Scheme I

the di-Grignard reagent prepared from 1,2-diethynyl-1,2-dimethyldiphenyldisilane (1a) and isopropylmagnesium chloride was allowed to react with 1,2-dichloro-1,2-dimethyldiphenyldisilane in THF. The mixture was heated to reflux for 15 h, and then it was hydrolyzed with water. After the solvent was evaporated, the residue was chromatographed on silica gel eluting with benzene. The resulting crystals were recrystallized from benzene to give 2a in 20% yield as a single isomer. Similar treatment of a di-Grignard reagent of 1,2-diethyl-1,2-diethynyldimethyldisilane (1b) with 1,2-dichloro-1,2-diethyldimethyldisilane afforded 1,2,5,6-tetraethyl(tetramethyl)-1,2,5,6-tetrasilacycloocta-3,7-diyne[8] (2b) in 47% yield.

The anionic ring-opening polymerization was carried out with the use of n-butyllithium as a catalyst in THF at room temperature. Thus, a mixture of 1.37 mmol of 1,2,5,6-tetrasilacycloocta-3,7-diyne (2a) with a catalytic amount of n-butyllithium (1.7 mol %) in 5 mL of dry THF[9] was stirred at room temperature in a sealed glass tube for 64 h. The mixture was poured into ethanol, and the resulting white-yellow solid was reprecipitated twice from benzene-ethanol to give 0.253 g (35% yield) of poly[(1,2-dimethyldiphenyldisilanylene)ethynylene] (3a)[10] (Scheme I). Molecular weight of the polymer 3a was determined to be $\bar{M}_w = 8.08 \times 10^4$ ($\bar{M}_w/\bar{M}_n = 4.08$), relative to polystyrene standards. The polymer 3a melts at 60-85 °C without decomposition and is soluble in common organic solvents, such as benzene, ethers, and halocarbons.

The structure of 3a was verified by IR and ^{1}H and ^{13}C NMR spectroscopic analysis.[11] The ^{13}C NMR spectrum revealed a single resonance at 114.4 ppm, indicating the presence of ethynylene carbons in the polymer chain.

The ring-opening polymerization catalyzed by butyllithium is remarkably general for tetrasilacycloocta-3,7-diynes. In fact, alkyl-substituted tetrasilacycloocta-3,7-diynes readily undergo ring-opening polymerization. Thus, when a solution of 1,2,5,6-tetraethyl(tetramethyl)-1,2,5,6-tetrasilacycloocta-3,7-diyne (2b) is stirred in the presence of a catalytic amount of n-butyllithium in THF at room temperature for 40 h, poly[(1,2-diethyldimethyldi-

silanylene)ethynylene][12] (3b) was obtained as a white solid in 92% yield. The polymer 3b melts at 140-145 °C and is soluble in common organic solvents. The molecular weight of 3b determined by GPC was calculated to be $\bar{M}_w = 1.05 \times 10^5$ ($\bar{M}_w/\bar{M}_n = 3.25$). The ^{13}C NMR spectrum of 3b reveals a resonance at 114.2 ppm, indicating the presence of the ethynylene group.

Similar reaction of 1,1,2,2,5,5,6,6-octamethyltetrasilacycloocta-3,7-diyne[5] (2c) with n-butyllithium under the same conditions gave a white polymer, poly[(tetramethyldisilanylene)ethynylene] (3c). In contrast to the ring-opening polymerization of 2a and 2b, in which no insoluble polymers were formed, in the case of 2c, the precipitation of the polymers was observed in the early stages of the polymerization. The polymer 3c thus obtained did not melt but decomposed at 205-210 °C and was scarcely soluble in common organic solvents. Insolubility for this polymer may be ascribed to the high crystallinity.

The polymer 3a and 3b can be cast to the film by spin coating of their methylene chloride solution. Characteristic of the polymers 3a and 3b is a strong absorption at 242 nm in the ultraviolet region. As expected, 3a and 3b are highly photoactive. Thus, irradiation of thin solid films of 3a and 3b with a low-pressure mercury lamp in air led to the disappearance of this absorption, indicating that homolytic scission of silicon-silicon bonds in the polymer backbone occurred, as observed in the photolyses of the polymers composed of a disilanylene unit and a π-electron system as a repeating unit.[1,3,4]

Interestingly, when the films of 3a and 3b were treated with SbF₅ vapor, the highly conducting films were obtained. The conductivity determined by the four-probe method was found to be 0.41 S·cm^{-1} for 3a and 1.96 S·cm^{-1} for 3b, respectively.[13]

Aluminum chloride also acts as a catalyst for ring-opening polymerization of 3a and 3b. However, at present, the molecular weights of the resulting polymers were determined to be 2500-4000.

