Organometallics **2008,** *27,* 1750–1757

Influence of Electron-Deficient Ruthenium(I) Carbonyl Carboxylates on the Vinylogous Reactivity of Metal Carbenoids

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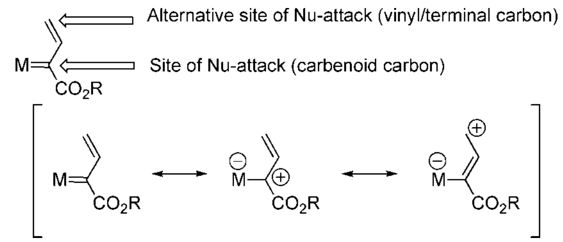
Received September 4, 2007

Highly electrophilic ruthenium(I) mixed carbonyl carboxylate complexes exhibit catalytic activity in the cyclopropanation of styrene with methyl phenyldiazoacetate. A particular advantage of these catalysts is their propensity to enhance vinylogous reactivity in the reactions of vinyldiazoacetates. The catalytic study was conducted on four known ruthenium(I) mixed carbonyl carboxylate complexes and four new complexes, namely, $[Ru_2(O_2C(2,3,4\text{-}F)_3C_6H_2)_2(CO)_5]$, $[Ru_2(O_2C(2,4,6\text{-}F)_3C_6H_2)_2(CO)_5]$, $[Ru_2(O_2CC_6F_5)_2(CO)_5]$, and $[Ru_2(O_2C(3,5\text{-}CF_3)_2C_6H_3)_2(CO)_4]$. All complexes have been prepared by a combination of solvent-free techniques: melt reactions of ruthenium carbonyl with a benzoic acid followed by gas-phase sublimation−deposition of the products under reduced pressure. X-ray crystallographic characterization revealed a tetranuclear “dimer of dimers” type of structure for the $[Ru_2(O_2CR)_2(CO)_5]$ complexes and a polymeric chain for $[Ru_2(O_2C(3,5\text{-}CF_3)_2C_6H_3)_2(CO)_4]$. Both motifs are built on diruthenium(I,I) units linked in the solid state by axial Ru···O interactions. The solution behavior of the polynuclear ruthenium(I) complexes in solvents of varying coordination ability has been investigated to show a breakage of weak Ru···O contacts, resulting in the formation of one- and two-end open dimetal units.

Introduction

The rhodium-catalyzed reactions of vinyldiazoacetates have been shown to have broad synthetic potential. A number of very powerful synthetic methods have been developed, which exploit the highly selective transformations of the rhodium-stabilized vinylcarbenoid intermediates generated under these conditions. These include a number of C−C bond formation reactions including cyclopropanations,[1,2] the tandem cyclopropanation/Cope rearrangement,[3–7] [3+2] cycloadditions,[8,9] C−H insertions,[10,11] and the combined C−H activation/Cope rearrangement.[11–13] All of these reactions involve initial attack of the vinylcarbenoids at the carbenoid center. An interesting phenomenon, however, associated with these vinylcarbenoids is that in certain systems it is possible to have competing electrophilic reactivity at the terminal site (Scheme 1).[14,15] This type of behavior is common in Fischer vinylcarbenes[16] but has not been extensively developed with the transient metal carbenoids derived from vinyldiazoacetates, primarily because convenient methods for controlling vinylogous reactivity have not been developed.

Scheme 1. Resonance Picture of Vinylogous Reactivity



One of the challenges associated with the use of vinyldiazoacetates in synthesis is the requirement of a very active catalyst to induce rapid nitrogen extrusion since many of the vinyldiazoacetates are prone to 6π-electrocyclization to form pyrazoles.[4] The dirhodium(II,II) tetracarboxylates were discovered to be the optimal catalysts for this chemistry, and they have been predominantly used in all the new vinylcarbenoid synthetic

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[1] (1) Doyle, M. P.; McKervey, M. A.; Ye, T. *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds: From Cyclopropanes to Ylides*; 1998.

[2] (2) Lebel, H.; Marcoux, J.-F.; Molinaro, C.; Charette, A. B. *Chem. Rev.* **2003**, *103*, 977–1050.

[3] (3) Davies, H. M. L. *Tetrahedron* **1993**, *49*, 5203–5223.

