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Facile Formation of Chloro–η^3-Allyl Complexes by Reaction of Vinyldiazoacetates and Ruthenium(II) Arene Complexes

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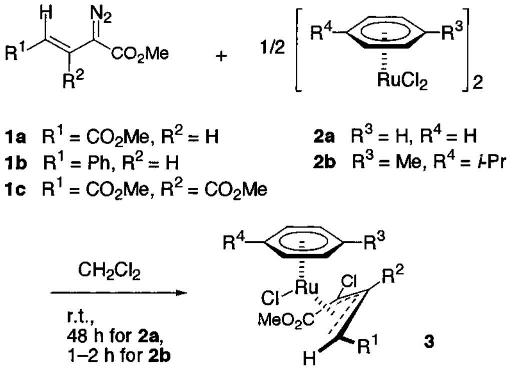
Summary: The reaction of vinyldiazoacetates ***1*** *and ruthenium arene complexes* ***2*** *at room temperature resulted in the formation of a new type of chloro-substituted* η^3*-allyl ruthenium complexes,* ***3****, in high yield. The structure of* ***3a*** *was determined by X-ray crystallographic 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**.

Scheme 1



	R^1	R^2	R^3	R^4	yield (%)
3a	CO_2Me	H	H	H	81
3b	CO_2Me	H	Me	*i*-Pr	96
3c	Ph	H	H	H	86
3d	Ph	H	Me	*i*-Pr	96
3e	CO_2Me	CO_2Me	H	H	76
3f	CO_2Me	CO_2Me	Me	*i*-Pr	94

Results and Discussion

Reaction of the vinyldiazoacetate **1a** and the (η^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 CO_2Me (*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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(1) Davies, H. M. L. *Curr. Org. Chem.* **1998**, *2*, 463. Davies, H. M. L. *Advances in Cycloaddition*; Harmata, M., Ed.; JAI Press: New York, 1999; Vol. 5, p 119. Selected papers: Davies, H. M. L.; Bruzinski, P. R.; Lake, D. H.; Kong, N.; Fall, M. J. *J. Am. Chem. Soc.* **1996**, *118*, 6879. Davies, H. M. L.; Hansen, T. *J. Am. Chem. Soc.* **1997**, *119*, 9075. Davies, H. M. L.; Xiang, B.; Kong, N.; Stafford, D. G. *J. Am. Chem. Soc.* **2001**, *123*, 7461.

(2) Doyle, M. P.; McKervey, M. A.; Ye, T. *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds*; Wiley: New York, 1998. Davies, H. M. L.; Antoulinakis, E. G. *Organic Reactions*; Overman, L. E., Ed.; Wiley: New York, 2001; Vol. 57, p 1.

(3) Nishiyama, H.; Itoh, Y.; Matsumoto, H.; Park, S.-B.; Itoh, K. *J. Am. Chem. Soc.* **1994**, *116*, 2223. Nishiyama, H.; Itoh, Y.; Sugawara, Y.; Matsumoto, H.; Park, S.-B.; Itoh, K. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 1247. Nishiyama, H.; Soeda, N.; Naito, T.; Motoyama, Y. *Tetrahedron: Asymmetry* **1998**, *9*, 2865. Iwasa, S.; Takezawa, F.; Tuchiya, Y.; Nishiyama, H. *Chem. Commun.* **2001**, 59. For vinylcarbene complexes of Ru, for example: Wu, Z.; Nguyen, S. T.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1995**, *117*, 5503. Schwab, P.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 100. Nishiyama, H.; Park, S.-B.; Itoh, K. *Chem. Lett.* **1995**, 599 and references therein.

(4) For (*arene*)ruthenium complex catalyzed cyclopropanations; see for example: Kücükbay, H.; Cetinkaya, B.; Guesmi, S.; Dixneuf, P. H. *Organometallics* **1996**, *15*, 2434. Simal, F.; Jan, D.; Demonceau, A.; Noels, A. F. *Tetrahedron Lett.* **1999**, *40*, 1653. Baratta, W.; Herrmann, W. A.; Kratzer, R. M.; Rigo, R. *Organometallics* **2000**, *19*, 3664.