(8) Compound 2b: mp 30-32 °C; MS m/e 336 (M$^+$); IR 1248, 1008, 955 cm^{-1}; UV λ_{max} (log ε) 211.0 (4.04), 248 nm (4.19); ^{1}H NMR (δ in CDCl₃) 0.22 (12 H, s, MeSi), 0.57-1.16 (20 H, m, EtSi); ^{13}C NMR (δ in CDCl₃) -5.1 (MeSi), 6.1 and 8.1 (EtSi), 119.5 (C≡C). Anal. Calcd for C₁₆H₃₂Si₄: C, 57.06; H, 9.58. Found: C, 57.27; H, 9.47.

(9) The solvent THF used for polymerization was dried over sodium-potassium alloy and transferred into a glass tube under reduced pressure.

(10) In this reaction, no insoluble polymers were formed. The evaporation of the solvent used in the reprecipitation of the polymer 3a gave 0.38 g of yellow liquid.

(11) Polymer 3a: mp 60-85 °C; IR 1428, 1248, 1108 cm^{-1}; UV λ_{max} (in solid film) 242.0 nm, λ_{max} (in THF) 249.0 nm; ^{1}H NMR (δ in CDCl₃) 0.42 and 0.55 (6 H, br s, MeSi), 7.02-7.80 (10 H, m, phenyl ring protons); ^{13}C NMR (δ in CDCl₃) -3.9 (MeSi), 114.4 (C≡C), 127.8, 129.2, 133.6, 134.5 (phenyl ring carbons).

(12) Polymer 3b: mp 140-145 °C; IR 1248, 1011, 957 cm^{-1}; UV λ_{max} (in solid film) 242.0, λ_{max} (in THF) 247.0 nm; ^{1}H NMR (δ in CDCl₃) 0.21 and 0.20 (6 H, s, MeSi), 0.56-1.16 (10 H, m, EtSi); ^{13}C NMR (δ in CDCl₃) -4.9 and -4.8 (MeSi), 6.3, 8.1 (EtSi), 114.2 (C≡C).

(13) For conducting polysilane, see: West, R.; David, L. D.; Djurovich, L.; Stearley, K. L.; Srinivasan, K. V. S.; Yu, H. *J. Am. Chem. Soc.* 1981, 103, 7352.

1,3-Scrambling of Chlorine in RhCl(PPh₃)₃-Catalyzed Decarbonylations of Allylic Acid Chlorides

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Summary: Reactions of RhCl(PPh₃)₃ with *trans*-3-pentenoyl chloride (at -20 °C), mixtures of *cis*-/*trans*-3-pentenoyl chloride (at -20 °C), and 2-methyl-3-butenoyl chloride (at room temperature) in CDCl₃ all produced the

rearranged products 1-chloro-2-butene and 3-chloro-1-butene. This 1,3-scrambling of chlorine is a direct consequence of the decarbonylation reaction, not of secondary rearrangements in the product. Reactions of *trans*-CH_3CH=$CHCH_2COCl$ with $RhCl(CO)(PPh_3)_2$ in the presence of ^{13}CO produced *trans*-CH_3CH=$CHCH_2$$^{13}COCl$ but no rearranged acid chloride ($CH_3CH(^{13}COCl)CH$=CH_2). Similar reactions of $CH_3CH(COCl)CH$=CH_2 produced $CH_3CH(^{13}COCl)CH$=CH_2 but no rearranged acid chloride (CH_3CH=$CHCH_2$$^{13}COCl$). Thus, a rearranged ($\eta^1$-allyl)Rh intermediate was conclusively ruled out as the reactive intermediate leading to the observed Cl scrambling. This loss of regiochemistry of chlorine is best explained by chloride attacks at 1- and 3-positions of (η^3-allyl)Rh$^+$ intermediates to form the 1- and 3-chloro products. These results provide clear evidence that the formation of RCl from decarbonylations of RCOCl in the so-called "reductive elimination" step is not a simple coupling of R,Cl from Rh, as has been indicated in some literature reports.