[4] (4) Davies, H. M. L.; Bruzinski, P.; Hutcheson, D. K.; Kong, N.; Fall, M. J. *J. Am. Chem. Soc.* **1996**, *118*, 6897–6907.

[5] (5) Davies, H. M. L.; Clark, T. J.; Smith, H. D. *J. Org. Chem.* **1991**, *56*, 3817–3824.

[6] (6) Davies, H. M. L.; Doan, B. D. *J. Org. Chem.* **1999**, *64*, 8501–8508.

[7] (7) Davies, H. M. L.; Stafford, D. G.; Doan, B. D.; Houser, J. H. *J. Am. Chem. Soc.* **1998**, *120*, 3326–3331.

[8] (8) Davies, H. M. L.; Romines, K. R. *Tetrahedron* **1988**, *44*, 3343–3348.

[9] (9) Davies, H. M. L.; Xiang, B.; Kong, N.; Stafford, D. G. *J. Am. Chem. Soc.* **2001**, *123*, 7461–7462.

[10] (10) Davies, H. M. L. *J. Mol. Catal. A: Chem.* **2002**, *189*, 125–135.

[11] (11) Davies, H. M. L.; Beckwith, R. E. J. *Chem. Rev.* **2003**, *103*, 2861–2903.

[12] (12) Davies, H. M. L.; Dai, X.; Long, M. S. *J. Am. Chem. Soc.* **2006**, *128*, 2485–2490.

[13] (13) Davies, H. M. L.; Jin, Q. *J. Am. Chem. Soc.* **2004**, *126*, 10862–10863.

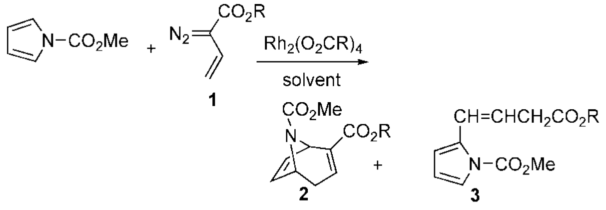
[14] (14) Davies, H. M. L.; Hu, B.; Saikali, E.; Bruzinski, P. R. *J. Org. Chem.* **1994**, *59*, 4535–4541.

[15] (15) Davies, H. M. L.; Saikali, E.; Clark, T. J.; Chee, E. H. *Tetrahedron Lett.* **1990**, *31*, 6299–6302.

[16] (16) Wulff, W. D.; Yang, D. C. *J. Am. Chem. Soc.* **1983**, *105*, 6726–6727.

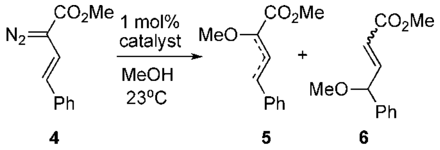
10.1021/om700888f CCC: $40.75

Scheme 2. Carbenoid vs Vinylogous Reactivity[15]



R	Reaction conditions	Ratio
Me	$Rh_2(OAc)_4/CH_2Cl_2$	55 : 45
Me	$Rh_2(TFA)_4/CH_2Cl_2$	15 : 85
Me	$Rh_2(OHex)_4$/hexane	>95 : 5
2,6-di-^{t}Bu-4-MeC_6H_2	$Rh_2(OAc)_4/CH_2Cl_2$	<5 : 95

Scheme 3. O−H Insertion[18]



Catalyst	Ratio
Rh_2(S-TBSP)$_4$	>95 : 5
$Rh_2(OAc)_4$	>95 : 5
$Mo(CO)_6$/S-TBSP-H	50 : 50

methods developed to date.[10,11,17] During these studies, it was discovered that vinylcarbenoids unsubstituted at the vinyl terminus could display electrophilic character at the vinylogous position. This is illustrated in the reaction of vinyldiazoacetate **1** with *N*-carbomethoxypyrrole, which resulted in the formation of a mixture of tropane **2**, derived from a tandem cyclopropanation/Cope rearrangement, and the alkylation product **3**, derived from reaction at the vinylogous site (Scheme 2).[15] The product distribution is dependent on the solvent and catalyst, where a more polar solvent and electron-deficient catalyst favor reaction at the vinylogous site. The only way to form exclusively the alkylation product was to use a very bulky ester to block reactivity at the carbenoid site.[15] This is not an ideal solution, however, because the ester is too bulky to be hydrolyzed, and due to its size, it triples the molecular weight of the vinyldiazoacetate.