(5) Maxwell, J. L.; Brown, K. C.; Bartley, D. W.; Kodadek, T. *Science* **1992**, *256*, 1544. An intermediate carbene species of the rhodium–porphyrin system was captured by iodine anion to form iodomethyl species in the absence of styrene.

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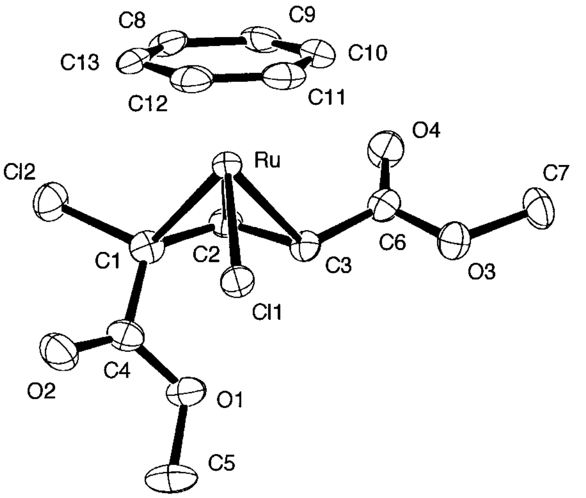


Figure 1. Molecular structure of **3a** showing 30% thermal ellipsoids.

Table 1. Crystal Data and Structure Refinement Details of 3a

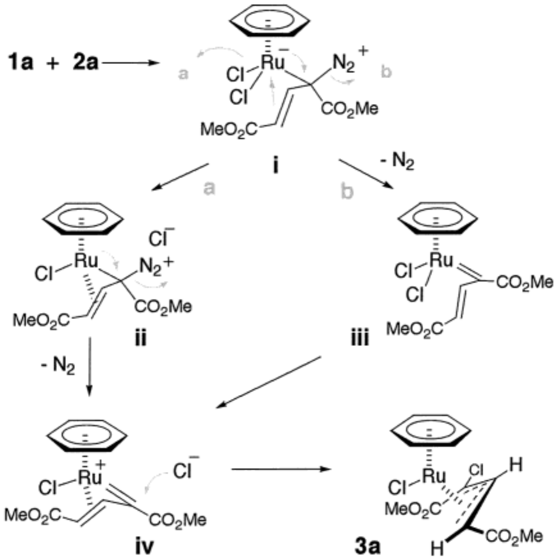
empirical formula	$C_{13}H_{14}O_4Cl_2Ru$
fw	406.22
cryst dimens	0.05 × 0.2 × 0.3 mm
cryst syst	monoclinic
space group	*C*2/*c* (No. 15)
lattice params	
a	19.333(2) Å
b	7.754(2) Å
c	19.931(2) Å
β	100.689(7)°
V	2935.7(9) $Å^3$
Z	8
density (calcd)	1.838 g/cm^3
F_{000}	1688.00
μ(Mo Kα)	14.40 cm^{-1}
$2\theta_{max}$	55°
no. of rflns	
measd	3727
unique	3619 ($R_{int} = 0.02$)
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.

Scheme 2



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 N_2 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*-CO_2Me 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, $Rh_2(OAc)_4$ (1 mol %), styrene (5 equiv with respect to vinyldiazoacetate), and CH_2Cl_2 (at reflux) give the corresponding vinylcyclopropane products in 96% yield (*trans*:*cis* = 89:11) from (*E*)-$C(N_2)(CO_2Et)CH{=}CHCO_2Et$.[8] These facts indicate that the reverse route (**3** → **iv** → **iii**) may be feasible at higher temper-

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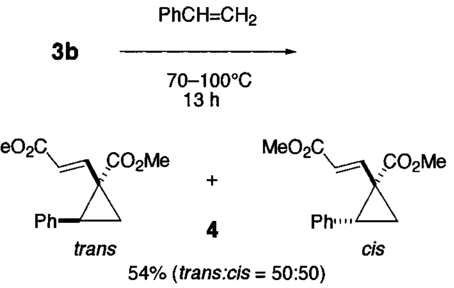
(6) Hofmann, P.; Hämmerle, M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 908. References for related metallacyclobutene MC_3H_4 systems derived from η^3-vinylcarbene moieties were cited therein.