The chemistry of palladium-catalyzed nucleophilic substitutions of allylic substrates in (η^3-allyl)Pd systems has been extensively studied and widely applied in organic synthesis.[1] It is generally assumed that the reactions proceed via cationic (η^3-allyl)Pd intermediates to lead to the regiochemical distribution of substitutions at the 1- or 3-positions of allyl substrates. However, the question of the nature of reactive intermediates, (η^3-allyl)Pd vs (η^1-allyl)Pd, has not been fully resolved.[2-4] A recent paper reported that (η^3-allyl)Pd is most probably the reactive intermediate, although dynamic (η^3-allyl)Pd $\rightleftharpoons$ (η^1-allyl)Pd interconversions could not be conclusively ruled out.[4b] Similar to the palladium systems, (η^3-allyl)Rh complexes have often been postulated as the intermediates in some chemical transformations, such as the alkylation of allyl carbonates[5] catalyzed by $RhCl(PR_3)_3$ and the aminations of butadiene[6] catalyzed by $RhCl_3$. No efforts have been made to probe the nature of the reactive intermediate, (η^3-allyl)Rh or (η^1-allyl)Rh, as has been debated in palladium systems. We now report our studies on Rh(I)-catalyzed decarbonylations of allylic acid chlorides.[7-9] Chlorine is scrambled between the 1- and 3-positions of the allyl chlorides that are the decarbonylation products. We have

conclusive evidence that there can be no rearranged (η^1-allyl)Rh intermediates in the reaction. The observed 1,3-scrambling of Cl is best explained by Cl$^-$ attack at the 1- or 3-position of an (η^3-allyl)Rh$^+$ complex.

The reaction of *trans*-CH_3CH=$CHCH_2COCl$ with $RhCl(PPh_3)_3$ in $CDCl_3$ at -20 °C produced $CH_3CH(Cl)CH$=CH_2 and *trans*-CH_3CH=$CHCH_2Cl$. The formation of the these decarbonylation products could be conveniently followed by ^1H NMR spectroscopy.[10] In the first spectrum (at 2 h 20 min), only the 3-Cl product was observed; no 1-Cl was detected. The 3-Cl/1-Cl ratio must be $\geq$50/1. The 3-Cl product slowly isomerized to the 1-Cl product. Thus, at 4 h 20 min the 3-Cl/1-Cl ratio became 18/1 and at 8 h 20 min, when the reaction was 95% complete, the ratio became 11/1. Therefore, the 3-Cl/*trans*-1-Cl product ratio from *trans*-CH_3CH=$CHCH_2COCl$ is at least 50/1. Since the secondary rearrangement in the products was slow and was in the opposite direction, i.e. from 3-chlorobutene (the product of regiochemical rearrangement) back to 1-chlorobutene (the product of regiochemical retention), the observed Cl rearrangement in the decarbonylation products must be a direct consequence of the decarbonylation reaction, not of secondary rearrangements of the products.

cis-CH_3CH=$CHCH_2COCl$ could not be easily obtained. Reactions of mixtures of *cis-/trans*-CH_3CH=$CHCH_2COCl$ with $RhCl(PPh_3)_3$ in $CDCl_3$ at -20 °C were examined. Decompositions of $RhCl_2(PPh_3)_2(COCH_2CH$=$CHCH_3)$ (double-bond cis/trans ratio 2/1 and 1/3, respectively) produced $CH_2CH(Cl)CH$=CH_2 and *cis*- and *trans*-CH_3CH=$CHCH_2Cl$. From the observed product ratios,[11] the 3-Cl/*cis*-1-Cl product ratio from *cis*-CH_3CH=$CHCH_2COCl$ could be deduced to be approximately 2/1.[12]

The reaction of $CH_3CH(COCl)CH$=CH_2 with $RhCl(PPh_3)_3$ in $CDCl_3$ at room temperature also produced $CH_3CH(Cl)CH$=CH_2 and *cis*- and *trans*-CH_3CH=$CHCH_2Cl$: the 3-Cl/1-Cl ratio was 3.5/1.[13]

The most likely mechanisms for this Cl scrambling seem to be (a) a 1,3-Rh shift in the (allyl)Rh complexes (eq 1)

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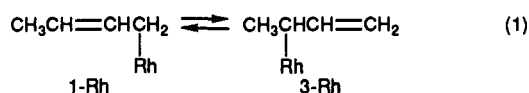(5) Tsuji, J.; Minami, I.; Shimizu, I. *Tetrahedron Lett.* **1984**, *25*, 5157–5160.

