Facile Formation of Chloro $-\eta^3$ -Allyl Complexes by Reaction of Vinyldiazoacetates and Ruthenium(II) Arene Complexes

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Summary: The reaction of vinyldiazoacetates **1** and ruthenium arene complexes **2** at room temperature resulted in the formation of a new type of chlorosubstituted η^3 -allyl ruthenium complexes, **3**, in high yield. The structure of **3a** was determined by X-ray crystallographic analysis. The reaction of the ruthenium complexes **3a**, **d** with styrene demonstrated that these complexes are capable of inducing a cyclopropanation reaction.

Introduction

The rhodium-catalyzed reactions of vinyldiazoacetates with olefins has been well-developed as a general method for the stereoselective synthesis of cyclopropanes and cyclopentenes, and these reactions are believed to proceed via metal carbenoids.^{1,2} The Nishiyama group has investigated the carbenoid reactions and the carbene complexes derived from the reaction of various ruthenium species with diazoacetates and diazomalonates.^{3,4} In this paper, we disclose our studies on the reaction of several vinyldiazoacetates **1** with ruthenium arene complexes **2**, which resulted in the unexpected formation of novel η^3 -allyl ruthenium complexes **3**.



Results and Discussion

Reaction of the vinyldiazoacetate **1a** and the $(\eta^{6}$ benzene)ruthenium complex 2a in dichloromethane at room temperature produced the new complex 3a (Scheme 1). The reaction was monitored by TLC, which showed the appearance of a new yellow spot. Purification by column chromatography gave a yellow solid, which on the basis of NMR analysis appeared to consist of two stereoisomers (ca. 94:6). X-ray crystallographic analysis of the main isomer demonstrated that it was not the anticipated ruthenium carbenoid complex. Instead, the quite unusual 1-chloro-substituted η^3 -allyl ruthenium complex **3a** was formed with a Cl (syn) and CO_2Me (anti) arrangement on the C1 carbon atom (Figure 1, Tables 1 and 2).⁵ Probably, the minor product is the isomer with Cl (anti) and CO₂Me (syn), but this cannot be fully characterized because the minor isomer was not isolated in pure form. When the (*p*-cymene)ruthenium

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Figure 1. Molecular structure of **3a** showing 30% thermal ellipsoids.

Table 1. Crystal Data and Structure RefinementDetails of 3a

empirical formula	$C_{13}H_{14}O_4Cl_2Ru$
fw	406.22
cryst dimens	$0.05 \times 0.2 \times 0.3 \text{ mm}$
cryst syst	monoclinic
space group	C2/c (No. 15)
lattice params	
а	19.333(2) Å
b	7.754(2) Å
С	19.931(2) Å
eta	100.689(7)°
V	2935.7(9) Å ³
Ζ	8
density (calcd)	1.838 g/cm ³
F_{000}	1688.00
μ(Μο Κα)	14.40 cm^{-1}
$2 heta_{ m max}$	55°
no. of rflns	
measd	3727
unique	$3619 \ (R_{\rm int} = 0.02)$
no. of observns ($I > 3.00\sigma(I)$)	2143
no. of variables	181
rfln/param ratio	11.84
residuals: R ; R_w	0.047; 0.050
goodness of fit indicator	1.21

Table 2. Selected Bond Lengths (Å) and Angles (deg) of 3a

Bond Lengths (Å)			
Ru-Cl(1)	2.399(2)	C(1)-C(2)	1.43(1)
Ru-C(1)	2.175(7)	C(2)-C(3)	1.42(1)
Ru-C(2)	2.137(7)	C(3)-C(6)	1.50(1)
Ru-C(3)	2.207(7)	C(1)-C(4)	1.51(1)
Cl(2) - C(1)	1.776(8)		
Bond Angles (deg)			
Cl(1)-Ru-C(1)	88.9(2)	C(2)-Ru-C(3)	38.0(3)
Cl(1)-Ru-C(2)	106.2(2)	C(1)-C(2)-C(3)	117.9(7)
Cl(1)-Ru-C(3)	86.0(2)	C(2) - C(1) - C(4)	125.8(7)
C(1)-Ru-C(2)	38.9(3)	C(2) - C(3) - C(6)	116.1(7)
C(1)-Ru-C(3)	67.8(3)	C(2)-C(1)-Cl(2)	114.6(6)

complex **2b** was treated with **1a**, a very fast reaction was observed to give the corresponding η^3 -allyl ruthenium complex **3b** within 1 h. In a similar manner, vinyldiazo compounds **1b**,**c** were also subjected to the reaction with **2a**,**b**, giving the complexes **3c**-**f**. In the case of vinyldiazoacetate **1c**, only a single stereoisomer was observed, probably attributed to the existence of an ester group at the C2 position.