A possible approach to enhance the vinylogous reactivity would be to use dimetal complexes that have different electronic properties from the dirhodium complexes previously used as catalysts (Scheme 2). Preliminary studies have been conducted with *in situ* generated dimolybdenum complexes, which demonstrate in O−H insertion reactions that vinylogous reactivity can be achieved even with vinylcarbenoids unsubstituted at the vinyl terminus (Scheme 3).[18] This system, however, was very limited, because it could only be applied to O−H insertions. Furthermore, the *in situ* generated complex was unstable and its actual structure remains uncertain. An alternative approach has been recently described for enhancing vinylogous reactivity in X−H insertions by using mononuclear metal complexes.[19] These transformations have been proposed to be Lewis acid catalyzed reactions and to not involve carbenoid intermediates. To further develop the use of dimetal complexes to enhance vinylogous reactivity, it would be highly desirable to have air-stable, structurally well-defined catalysts. This paper describes diruthenium(I,I) carbonyl dicarboxylates that are effective catalysts for the decomposition of diazoacetates and that they strongly enhance vinylogous reactivity over the traditional chemistry at the carbenoid site.

Diruthenium(I,I) carbonyl carboxylates of the general formula $[Ru_2(\mu_2\text{-}O_2CR)_2(CO)_4L_2]$ and polymeric compounds of the composition $[Ru_2(\mu_2\text{-}O_2CR)_2(CO)_4]$ have been utilized in inter- and intramolecular reactions of diazoacetates and diazoacetamides by Maas and co-workers.[20–27] The complexes are air stable, and since Ru(I) is isoelectronic to Rh(II), one can expect roughly a similar reactivity profile between the two classes of complexes. The diruthenium(I,I) carbonyl carboxylate complexes have not been explored as catalysts for the reactions of vinyldiazoacetates. As our goal was to enhance vinylogous reactivity, we tested a family of electrophilic diruthenium(I,I) mixed carbonyl carboxylate complexes of the general formula $[Ru_2(O_2CR)_2(CO)_n]$: $n = 5$, R = CF_3 (**I**), $(2,4\text{-}CF_3)_2C_6H_3$ (**II**), $(3,5\text{-}CF_3)_2C_6H_3$ (**III**), $(2,3,4\text{-}F)_3C_6H_2$ (**IV**), $(2,4,6\text{-}F)_3C_6H_2$ (**V**), C_6F_5 (**VI**); $n = 4$, R = CF_3 (**VII**), $(3,5\text{-}CF_3)_2C_6H_3$ (**VIII**). The synthesis of and structural information on **I**−**III** and **VII** have been reported previously, while compounds **IV**−**VI** and **VIII** are reported here for the first time (Scheme 4). In this paper we first describe the syntheses, characterization, and solution behavior of these complexes, followed by their catalytic activity.

Results and Discussion

Synthesis. The synthetic methods to isolate complexes **I**−**VIII** in pure crystalline form have been developed in our group.[28] The first diruthenium(I,I) carbonyl carboxylate $[Ru_2(O_2CCF_3)_2(CO)_5]$ (**I**) was prepared by refluxing $Ru_3(CO)_{12}$ with trifluoroacetic acid in a mixture of noncoordinating solvents, while $[Ru_2(O_2CCF_3)_2(CO)_4]$ (**VII**) was synthesized in a ligand exchange reaction from commercially available $[Ru_2(O_2CCH_3)_2(CO)_4]$.[29] Recently, we have prepared a series of the mixed carbonyl fluorinated benzoates of ruthenium(I) by adapting the procedures reported by Strähle based on melt reactions of $Ru_3(CO)_{12}$ with a corresponding benzoic acid.[30,31] As a result, products of the composition $[Ru_2(O_2CR)_2(CO)_n]$ [$n = 5$, R = $(2,4\text{-}CF_3)_2C_6H_3$ (**II**), $(3,5\text{-}CF_3)_2C_6H_3$ (**III**),[28] $(2,3,4\text{-}F)_3C_6H_2$ (**IV**), $(2,4,6\text{-}F)_3C_6H_2$ (**V**), and C_6F_5 (**VI**); $n = 4$, R = $(3,5\text{-}CF_3)_2C_6H_3$ (**VIII**)] were isolated as air-stable crystalline solids. While **I**−**VI** are soluble in most organic solvents, **VIII** shows a very limited solubility in noncoordinating solvents. The synthetic route for each compound combined a melt reaction at the temperature slightly above the melting point of an acid with consequent removal of unreacted acid by several resublimations under reduced pressure. This was followed by crystal growth using a gas-phase sublimation−deposition technique that was proven

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(17) Davies, H. M. L. *Eur. J. Org. Chem.* **1999**, 2459–2469.