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(7) For a recent review of this decarbonylation chemistry, see: Doughty, D. H.; Pignolet, L. H. In *Homogeneous Catalysis with Metal Phosphine Complexes*; Pignolet, L. H., Ed.; Plenum Press: New York, 1983; pp 343–375.

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(10) ^1H NMR spectra were obtained on a General Electric QE-300 spectrometer. The following characteristic absorptions were monitored for each decarbonylation product: δ 4.11, d, ^3J = 7.4 Hz (*cis*-CH_3CH=$CHCH_2Cl$); δ 4.02, d, ^3J = 7.0 Hz (*trans*-CH_3CH=$CHCH_2Cl$); δ 4.52, quintet ($CH_3CH(Cl)CH$=CH_2).

(11) Mixtures of *cis-/trans*-CH_3CH=$CHCH_2COCl$ were obtained in 4/1 and 1/2 ratios. Both cis and trans acid chlorides react very rapidly with $RhCl(PPh_3)_3$ at -20 °C in $CDCl_3$ and at similar rates because the cis/trans ratios in the excess acid chlorides remained unchanged (4/1 and 1/2, respectively). Since the product isomerize under the reaction conditions, it is necessary to analyze the reaction system at partial decomposition. The formation of the two Rh-acyl complexes could be clearly observed, and their decompositions were followed by ^1H NMR spectroscopy: δ 4.93, d, ^3J = 6.1 Hz ($RhCl_2(COCH_2CH$=$CHCH_3)L_2$, cis double bond, 1); δ 4.83, d, ^3J = 6.4 Hz ($RhCl_2(COCH_2CH$=$CHCH_3)L_2$, trans double bond, 2). 2 decomposed faster than 1. Thus, from a cis/trans ratio of 4/1, at 2.3 h the residual 1/2 ratio became 7.6/1 and the observed 3-Cl/cis-1-Cl, 3-Cl/1-Cl, and cis-1-Cl/trans-1-Cl ratios were 2.4/1, 2.2/1, and 8.0/1. It can be calculated that this product distribution was the result of the decompositions of 1 and 2 in a 2/1 ratio. Similarly, from a cis/trans ratio of 1/2, at 3 h the residual 1/2 ratio became 1/1.5 and the observed 3-Cl/cis-1-Cl, 3-Cl/1-Cl, and cis-1-Cl/trans-1-Cl ratios were 8.1/1, 6.4/1, and 3.8/1. It can be calculated that this product distribution was the result of the decompositions of 1 and 2 in a 1/3 ratio.

(12) By using 3-Cl/*trans*-1-Cl = 50/1 from *trans*-CH_3CH=$CHCH_2COCl$ and by using the observed product composition and the ratios of 1 and 2 decomposed, as described above, we can calculate that a 3-Cl/cis-1-Cl ratio from *cis*-CH_3CH=$CHCH_2COCl$ of 2/1 gives the best fit to the data. Using this ratio (3-Cl/cis-1-Cl = 2/1), we can back-calculate 3-Cl/1-Cl product ratios from cis/trans mixtures of starting acid chlorides: CH_3CH=$CHCH_2COCl$ with cis/trans ratios 2/1 and 1/3 should give 3-Cl/cis-1-Cl, 3-Cl/1-Cl, and cis-1-Cl/trans-1-Cl ratios of 3.5/1, 3.4/1, 31.7/1 and 10.9/1, 9.2/1, 5.5/1, respectively. The experimental results were 2.4/1, 2.2/1, 8.0/1 and 8.1/1, 6.4/1, 3.8/1, respectively. Because of the secondary 3-Cl → 1-Cl and cis-1-Cl → trans-1-Cl isomerizations under the reaction conditions, it is understandable that the experimental ratios are lower than the calculated ratios.

followed by product formation from both η^1 complexes, (b) S_N2 and S_N2' nucleophilic attacks by chloride on a single, unrearranged (η^1-allyl)Rh complex, and (c) product formations from both ends of the η^3-allyl ligand in an (η^3-allyl)Rh intermediate.

$$CH_3CH\!\!=\!\!CHCH_2 \underset{\longleftarrow}{\overset{\longrightarrow}{\rule{0pt}{0pt}}} CH_3CHCH\!\!=\!\!CH_2 \qquad (1)$$
$$\underset{\text{1-Rh}}{\overset{|}{Rh}} \qquad\qquad \underset{\text{3-Rh}}{\overset{|}{Rh}}$$

