was solved from direct and Fourier methods and refined by block-diagonal least squares with anisotropic thermal parameters in the last cycles for all nonhydrogen atoms. Hydrogen atoms for the six phenyl rings were placed in calculated positions, while the vinylic proton was located from a difference Fourier map. However, the protons for the methyl groups could not be located. In the refinements, unit weight was applied. The function minimized in the least-squares refinement was $\sum w(|F_o| - |F_c|)^2$. The computational program package used in the analysis was the UNICS 3 program system.[21] Neutral atomic scattering factors were taken from International Tables.[22] Final atomic parameters

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for the nonhydrogen atoms and important bond lengths and angles are given in Tables II and III, respectively.

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Registry No. 1. 25360-32-1; **2.** 125615-88-5; **3**, 125615-89-6; **5**, 137039-44-2; **6**, 125615-91-0; **11a**, 137039-45-3; **11b**, 137039-49-7; **12**, 125615-90-9; **13**, 137039-46-4; (*Z*)-dbb, 57788-53-1; (*E*)-dbb, 62444-32-0; HC≡C^{t}Bu, 917-92-0; $Ru(CO)(PPh_3)_3(H)(C{\equiv}CPh)$, 125615-95-4; $Ru(CO)(PPh_3)_3(H)(C{\equiv}CSiMe_3)$, 125615-96-5; $HC{\equiv}CSiMe_3$, 1066-54-2; $Ru(CO)(PPh_3)_3(C{\equiv}CSiMe_3)_2$, 137039-47-5; $Ru(CO)(PPh_3)_3(C{\equiv}CPh)_2$, 137039-48-6; $RuCl(CO)(PPh_3)_3H$, 16971-33-8; $RuCl_2(PPh_3)_3$, 15529-49-4; $RuBr_2(PPh_3)_3$, 15709-75-8; $C(C{\equiv}C^tBu){\equiv}C^tBu$, 6130-98-9; Ru(cod)(cot), 42516-72-3.

Supplementary Material Available: Tables of positional and thermal parameters for **12** and a full tabulation of bond distances and angles (5 pages); a listing of observed and calculated structure factors (23 pages). Ordering information is given on any current masthead page.

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Ab Initio and Crystal Structure Analysis of Like-Charged Ion Pairs

Jiali Gao,*[1a] Stephane Boudon,[1b,c] and Georges Wipff[1c]

Contribution from the Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214, and Institut le Bel, Universite Louis Pasteur de Strasbourg, 4 rue Blaise Pascal, 67000 Strasbourg, France. *Received April 24, 1991*

Abstract: A combined approach of crystallographic analyses and ab initio molecular orbital computations provides strong support to the previous theoretical finding of the possible existence of a stable Cl_2^{2-} aggregate in water. Consistent with previous explanations, the stabilization of like-charged ion pairs in aqueous solution was rationalized by the Born model of solvation and the solvent-bridged hydrogen-bonding interactions that offset Coulombic repulsion between the two anions. Analysis of the Cambridge Structural Database revealed correlation patterns in hydrogen-bonding interaction. Further, the ab initio results were compared with those predicted using empirical potential functions and good agreement was obtained.

Introduction

Electrostatic interactions play a key role in determining the function and reactivity of biological molecules in aqueous solution.[2] Consequently, the study of ionic solvation has been a central theme in physical chemistry.[3] An important phenomenon of electrolytic solution is the formation of ion pairs consisting of oppositely charged species proposed in the Bjerrum theory.[3b,4] This has now been supported by many experimental investigations including neutron and X-ray diffraction studies.[5-7] However, more detailed understanding of the molecular interactions in solution was aided through computer simulations of ion pairs in water. These computations revealed an oscillatory behavior in the potential of mean force (pmf) for cation–anion interactions, corresponding to contact and solvent separated ion pairs.[8-12] Moreover, a striking finding in both integral equation computations and simulation studies is the observation of a stable, like-charged ion pair in aqueous solution near contact distance between two chloride ions.[9,10,13,14] Stabilization of the anion pairing has been attributed to the formation of several bridging hydrogen bonds between water molecules and the two Cl^- ions.[13,14]

Experimental evidence for the possible existence of halide ion pairs in solution was provided by NMR and diffraction measurements. The NMR relaxation data for aqueous alkali halide indicated long-lived anion pairing with strong stabilization for $F^-\cdots F^-$.[15] Further, X-ray diffraction patterns obtained by Smith and Wertz for aqueous lanthanum(III) chloride supported a $Cl^-\cdots Cl^-$ distance of 4.7 Å at high concentrations.[16] Similar results were obtained by neutron diffraction studies.[5,6] However, these experiments were typically performed at high salt concentrations, making comparison with the computed pmf difficult. Convincing evidence is now provided from the analysis of X-ray crystal structures containing halide ions. A survey of the Cambridge Structural Database (CSD) revealed that contact chloride pairs are common in the crystalline state.

Questions concerning the accuracy of the theoretical results still remain in computer simulation studies of ion pair in solution because pair-wise, effective potential functions are typically

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