A reasonable mechanism for the formation of the η^{3} allyl ruthenium complexes 3 is illustrated in Scheme 2 for the conversion of 1a + 2a to 3a. The first step is likely to be the nucleophilic addition of the vinyldiazoacetate 1a to the ruthenium complex 2a to form the monomeric betaine complex i. Coordination of the alkene moiety, giving the complex ii (path a), followed by spontaneous elimination of N₂ from ii would produce the η^3 -vinylcarbene species **iv**. Alternatively, **iv** may be generated via the η^1 -vinylcarbene complex **iii** (path **b**). Chloride ion attacks the carbene carbon atom in iv from the exo site to give syn-Cl and anti-CO2Me stereochemistry of the allylic moiety in **3a**. The intermediacy of the η^3 -vinylcarbene species **iv** would explain the stereochemical outcome of the chloride addition and why the incorporation of chloride is unique to the vinyldiazoacetate system. All of the intermediates described are reasonable structures, because they have coordinatively saturated 18-electron Ru(II) species.⁶ In this context, similar nucleophilic addition of hydride (H⁻) to the vinylcarbene moiety of tungsten complexes CpW(CO)2-(vinylcarbene) was reported to be likely to form the corresponding η^3 -allylic complexes.⁷

Preliminary studies have also been carried out on the reactivity of the η^3 -allyl ruthenium complexes. Heating of the complex **3b** with styrene at 70–100 °C generated a mixture of the corresponding cyclopropanes **4** in 54% yield (Scheme 3; *trans:cis* = 50:50). Similarly, the cyclopropanes from **3d** were also obtained, but in a lower yield (20%, *trans:cis* = 50:50). Interestingly, the diastereoselectivity of these cyclopropanations is quite different from that observed in the rhodium-catalyzed reactions; for example, Rh₂(OAc)₄ (1 mol %), styrene (5 equiv with respect to vinyldiazoacetate), and CH₂Cl₂ (at reflux) give the corresponding vinylcyclopropane products in 96% yield (*trans:cis* = 89:11) from (*E*)-C(N₂)(CO₂-Et)CH=CHCO₂Et.⁸ These facts indicate that the reverse route (**3** \rightarrow **iv** \rightarrow **iii**) may be feasible at higher temper-

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atures, as the carbene complex **iii** would be an active species expected to undergo a cyclopropanation reaction with styrene.

In summary, we have discovered a facile method for the preparation of chloro-substituted η^3 -allyl ruthenium complexes by using vinyldiazoacetates. These η^3 -allyl ruthenium complexes are capable of undergoing cyclopropanations, presumably via vinylcarbene ruthenium intermediates. These findings give useful information for the further development of metal carbenoid chemistry and catalysis.

Experimental Section

General Considerations. The vinyldiazoacetates 1 were synthesized from commercially available trans-glutaconic acid (Aldrich), trans-styrylacetic acid (Aldrich), and trans-aconitic acid (Tokyo Kasei) in two steps: methyl esterification with orthoformate in methanol catalyzed by a few drops of concentrated H₂SO₄ followed by transformation to the corresponding diazoacetates with 4-acetamidobenzenesulfonyl azide9 (ABSA) (Aldrich) and 1,8-diazabicyclo[5.4.0]-7-undecene (DBU) in CH₃-CN. See the Supporting Information for the procedure and spectroscopic data. ¹H and ¹³C NMR spectra were measured on Varian Inova-400 and Mercury-300 spectrometers. IR spectra were measured on a Jasco FT/IR-230 spectrometer. Melting points were measured on a Yanaco MP-J3. Elemental analyses were measured on a Yanaco CHN Corder, Model MT-6. Column chromatography was performed with silica gel (Merck, Art. No. 7734). Analytical thin-layer chromatography (TLC) was performed on glass plates with silica gel (Merck, Art. No. 5715).