(1) In (a), we do not distinguish between a direct 1,3-Rh shift and dynamic (η^1-allyl)Rh interconversions by way of an (η^3-allyl)Rh intermediate. The key proposal in (a) is that rearrangement of the (η^1-allyl)Rh intermediate is responsible for the observed rearrangement of Cl in the allyl chloride product. We have previously established that a wide variety of acid chlorides (RCOCl, R = methyl, propyl, vinyl, phenyl, benzyl, etc.) can be conveniently labeled by ^{13}CO at the carbonyl position by reaction with RhCl(CO)(PPh₃)₂ in the presence of ^{13}CO and that the labeling process is always much faster than the formation of the decarbonylation product (RCl or olefin);[8c,9a] i.e., recarbonylation of any Rh–R intermediate during the reaction by ^{13}CO to give R$^{13}COCl$ is much faster than the decomposition of the Rh–R intermediate to form RCl. Therefore, if a 1,3-Rh shift is involved in the reaction, the rearranged (η^1-allyl)Rh intermediate must lead to the formation of rearranged ^{13}CO-labeled acid chloride. Reactions of trans-CH₃CH=CHCH₂COCl with RhCl(CO)(PPh₃)₂ in the presence of ^{13}CO produced trans-CH₃CH=CHCH₂$^{13}COCl$, CH₃CH=CHCH₂Cl, and CH₃CH(Cl)CH=CH₂.[14] However, no rearranged acid chloride (CH₃CH($^{13}COCl$)CH=CH₂) was formed (confirmed by both ^1H and ^{13}C NMR spectroscopy). Similar reactions of CH₃CH(COCl)CH=CH₂ produced CH₃CH($^{13}COCl$)CH=CH₂, CH₃CH=CHCH₂Cl, and CH₃CH(Cl)CH=CH₂. Again, no rearranged acid chloride (CH₃CH=CHCH₂$^{13}COCl$) was formed. For (a) to be true, the 1,3-Rh shift must be competitive with product formations from 1-Rh and 3-Rh to account for the direct formation of 1- and 3-chlorobutenes at low temperatures. Since we observe the ^{13}CO labeling and the formation of decarbonylation products, starting from either acid chloride, without observing the rearranged acid chloride, we conclude that there cannot be any rearranged (η^1-allyl)Rh intermediates in the course of these decarbonylation reactions, i.e., no 3-Rh in the reaction of CH₃CH=CHCH₂COCl and no 1-Rh in the reaction of CH₃CH(COCl)CH=CH₂. Thus, (a) is ruled out.

(2) In (b), the product formation is not a simple coupling of R,Cl from Rh but is instead a nucleophilic attack of chloride at the 1- or 3-position in the η^1-allyl ligand with Rh as the leaving group. One would expect that γ-methyl substitution in the allyl system would increase the S_N2/S_N2' ratio whereas α-methyl substitution would decrease the S_N2/S_N2' ratio, as has been observed in nucleophilic substitution reactions of γ- and α-methylallyl chlorides.[15] However, the observed product distributions in these decarbonylation reactions show just the opposite trend: trans- and cis-CH₃CH=CHCH₂COCl (γ-methyl substitution) gave "S_N2/S_N2'" ratios of 1/50 and 1/2, respectively, and CH₃CH(COCl)CH=CH₂ (α-methyl substitution) gave an "S_N2/S_N2'" ratio of 3.5/1. Therefore, (b) is not satisfactory.

(3) The formation of an (η^3-allyl)Rh intermediate requires loss of one of the ligands (PPh₃, CO, or Cl⁻). It has been shown that added free PPh₃ does not affect the rates of the decomposition of RhCl₂(CO)(benzyl)L₂ and RhCl₂(CO)(styryl)L₂ to give the corresponding decarbonylation products.[8a,16] The ^{13}CO-labeling experiments require that CO be labile, yet the decarbonylation product RCl is usually not formed.[8c,9a,17] Therefore, dissociation of PPh₃ or CO does not induce the RCl formation. On the other hand, the ionization of chloride can easily accommodate the formation of an (η^3-allyl)Rh⁺ intermediate. Exactly this process has been observed in a similar Ir complex.[18] Attacks of Cl⁻ at both ends of (η^3-allyl)Rh⁺ lead naturally to the scrambling of regiochemistry of Cl in the product allyl chloride, with the reactions at the more substituted position (secondary carbon) being favored over those at the less substituted position (primary carbon.)[19] This proposal is quite consistent with the previously observed solvent effects (the formation of benzyl chloride is much faster in chloroform or acetonitrile than in benzene).[9a,20,21] It is also consistent with a previous kinetic study which showed that the ionization of chloride from RhCl₂(CO)(styryl)L₂ is the rate-determining step in the decomposition of this complex to give the decarbonylation product.[8a,22]