(18) Davies, H. M. L.; Yokota, Y. *Tetrahedron Lett.* **2000**, *41*, 4851–4854.

(19) Yue, Y.; Wang, Y.; Hu, W. *Tetrahedron Lett.* **2007**, *48*, 3975–3977.

(20) Buck, S.; Maas, G. *J. Organomet. Chem.* **2006**, *691*, 2774–2784.

(21) Grohmann, M.; Buck, S.; Schaeffler, L.; Maas, G. *Adv. Synth. Catal.* **2006**, *348*, 2203–2211.

(22) Leger, C.-D.; Maas, G. *Z. Naturforsch. (B)* **2004**, *59*, 573–578.

(23) Maas, G. *Chem. Soc. Rev.* **2004**, *33*, 183–190.

(24) Maas, G.; Seitz, J. *Tetrahedron Lett.* **2001**, *42*, 6137–6140.

(25) Maas, G.; Werle, T.; Alt, M.; Mayer, D. *Tetrahedron* **1993**, *49*, 881–888.

(26) Werle, T.; Maas, G. *Adv. Synth. Catal.* **2001**, *343*, 37–40.

(27) Werle, T.; Schaeffler, L.; Maas, G. *J. Organomet. Chem.* **2005**, *690*, 5562–5569.

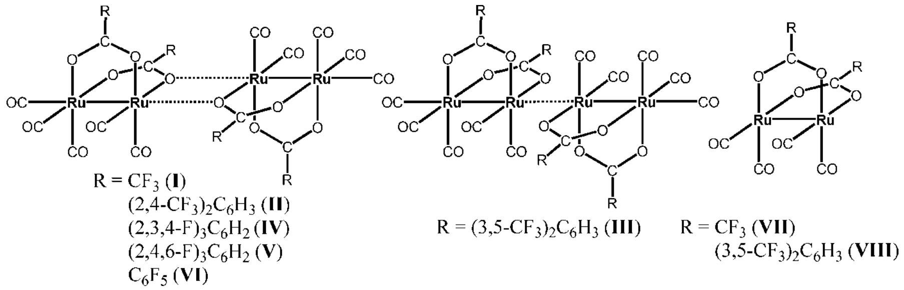
(28) Sevryugina, Y.; Olenev, A. V.; Petrukhina, M. A. *J. Cluster Sci.* **2005**, *16*, 217–229.

(29) Petrukhina, M. A.; Sevryugina, Y.; Andreini, K. W. *J. Cluster Sci.* **2004**, *15*, 451–467.

(30) Spohn, M.; Straehle, J.; Hiller, W. *Z. Naturforsch. (B)* **1986**, *41B*, 541–547.

(31) Spohn, M.; Vogt, T.; Straehle, J. *Z. Naturforsch. (B)* **1986**, *41B*, 1373–1380.

Scheme 4. Schematic Representation of Structures of I−VIII



to be very effective for crystallization of volatile electrophilic metal complexes in the absence of exogenous ligands.[32] Additionally, all diruthenium(I,I) carbonyl carboxylates presented in this study were structurally characterized to allow direct structure–reactivity correlations. It is important to emphasize the advantage of the gas-phase deposition technique that affords new metal catalysts in high yields as pure single-phase crystalline materials. Their use in catalytic transformations may allow a direct estimate of the structural and electronic differences in the catalytic properties of diruthenium(I,I) complexes.