(7) Garrett, K. E.; Sheridan, J. B.; Pourreau, D. B.; Feng, W. C.; Geoffroy, G. L.; Staley, D. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1989**, *111*, 8383. Mitsudo, T. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 1525.

Scheme 3



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 H_2SO_4 followed by transformation to the corresponding diazoacetates with 4-acetamidobenzenesulfonyl azide[9] (ABSA) (Aldrich) and 1,8-diazabicyclo[5.4.0]-7-undecene (DBU) in CH_3CN. See the Supporting Information for the procedure and spectroscopic data. ^1H and ^{13}C 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)[η^3-CCl(CO_2Me)CH=CH(CO_2Me)]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. CH_2Cl_2 (6 mL) was then added. The mixture was stirred at room temperature for 48 h; TLC: $R_f = 0.53$ (CH_2Cl_2:MeOH = 10:1) for the product and $R_f = 0.83$ for **1a**. After concentration, the residue was purified by silica gel column chromatography (SiO_2, 10 g; CH_2Cl_2/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): ν 1720, 1703, 1275 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 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. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 52.31, 52.94, 61.02, 78.96, 86.03, 92.15, 166.62, 174.34. Anal. Calcd for $C_{13}H_{14}Cl_2O_4Ru$: C, 38.44; H, 3.47. Found: C, 38.17; H, 3.37.

Ru(p-MeC_6H_4-i-Pr)[η^3-CCl(CO_2Me)CH=CH(CO_2Me)]Cl (3b). $[Ru(p\text{-}MeC_6H_4\text{-}i\text{-}Pr)Cl_2]_2$ (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: $R_f = 0.76$ (CH_2Cl_2:EtOAc = 10:1) for the product and $R_f = 0.81$ for **1a**. After concentration, the residue was purified by silica gel column chromatography (SiO_2, 10 g; CH_2Cl_2/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): ν 1722, 1700, 1275, 1195, 1190 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 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. ^{13}C NMR (100 MHz, $CDCl_3$, 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 $C_{17}H_{22}Cl_2O_4Ru$: C, 44.16; H, 4.80. Found: C, 44.24; H, 4.84.

Ru(C_6H_6)[η^3-CCl(CO_2Me)CH=CHPh]Cl (3c). $[Ru(C_6H_6)Cl_2]_2$ (50.0 mg, 0.10 mmol) and vinyldiazoacetate **1b** (48.5 mg, 0.24 mmol) were reacted in CH_2Cl_2 (6 mL) at room temperature for 48 h. TLC: $R_f = 0.60$ (CH_2Cl_2:acetone = 5:1) for the product and $R_f = 0.84$ for **1b**. After concentration, the residue was purified by silica gel column chromatography (SiO_2, 13.5 g; CH_2Cl_2/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): ν 1714, 1433, 1297, 1206 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 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 = 11.8 Hz), 5.32 (s), 6.17 (d, J = 11.8 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 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 $C_{17}H_{16}Cl_2O_2Ru$: C, 48.12; H, 3.80. Found: C, 48.05; H, 3.95.