(13) The reaction was done in CDCl₃ at room temperature. Some ^1H absorptions of RhCl₂(COCH(CH₃)CH=CH₂)(PPh₃)₂ (δ 4.08, quintet, the methine proton; δ 4.54, d, ^3J = 17.1 Hz, the terminal vinyl proton trans to the geminal vinyl proton) overlap with ^1H absorptions of the products (cis-CH₃CH=CHCH₂Cl, δ 4.09, d, ^3J = 7.4 Hz; trans-CH₃CH=CHCH₂Cl, δ 4.00, d, ^3J = 6.6 Hz; CH₃CH(Cl)CH=CH₂, δ 4.50, quintet). The formation of decarbonylation products was followed by the signals δ 1.58 (d, ^3J = 6.7 Hz, CH₃CH(Cl)CH=CH₂) and δ 1.71 (d, ^3J = 6.4, CH₃CH=CHCH₂Cl, both cis and trans). Therefore, the 3-Cl/1-Cl ratio could be readily determined, but the cis/trans ratio in 1-Cl products could not be determined until late stages of the reaction when the amount of RhCl₂(COCH(CH₃)CH=CH₂)(PPh₃)₂ decreased to the point to allow clear observations of δ 4.09 (d) vs δ 4.00 (d). At 4 h when the decarbonylation was 68% complete, the ratio δ 4.09/δ 4.00 was about 4/1. The ratio δ 4.09/δ 4.00 decreased with time, due to secondary isomerizations cis → trans. Finally the ratio δ 4.09/δ 4.00 became 1/2. Therefore, the actual cis-1-Cl/trans-1-Cl ratio must be >4.
(14) (a) For more information on the ^{13}CO-labeling experiment, see ref 8c and 9a. Reactions were done in CDCl₃, at 110 °C (to induce reactions of the acid chlorides with RhCl(CO)(PPh₃)₂). At this temperature the decarbonylation products (cis- and trans-CH₃CH=CHCH₂Cl and CH₃CH(Cl)CH=CH₂) are fully equilibrated (3-Cl/1-Cl was about 1/2 and cis-1-Cl/trans-1-Cl was about 1/5).[14b] Therefore, the product ratios do not have mechanistic significance. (b) Kharasch, M. S.; Kritchevsky, J.; Mayo, F. R. J. Org. Chem. 1938, 2, 489–496.

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(17) The observed retention of structure in the ^{13}CO-labeling experiments shows that an (η^3-allyl)Rh complex cannot be an intermediate in the labeling process. If an (η^3-allyl)Rh complex were formed irreversibly, no labeling would occur. If an (η^3-allyl)Rh complex were formed reversibly, both labeled acid chlorides would be formed. Therefore, the loss of CO cannot be the route to the (η^3-allyl)Rh intermediate.
(18) A similar (η^1-allyl)Ir complex, Ir(Cl)(X)(CO)(CH₂CH=CH₂)L₂ (X = halide), forms the corresponding (η^3-allyl)Ir⁺ complex upon ionization of X, and the structure of the (η^3-allyl)Ir⁺ complex thus obtained has been determined from X-ray data: (a) Deeming, A. J.; Shaw, B. L. J. Chem. Soc. A 1969, 1562–1567. (b) Kaduk, J. A.; Poulos, A. T.; Ibers, J. A. J. Organomet. Chem. 1977, 127, 245–260.
(19) It is interesting to compare this observation with the literature report which showed that nucleophilic attacks at more substituted positions in (η^3-allyl)Pd systems (with PPh₃ ligands) are the dominant route: Åkermark, B.; Krakenberger, B.; Hansson, S. Organometallics 1987, 6, 620–628. See also ref 4b.
(20) Stille, J. K.; Fries, R. W. J. Am. Chem. Soc. 1974, 96, 1514–1518.
(21) The ^{13}CO incorporation in PhCH₂COCl proceeds at about the same rate in chloroform and benzene.[9a] Since the rate of ^{13}CO labeling is not affected by the solvent change, but the rate of benzyl chloride formation is, the solvent effect is not on the oxidative-addition or alkyl-migration steps and must be on the benzyl chloride formation step; i.e., the ionization of chloride is faster in chloroform or acetonitrile than in benzene.
(22) Two more examples of the rate-determining ionization of halide from octahedral metal complexes are as follows: (a) Chloride ionization is the rate-determining step in the cis/trans isomerization of the similar Ir complex IrCl₂(CO)(R)L₂: Bennett, M. A.; Jeffery, J. C. Inorg. Chem. 1980, 19, 3763–3767. (b) Iodide ionization is the rate-determining step in the formation of iodobenzene from PtI₂(Ph)₂L₂: Ettorre, R. Inorg. Nucl. Chem. Lett. 1969, 5, 45–49.