Structural Characterization. The X-ray structural analysis of the newly prepared diruthenium(I,I) pentacarbonyl fluorobenzoates **IV**−**VI** displayed a centrosymmetric tetranuclear core that may be viewed as a "dimer of dimers" structure $[Ru_2(O_2CR)_2(CO)_5]_2$ (Figure 1), similar to that in previously reported compounds of this series, **I**[29] and **II**.[28] Two ruthenium centers within the dimer are *cis*-bridged by two carboxylate ligands at a Ru−Ru distance ranging from 2.6579(2) Å in **IV** to 2.6710(2) Å in **V**. Interestingly, the intermetallic separation is noticeably different for the two compounds **IV** and **V**, having the same molecular formula, $[Ru_2(O_2CF_3C_6H_2)_2(CO)_5]_2$, but different disposition of the fluorine substituents (2,3,4- vs 2,4,6-). Additionally, each dinuclear core accommodates five carbonyl groups: one at an axial position and the remaining four at equatorial sites. The Ru−C distances to equatorial carbonyl groups are considerably shorter (1.855(5)−1.859(2) Å) than those to axial carbonyl groups (1.993(5)−2.009(2) Å). The diruthenium units are linked together by two weak Ru···O axial contacts ranging from 2.302(3) in **VI** to 2.3234(14) Å in **V**. The geometric parameters of **IV**−**VI**, together with those for previously reported **I**−**III**, are summarized in Table 1. No significant discrepancies in bond lengths and angles are noticed in this series of compounds.

The newly prepared complex **VIII** exhibits a polymeric structure similar to that of **VII** formed by axial ruthenium−oxygen interactions between neighboring dimetal blocks (Figure 2). The Ru−Ru distance within the dimetal unit is 2.6343(7) Å, which is longer than that in **VII** of 2.6271(9) Å, while the axial Ru···O contacts of 2.294(4) Å are shorter in **VIII** vs **VII** (2.325(6) Å). Each Ru atom also has two equatorial carbonyl groups with an average Ru−C distance of 1.849(7) Å.

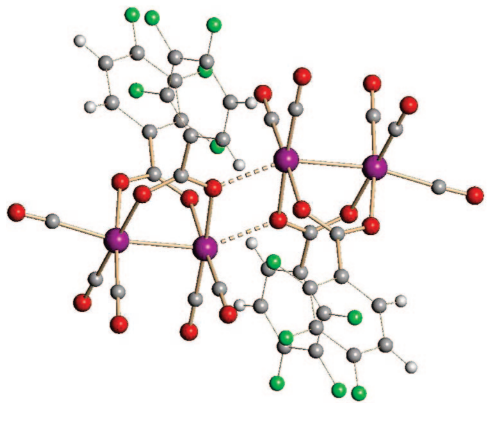


Figure 1. Molecular view of complex **IV**. Ru purple, O red, C gray, F green, H light gray. Complexes **V** and **VI** have similar structures.

On the basis of structural characteristics of **I**−**VIII**, we expect that carbenoid formation occurs through axial coordination of the diruthenium(I,I) unit to a diazoacetate. A necessary preliminary step would involve cleavage of weak Ru···O interdimer contacts to produce open Lewis acidic metal centers, which will become sites of catalytic activity (Scheme 5). This is illustrated here by solution crystallization of a toluene adduct of complex **III**, $[Ru_2(O_2C(3,5\text{-}CF_3)_2C_6H_3)_2(CO)_5\cdot(C_6H_5CH_3)]$ (**IX**), and a water adduct of complex **I**, $[Ru_2(O_2CCF_3)_2(CO)_4\cdot(H_2O)_2]$ (**X**) (Figure 3). In our previous work[28] we established similar dissociation processes in the gas phase through isolation of adducts with aromatic donor substrates, which additionally illustrated high electrophilicity of the prepared diruthenium(I,I) complexes. In contrast to the gas-phase reactions resulting in a breakage of intermolecular contacts between the dimetal units in both classes of ruthenium complexes, in solution strong coordinating solvents (like water, tetrahydrofuran, or alcohols) are required to break the chain polymeric structures of **VII** and **VIII**.