 $Ru(C_6H_6)[\eta^3$ -CCl(CO₂Me)CH=CH(CO₂Me)]Cl (3a). In a 20 mL flask were placed $[Ru(C_6H_6)Cl_2]_2$ (79.5 mg, 0.159 mmol) and the vinyldiazoacetate 1a (58.0 mg, 0.315 mmol) under an argon atmosphere. CH₂Cl₂ (6 mL) was then added. The mixture was stirred at room temperature for 48 h; TLC: $R_f =$ 0.53 (CH₂Cl₂:MeOH = 10:1) for the product and $R_f = 0.83$ for 1a. After concentration, the residue was purified by silica gel column chromatography (SiO₂, 10 g; CH₂Cl₂/MeOH as eluent) and a yellow band was collected to give yellow solids (105 mg, 0.26 mmol, 81%); mp 179-180 °C dec. IR (KBr disk): v 1720, 1703, 1275 cm⁻¹. ¹H NMR (400 MHz, CDCl₃, TMS): δ 3.55 (d, J = 10.0 Hz, 1H), 3.62 (s, 3H), 3.82 (s, 3H), 5.75 (s, 6H), 5.77 (d, J = 10.0 Hz, 1H); ca. 6% of the stereoisomer was obtained, 3.57 (d, J = 10.3 Hz, 1H), 3.84 (s, 3H), 3.93 (s, 3H), 5.71 (s, 6H), 6.26 (d, J = 10.3 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃, TMS): δ 52.31, 52.94, 61.02, 78.96, 86.03, 92.15, 166.62, 174.34. Anal. Calcd for C13H14Cl2O4Ru: C, 38.44; H, 3.47. Found: C, 38.17; H, 3.37.

 $Ru(p-MeC_6H_4-i-Pr)[\eta^3-CCl(CO_2Me)CH=CH(CO_2Me)]$ -**Cl** (3b). $[Ru(p-MeC_6H_4-i-Pr)Cl_2]_2$ (91.9 mg, 0.150 mmol) and vinyldiazoacetate 1a (58.0 mg, 0.315 mmol) were reacted in CH_2Cl_2 (4 mL) at room temperature for 1 h. TLC: $R_f = 0.76$ (CH₂Cl₂:EtOAc = 10:1) for the product and $R_f = 0.81$ for **1a**. After concentration, the residue was purified by silica gel column chromatography (SiO₂, 10 g; CH₂Cl₂/EtOAc as eluent) and a yellow band was collected to give yellow solids (133 mg, 0.288 mmol, 96%); mp 137-138 °C dec. IR (KBr disk): v 1722, 1700, 1275, 1195, 1190 cm⁻¹. ¹H NMR (400 MHz, CDCl₃, TMS): δ 1.29 (d, J = 6.8 Hz, 3H), 1.35 (d, J = 6.8 Hz, 3H), 2.25 (s, 3H), 2.85 (m, 1H), 3.52 (d, J = 10.0 Hz, 1H), 3.58 (s, 3H), 3.80 (s, 3H), 5.23 (dd, J = 6.0, 0.8 Hz, 1H), 5.27 (dd, J =5.6, 1.2 Hz, 1H), 5.35 (dd, J = 6.0, 0.8 Hz, 1H), 5.43 (dd, J = 5.6, 1.2 Hz, 1H), 5.56 (d, J = 10.0 Hz, 1H) ppm; <ca. 9% of the stereoisomer, 6.18 (d, J = 10.1 Hz) ppm. ¹³C NMR (100 MHz, CDCl₃, TMS): δ 16.34, 22.66, 22.97, 29.39, 51.66, 51.79, 61.10, 77.38, 84.70, 88.74, 88.92, 89.30, 90.89, 109.06, 118.77, 167.09, 173.90. Anal. Calcd for C17H22Cl2O4Ru: C, 44.16; H, 4.80. Found: C, 44.24; H, 4.84.