Ru(p-MeC_6H_4-i-Pr)[η^3-CCl(CO_2Me)CH=CHPh]Cl (3d). $[Ru(p\text{-}MeC_6H_4\text{-}i\text{-}Pr)Cl_2]_2$ (91.9 mg, 0.150 mmol) and vinyldiazoacetate **1b** (72.8 mg, 0.36 mmol) were reacted in CH_2Cl_2 (2 mL) at room temperature for 2 h. TLC: $R_f = 0.61$ (CH_2Cl_2:acetone = 10:1) for the product and $R_f = 0.88$ for **1b**. After concentration, the residue was purified by silica gel column chromatography (SiO_2, 35 g; CH_2Cl_2/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): ν 1718, 1435, 1297, 1202 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, 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. ^{13}C NMR (75 MHz, $CDCl_3$, 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 $C_{21}H_{24}Cl_2O_2Ru$: C, 52.50; H, 5.04. Found: C, 52.34; H, 5.07.

Ru(C_6H_6)[η^3-CCl(CO_2Me)C(CO_2Me)=CH(CO_2Me)]Cl (3e). $[Ru(C_6H_6)Cl_2]_2$ (35.0 mg, 0.07 mmol) and vinyldiazoacetate **1c** (36.3 mg, 0.15 mmol) were reacted in CH_2Cl_2 (4 mL) at room temperature for 48 h. TLC: $R_f = 0.64$ (CH_2Cl_2:acetone = 5:1) for the product and $R_f = 0.88$ for **1c**. After concentration, the residue was purified by silica gel column chromatography (SiO_2, 8 g; CH_2Cl_2/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, $CDCl_3$, 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. ^{13}C NMR (100 MHz, $CDCl_3$, 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 $C_{15}H_{16}Cl_2O_6Ru$: C, 38.81; H, 3.47. Found: C, 38.80; H, 3.46.

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(8) Davies, H. M. L.; Clark, T. J.; Church, L. A. *Tetrahedron Lett.* **1989**, *30*, 5057. For asymmetric versions, see: Davies, H. M. L.; Huby, N. J. S.; Cantrell, W. R., Jr.; Olive, J. L. *J. Am. Chem. Soc.* **1993**, *115*, 9468. Davies, H. M. L.; Panaro, S. A. *Tetrahedron Lett.* **1999**, *40*, 5287 and related references cited in ref 1.

(9) Davies, H. M. L.; Cantrell, W. R., Jr.; Romines, K. R.; Baum, J. S. *Org. Synth.* **1991**, *70*, 93.

Ru(p-MeC$_6$H$_4$-i-Pr)[η^3-CCl(CO$_2$Me)C(CO$_2$Me)=CH-(CO$_2$Me)]Cl (3f). [Ru(p-MeC$_6$H$_4$-i-Pr)Cl$_2$]$_2$ (15.3 mg, 0.025 mmol) and vinyldiazoacetate **1c** (13.3 mg, 0.055 mmol) were reacted in CH$_2$Cl$_2$ (0.5 mL) at room temperature for 1 h. TLC: $R_f = 0.55$ (CH$_2$Cl$_2$:EtOAc = 10:1) for the product and $R_f = 0.74$ for **1c**. After concentration, the residue was purified by silica gel column chromatography (SiO$_2$, 6 g; CH$_2$Cl$_2$/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): ν 1750, 1713, 1448, 1229 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$, 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, $J = 5.58$ Hz, 1H), 5.59 (d, $J = 5.58$ Hz, 1H), 5.69 (d, $J = 5.6$ Hz, 1H) ppm; no stereoisomer was observed. ^{13}C NMR (100 MHz, CDCl$_3$, 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 C$_{19}$H$_{24}$Cl$_2$O$_6$Ru: 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 × 0.2 × 0.3 mm) was obtained by recrystallization from CH$_2$Cl$_2$/n-hexane. The intensity data ($2\theta < 55.0°$, $\omega-2\theta$ scan technique) were collected on a Rigaku AFC-7R diffractometer with graphite-monochromated Mo Kα 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 ClCH$_2$CH$_2$Cl (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 ^{1}H 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.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture of Japan (Tokutei A, 412).

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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