Determination of Catalytic Activity of Ru(I) Complexes. The activities of ruthenium complexes **I**−**VIII** as catalysts for carbenoid transformations were initially evaluated in the cyclopropanation reaction between methyl phenyldiazoacetate (**7**) and styrene (Scheme 6). This transformation is effective with various dirhodium catalysts and was thus considered an appropriate test reaction for catalytic activity. The reactions were conducted in dichloromethane by syringe pump addition of phenyldiazoacetate **7** to a solution of excess styrene and the ruthenium catalyst (1 mol%). Reactions at room temperature gave fairly low yields for all complexes **I**−**VIII** (0−26%). The highest yields were obtained with complexes **I** and **IV**−**VI** (13−26%). Reactions in refluxing dichloromethane, however, produced the cyclopropane in moderate to good yields for all the catalysts (42−69% yield). The main side-reaction was the formation of carbene dimers. The significant improvement in yields and reactivity with temperature may be attributed to thermally enhanced dissociation of dimeric and polymeric complexes of these species to open up the axial active sites for catalysis. The lowest yields were obtained with complexes **VII** and **VIII** in reactions conducted both at room temperature and at reflux. These two catalysts lack axial CO ligands and have chain polymeric structures in the solid state and are therefore expected to have lower solubility in dichloromethane compared to complexes **I**−**VI**. The latter complexes, containing axial CO ligands, which form "dimer of dimer" type structures, dissociate in solutions more easily than **VII** and **VIII**.

Table 1. Selected Bond Distances (Å) and Angles (deg) in a Series of Ruthenium(I) Carbonyl Carboxylates of the General Formula $[Ru_2(O_2CR)_2(CO)_5]_2$

		$(CF_3)_2C_6H_3$[28]		$F_3C_6H_2$		
	CF_3[29]	2,4-	3,5-	2,3,4-	2,4,6-	C_6F_5
R	**I**	**II**	**III**	**IV**	**V**	**VI**
Ru(1)−Ru(2)	2.6728(2)	2.6654(7)	2.6859(8)	2.6579(2)	2.6710(2)	2.6671(5)
$Ru-O_{carboxylate}$[a]	2.1394(12)	2.130(3)	2.098(3)	2.1275(14)	2.1307(14)	2.125(3)
Ru(1)···O(1A)	2.3437(12)	2.301(2)		2.3162(13)	2.3234(14)	2.302(3)
Ru(1)···Ru(1A)			2.9065(9)			
$Ru-CO_{eq}$[a]	1.864(2)	1.863(4)	1.866(5)	1.859(2)	1.858(2)	1.855(5)
$Ru(2)-CO_{ax}$	1.991(2)	2.002(4)	1.969(5)	2.009(2)	2.007(2)	1.993(5)
$C-O_{eq}$[a]	1.139(2)	1.134(5)	1.134(5)	1.139(3)	1.140(3)	1.144(6)
$C-O_{ax}$	1.126(2)	1.114(5)	1.116(6)	1.114(3)	1.115(3)	1.118(6)
Ru−Ru···Ru			173.961(19)			
$Ru-Ru\cdots O_{ax}$	157.56(3)	157.66(6)		154.31(3)	157.93(3)	156.11(7)
$Ru-Ru-C_{ax}$	170.43(5)	166.56(13)	169.28(13)	168.61(6)	168.27(6)	166.99(13)

[a] Averaged.

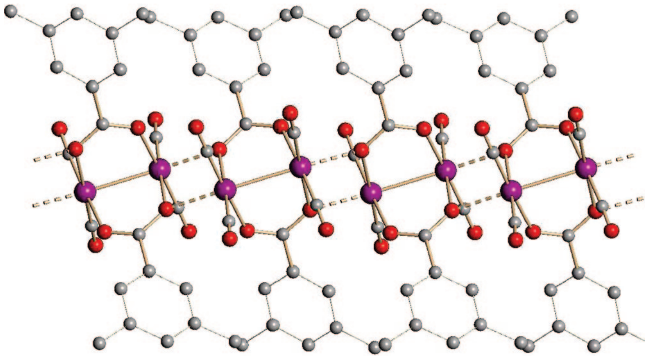


Figure 2. Fragment of a polymeric chain in complex **VIII**. Ru purple, O red, C gray. F and H atoms are omitted for clarity.

The diastereoselectivity of the reaction of **7** with styrene is generally very high with dirhodium(II,II) complexes as catalysts (>94% de).[33] With the diruthenium(I,I) catalysts the diastereoselectivities are not as high (50−83% de). The attenuated diastereoselectivity observed for the ruthenium-catalyzed reactions is presumably due to the higher electrophilic character of these complexes compared to previously used dirhodium catalysts, which lowers the discriminating abilities of the resulting carbenoid intermediates.