 $Ru(C_6H_6)[\eta^3$ -CCl(CO₂Me)CH=CHPh]Cl (3c). [Ru(C₆H₆)- Cl_2 (50.0 mg, 0.10 mmol) and vinyldiazoacetate **1b** (48.5 mg, 0.24 mmol) were reacted in CH₂Cl₂ (6 mL) at room temperature for 48 h. TLC: $R_f = 0.60$ (CH₂Cl₂:acetone = 5:1) for the product and $R_f = 0.84$ for **1b**. After concentration, the residue was purified by silica gel column chromatography (SiO₂, 13.5 g; CH₂Cl₂/acetone as eluent) and a yellow band was collected to give yellow solids (72.9 mg, 0.17 mmol, 86%); mp 153-154 °C dec. IR (KBr disk): v 1714, 1433, 1297, 1206 cm⁻¹. ¹H NMR (400 MHz, CDCl₃, TMS): δ 3.68 (s, 3H), 4.88 (d, J = 11.7 Hz, 1H), 5.42 (s, 6H), 5.67 (d, J = 11.7 Hz, 1H), 7.3–7.4 (m, 5H) ppm; <ca. 9% of the stereoisomer, 3.95 (s), 4.99 (d, J = 11.8Hz), 5.32 (s), 6.17 (d, J = 11.8 Hz) ppm. ¹³C NMR (100 MHz, CDCl₃, TMS): δ 51.98, 79.37, 80.93, 83.04, 90.94, 126.19, 128.00, 129.08, 140.25, 167.75. Anal. Calcd for C17H16Cl2O2-Ru: C, 48.12; H, 3.80. Found: C, 48.05; H, 3.95.

 $Ru(p-MeC_6H_4-i-Pr)[\eta^3-CCl(CO_2Me)CH=CHPh]Cl (3d).$ [Ru(p-MeC₆H₄-i-Pr)Cl₂]₂ (91.9 mg, 0.150 mmol) and vinyldiazoacetate 1b (72.8 mg, 0.36 mmol) were reacted in CH₂Cl₂ (2 mL) at room temperature for 2 h. TLC: $R_f = 0.61$ (CH₂Cl₂: acetone = 10:1) for the product and $R_f = 0.88$ for **1b**. After concentration, the residue was purified by silica gel column chromatography (SiO₂, 35 g; CH₂Cl₂/acetone as eluent) and a yellow band was collected to give yellow solids (138 mg, 0.29 mmol, 96%); mp 127-128 °C dec. IR (KBr disk): v 1718, 1435, 1297, 1202 cm⁻¹. ¹H NMR (300 MHz, CDCl₃, TMS): δ 1.18 (d, J = 6.9 Hz, 3H), 1.33 (d, J = 6.9 Hz, 3H), 1.56 (s, 3H), 2.50 (m, 1H), 3.65 (s, 3H), 4.64 (dd, J = 6.0, 0.9 Hz, 1H), 4.73 (d, J= 11.7 Hz, 1H), 4.93 (dd, J = 6.9 Hz, 0.9 Hz, 1H), 5.29 (dd, J = 6.9 Hz, 0.9 Hz, 1H), 5.32 (dd, J = 6.9 Hz, 0.9 Hz, 1H), 5.36 (d. J = 11.7 Hz, 1H), 7.27–7.40 (m, 5H) ppm; <ca. 6% of the stereoisomer, 6.02 (d, J = 10.0 Hz) ppm. ¹³C NMR (75 MHz, CDCl₃, TMS): *δ* 15.41, 22.04, 23.45, 29.01, 52.85, 77.46, 78.29, 83.98, 86.46, 89.12, 92.21, 108.30, 117.79, 126.49, 127.37, 129.19, 129.22, 138.98, 168.16. Anal. Calcd for C₂₁H₂₄Cl₂O₂-Ru: C, 52.50; H, 5.04. Found: C, 52.34; H, 5.07.

Ru(C₆H₆)[η³-CCl(CO₂Me)C(CO₂Me)=CH(CO₂Me)]Cl (3e). [Ru(C₆H₆)Cl₂]₂ (35.0 mg, 0.07 mmol) and vinyldiazoacetate 1c (36.3 mg, 0.15 mmol) were reacted in CH₂Cl₂ (4 mL) at room temperature for 48 h. TLC: R_f = 0.64 (CH₂Cl₂:acetone = 5:1) for the product and R_f = 0.88 for 1c. After concentration, the residue was purified by silica gel column chromatography (SiO₂, 8 g; CH₂Cl₂/acetone as eluent) and a yellow band was collected to give yellow solids (49.2 mg, 0.11 mmol, 76%); mp 179–181 °C dec. IR (KBr disk): ν 1748, 1715, 1445, 1238 cm⁻¹. ¹H NMR (400 MHz, CDCl₃, TMS): δ 3.46 (s, 1H), 3.63 (s, 3H), 3.79 (s, 3H), 3.86 (s, 3H), 6.00 (s, 6H) ppm; no stereoisomer was observed. ¹³C NMR (100 MHz, CDCl₃, TMS): δ 52.13, 52.31, 52.44, 54.19, 75.23, 95.79, 97.42, 166.28, 166.92, 174.02. Anal. Calcd for C₁₅H₁₆Cl₂O₆Ru: C, 38.81; H, 3.47. Found: C, 38.80; H, 3.46.