Scheme I
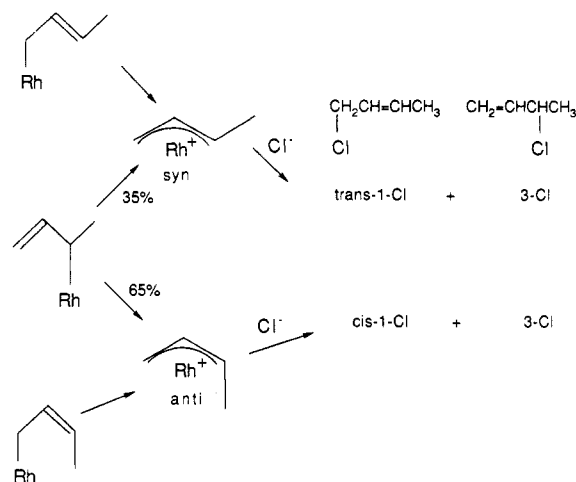
The regiochemical distribution of products (3-Cl/1-Cl) from $CH_3CH(COCl)CH=CH_2$ is consistent with that predicted from 3-Cl/1-Cl ratios from *trans*-$CH_3CH=CHCH_2COCl$ (50/1, via the *syn*-(η^3-1-methylallyl)Rh intermediate) and *cis*-$CH_3CH=CHCH_2COCl$ (2/1, via the *anti*-(η^3-1-methylallyl)Rh intermediate): $CH_3CH(COCl)$-$CH=CH_2$ forms approximately 35/65 *syn*-/*anti*-(η^3-1-methylallyl)Rh intermediates to give the observed 3-Cl/1-Cl ratio of 3.5/1 (Scheme I).[23] Although we do not have the clear experimental cis/trans ratio in the 1-Cl product, the observation of more cis 1-Cl product is certainly consistent with the analysis.[23]

In summary, we have provided conclusive evidence that there cannot be any rearranged (η^1-allyl)Rh intermediates during the reaction in which the regiochemistry of chlorine is lost in the formation of allyl chlorides from β,γ-unsaturated acid chlorides. The observed 1,3-scrambling of chlorine is best explained by Cl⁻ attacks at the 1- and 3-positions of an (η^3-allyl)Rh⁺ intermediate[24] to form the 1- and 3-chloro products. This conclusion may shed some light on the general question of (η^3-allyl)M vs (η^1-allyl)M as reactive intermediates in similar reactions of other (allyl)M systems. In addition, these results provide clear evidence that the formation of RCl from the decarbon-

ylations of RCOCl in the so-called "reductive elimination" step is not a simple coupling of R,Cl from Rh, as has been indicated in a number of literature reports.[16b,29]

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(26) (a) As reported in ref 8a, the rate of decomposition of $RhCl_2$-$(CO)(styryl)(PPh_3)_2$ in the presence of excess PPh_3 is proportional to $k_2[PPh_3]/(k_{-1}[Cl^-] + k_2[PPh_3])$, where k_{-1} is the rate constant of Cl⁻ returning to (Rh–R)⁺ at Rh and k_2 is the rate constant of nucleophilic attack by PPh_3 at carbon to form the decarbonylation product. In the absence of other nucleophiles, this term becomes $k_2/(k_{-1} + k_2)$. Vinyl and aryl are poor substrates for substitution reactions, so that k_2 is much smaller than k_2 for substitutions at methyl. Therefore, the overall rate of formation of methyl chloride is much greater than that of vinyl or aryl chloride. (b) Nucleophilic attacks of halide at the α-carbon in alkyl ligands in cationic metal complexes (preformed by oxidation of the corresponding neutral complexes) have been well-established in the literature.[27,28] Thus, it seems that nucleophilic substitutions of chloride at the α-carbon in metal–R complexes is common in cleavages of metal–carbon bond.