Vinylogous Reactivity in O−H Insertions. The crucial question regarding the diruthenium(I,I)-catalyzed reactions of vinyldiazoacetates was whether these electrophilic catalysts would enhance reactivity at the terminal position of the vinylcarbenoid intermediate. As discussed in the introduction, a test reaction for vinylogous *vs* carbenoid reactivity is the metal-catalyzed decomposition of a vinyldiazoacetate in methanol (Scheme 7).[18] The resulting distribution of products, arising from nucleophilic attack of methanol at the terminal position (products *E*-**6** and *Z*-**6**) or the carbenoid carbon (products **5a**,**b**), reflects vinylogous vs carbenoid reactivity. Results from O−H insertion reactions of methyl phenylvinyldiazoacetate (**4**) and methanol catalyzed by diruthenium(I,I) complexes **I**−**III** in comparison with previously reported Mo species and dirhodium complexes Rh_2(*S*-TBSP)$_4$ and $Rh_2(OAc)_4$ are shown in Scheme 7. Dirhodium complexes typically give only products arising from nucleophilic attack at the carbenoid carbon (entries 5 and 6), while Mo complexes have been shown to shift the reactivity more toward vinylogous reactivity (entry 4).[18] Reactions with Ru(I) catalysts **I**−**III** show an even more pronounced shift toward vinylogous reactivity. For these complexes, the products derived from vinylogous reactivity always constitute >80% of the products. The *E/Z* distribution of **6** varies somewhat as well and may reflect the preference of the carbenoid to exist in an *s-trans* conformation. The product yields are relatively low, possibly due to reduced reactivity of the catalysts at room temperature, but the trend toward vinylogous reactivity is very pronounced. The ruthenium-catalyzed reactions gave a 4:1 ratio of products favoring terminus reactivity in a system, which under the standard rhodium-catalyzed reaction gave exclusive reaction at the carbenoid site.

Enhancing Vinylogous Reactivity in C−C Bond Forming Reactions. The scope of the ruthenium-catalyzed reactions would be greatly enhanced if selective vinylogous reactivity could be achieved in C−C bond forming reactions. Rhodium-catalyzed vinyldiazoacetates unsubstituted at the vinyl terminus can give rise to vinylogous reactivity, but the selectivity is poor unless a very bulky ester group is used.[14] In order to test this possibility, the reaction of vinyldiazoacetate **9** with cyclopentadiene was examined. Previously, this transformation has been conducted with dirhodium(II,II) systems, which gave a mixture of compounds **10** and **11** (Scheme 8), where **10** arises from initial nucleophilic attack at the terminal position of the intermediate vinylcarbenoid and **11** is the product of a tandem cyclopropanation/Cope rearrangement (carbenoid reactivity).[14] The reactions were conducted at room temperature, due to the intrinsic thermal instability of the vinyldiazoacetate, with a large excess of trapping agent (20 equiv). Reaction between methyl vinyldiazoacetate **9** and cyclopentadiene in the presence of diruthenium(I,I) complexes **I**, **II**, and **VI** led cleanly to the bicyclic products *cis/trans*-**10** in moderate yields (37−54%) with an isomer ratio of about 2:1 in all cases. Compared to previously reported dirhodium(II,II)-catalyzed reactions, there is remarkable control of site selectivity, and only the product(s) **10** arising from vinylogous reactivity can be observed. Only partial control is achieved, even with the highly electron-deficient $Rh_2(TFA)_4$, for dirhodium(II,II) complexes.[14]

The proposed reaction mechanism[14,15] (Scheme 9) is considered to proceed by initial nucleophilic attack at the vinylogous site to form zwitterionic intermediate **13**. This intermediate then cyclizes to form a second metal carbenoid intermediate **14**, which then undergoes a [1,2]-hydride shift and elimination to form **10**. The dependence of the isomer ratio of **10** on catalyst structure supports the existence of the second carbene intermediate **14**.