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 $Ru(p-MeC_6H_4-i-Pr)[\eta^3-CCl(CO_2Me)C(CO_2Me)=CH-$ (CO₂Me)]Cl (3f). [Ru(p-MeC₆H₄-*i*-Pr)Cl₂]₂ (15.3 mg, 0.025 mmol) and vinyldiazoacetate 1c (13.3 mg, 0.055 mmol) were reacted in CH₂Cl₂ (0.5 mL) at room temperature for 1 h. TLC: $R_f = 0.55$ (CH₂Cl₂:EtOAc = 10:1) for the product and $R_f = 0.74$ for 1c. After concentration, the residue was purified by silica gel column chromatography (SiO2, 6 g; CH2Cl2/EtOAc as eluent) and a yellow band was collected to give yellow solids (24.5 mg, 0.047 mmol, 94%): mp 129-130 °C dec. IR (KBr disk): v 1750, 1713, 1448, 1229 cm⁻¹. ¹H NMR (400 MHz, CDCl₃, TMS): δ 1.29 (d, J = 6.8 Hz, 3H), 1.37 (d, J = 6.8 Hz, 3H), 2.29 (s, 3H), 2.85 (m, 1H), 3.47 (s, 1H), 3.60 (s, 3H), 3.79 (s, 3H), 3.85 (s, 3H), 5.46 (d, J = 5.6 Hz, 1H), 5.58 (d, J = 5.58Hz, 1H), 5.59 (d, J = 5.58 Hz, 1H), 5.69 (d, J = 5.6 Hz, 1H) ppm; no stereoisomer was observed. ¹³C NMR (100 MHz, CDCl₃, TMS): δ 16.44, 22.54, 22.79, 29.41, 51.77, 51.80, 53.96, 56.79, 73.55, 91.27, 91.71, 91.91, 94.17, 95.21, 114.02, 122.47, 166.63, 167.40, 173.22. Anal. Calcd for C19H24Cl2O6Ru: C, 43.85; H, 4.65. Found: C, 43.83; H, 4.61.

Crystallographic Structure Determination of 3a. A single orange prismatic crystal ($0.05 \times 0.2 \times 0.3$ mm) was obtained by recrystallization from CH₂Cl₂/*n*-hexane. The intensity data ($2\theta < 55.0^{\circ}$, $\omega - 2\theta$ scan technique) were collected on a Rigaku AFC-7R diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.710$ 69 Å), and the structure was solved by direct methods (SAPI91). The final cycle of refinement was based on 2143 observed reflections ($I > 3.00\sigma(I)$) and 181 variable parameters and converged with R = 4.7% and $R_w = 5.0\%$. Relevant data are listed in Table 1.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (No. CCDC-179396). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CD21EZ, U.K. (e-mail, deposit@ccdc.cam.ac.uk; web, http://www.ccdc.cam.ac.uk/).

Reaction of 3b with Styrene. A mixture of **3b** (69.3 mg, 0.15 mmol) and styrene (0.17 mL, 1.5 mmol) in toluene (0.7 mL) and ClCH₂CH₂Cl (0.7 mL) was heated to 70–100 °C for 13 h. After concentration, the residue was purified by column chromatography with ether—hexane as eluent to give the oily product **4** (21.2 mg, 0.081 mmol) in 54% yield. The trans:cis ratio was determined by ¹H NMR: olefinic part, *trans* δ 6.63 (d, J = 15.9 Hz, 0.50H), *cis* δ 5.82 (d, J = 15.9 Hz, 0.50H) ppm.

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Supporting Information Available: Tables of atomic coordinates and anisotropic displacement parameters, bond lengths, and torsion angles for **3a**, figures and tables giving molecular structures and atomic coordinates for **3b,f**, and text detailing the preparation of vinyldiazoacetates. This material is available free of charge via the Internet at http://pubs.acs.org.

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