(27) (a) Sanderson, L. J.; Baird, M. C. *J. Organomet. Chem.* 1986, *307*, C1–C4. (b) Rogers, W. N.; Page, J. N.; Baird, M. C. *Inorg. Chem.* 1981, *20*, 3521–3528.

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(29) Weinberg, E. L.; Baird, M. C. *J. Organomet. Chem.* 1979, *179*, C61–C64.

Organometallic Clusters with Face-Capping Arene Ligands. 3.[†] [(β,α,1,2-η)-1-Vinylnaphthalene]cyclopentadienylcobalt and [μ_2-(1–3–6–η:4–6–η)-1,6-Diphenylhexatriene]bis(cyclopentadienylcobalt)(*Co–Co*): Model Compounds for Intermediates in the Synthesis of (CpCo)$_3$[μ_3-(η^2:η^2:η^2)-arene] Clusters

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Summary: Reaction of 1-phenylbuta-1,3-diene (**3a**), 1,4-diphenylbuta-1,3-diene (**3b**), and 1,6-diphenylhexa-1,3,5-triene (**5**) with CpCo(C_2H_4)$_2$ (**2**) results in the complexes CpCo(η^4-CHR=CHCH=CHR') (R = H, R' = Ph, **4a**; R = R' = Ph, **4b**; R = Ph, R' = CH=CHPh, **6**). **6** reacts further with **2** to give (CpCo)$_2$[μ_2-(1–3–η:4–6–η)-1,6-diphenylhexatriene] (**7**) with a *syn*-(CpCo)$_2$[bis(enyl)] structure. From 1-vinylnaphthalene and **2** CpCo[(β,-α,1,2-η)-1-vinylnaphthalene] (**11**) is obtained. **7** and **11** are model compounds for mono- and dinuclear intermediates in the synthesis of (CpCo)$_3$[μ_3-(η^2:η^2:η^2)-arene] clusters.

We have recently published a simple high yield synthetic route to a novel class of transition-metal clusters with face-capping arene ligands.[1] The compounds (CpCo)$_3$-[μ_3-(η^2:η^2:η^2)-arene] [arene = α- and β-methylstyrene (**1a,b**), *o*-, *m*-, and *p*-methyl-β-methylstyrene (**1c–e**), stilbene (**1f**),

(23) The 50/1 ratio of 3-Cl/*trans*-1-Cl products from *trans*-$CH_3CH=CHCH_2COCl$ must be the product distribution from the *syn*-(η^3-1-methylallyl)Rh⁺ intermediate. Similarly, the 2/1 ratio of 3-Cl/*cis*-1-Cl products from *cis*-$CH_3CH=CHCH_2COCl$ must be the product distribution from the *anti*-(η^3-1-methylallyl)Rh⁺ intermediate. However, CH_3C-H(COCl)CH=CH$_2$ can form both *syn*- and *anti*-(η^3-1-methylallyl)Rh⁺ intermediates. Partition between *syn*- and *anti*-(η^3-1-methylallyl)Rh⁺ intermediates must lead to a product distribution between 50/1 and 2/1. It can be calculated that decarbonylations of $CH_3CH(COCl)CH=CH_2$ via 35/65 *syn*-/*anti*-(η^3-1-methylallyl)Rh⁺ intermediates (35% is the upper limit for the syn intermediate) will give the observed 3.5/1 ratio of 3-Cl/1-Cl products. In addition, the cis/trans ratio in $CH_3CH=CHCH_2Cl$ should be approximately 31/1.

(24) The formation of a (η^3-allyl)Rh⁺ intermediate in the rate-determining step suggests a way to understand the reactivity sequence we have observed. The rate of the product formation from decarbonylations of RCOCl follows the sequence

R = allyl > benzyl > methoxymethyl ≫ methyl ≫ vinyl, aryl[8,9,25]

Thus for allyl, benzyl, and methoxymethyl (substrates having electron pairs at β-positions), the ionization of chloride is much faster because of the participation and assistance of the electron pair. This proposal is also consistent with the fairly large negative entropy of activation (–12.2 eu) observed for the benzyl chloride formation step in the decarbonylation of phenylacetyl chloride.[9b] For methyl, vinyl, and aryl (substrates not having electron pairs at β-positions), the ionization of chloride is much slower. The formation of methyl chloride is faster than that of vinyl or aryl chlorides because the last two are poor substrates for nucleophilic substitutions.[26]

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