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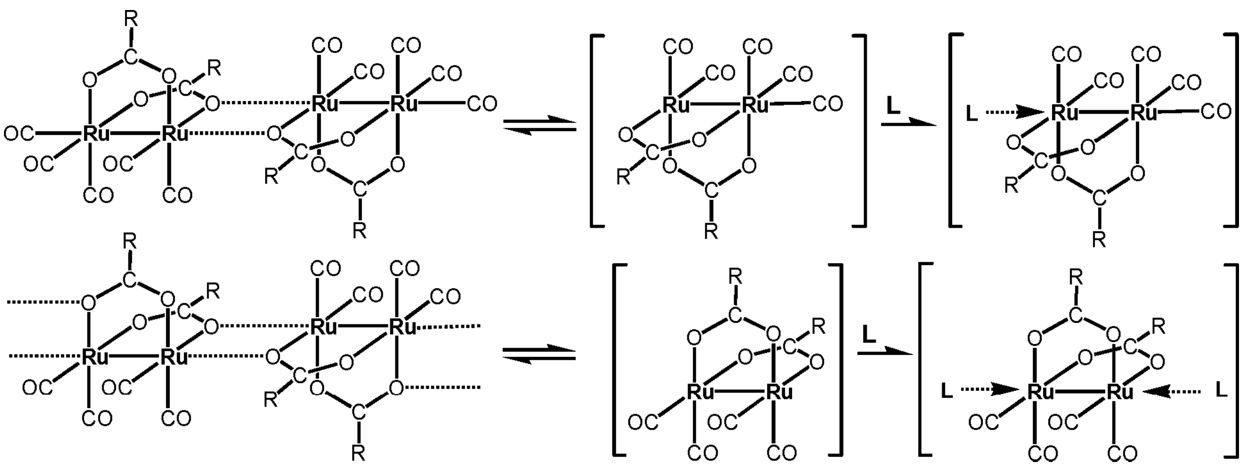
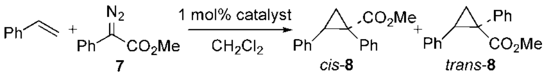
(32) Dikarev, E. V.; Filatov, A. S.; Clerac, R.; Petrukhina, M. A. *Inorg. Chem.* **2006**, *45*, 744–751.

(33) Davies, H. M. L.; Rusiniak, L. *Tetrahedron Lett.* **1998**, *39*, 8811–8812.

Scheme 5. Dissociation of Tetra- and Polynuclear Complexes to Form Diruthenium(I,I) Units

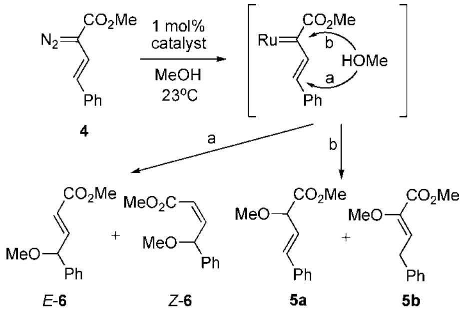


Scheme 6. Cyclopropanation of Styrene



Catalyst	Yield, % at 23 °C	Yield, % at 40 °C	de, % at 40 °C
I	16	55	50
II	9	69	83
III	9	67	69
IV	13	60	51
V	26	47	59
VI	16	69	72
VII	0	45	59
VIII	3	42	64

Scheme 7. O–H Insertion



Catalyst	Yield, %	Product ratio			
		Z-**6**	*E*-**6**	**5a**	**5b**
I	45	75	11	14	0
II	26	67	15	18	0
III	28	62	18	20	0
$Mo(CO)_6$/*S*-TBSP-H[a]	93	34	17	40	9
Rh_2(*S*-TBSP)$_4$[a]	86	0	0	89	11
$Rh_2(OAc)_4$	85	0	0	100	0

[a] Values from the literature.[18]

Enhancement of vinylogous reactivity appears to be a general phenomenon, as illustrated for the reaction using *N*-Boc pyrrole as the trapping agent (Scheme 10). This reaction afforded *cis/trans* isomers of the alkylation product **15**, presumably arising from initial nucleophilic attack at the terminal position of the vinylcarbenoid. The yields of **15** were somewhat higher but comparable to those obtained with cyclopentadiene (45–57%). Again, only the products derived from vinylogous reactivity were observed, and the formation of *Z*-**15** was strongly preferred over *E*-**15**.

In conclusion, the diruthenium(I,I) complexes investigated here can be active catalysts in carbenoid transformations at low catalyst loadings (1 mol %). The activity can be modulated by the association propensity of the active complexes in solution. The diruthenium catalysts require more vigorous reaction temperatures than dirhodium(II,II) catalysts, but they have promising synthetic potential because they cause significant enhancement of vinylogous vs carbenoid reactivity of vinylcarbenoids. The study demonstrates that the catalyst is an essential control element for enhancing reactivity at the terminal position of vinylcarbenoids. Future studies will be directed toward further optimization of the diruthenium catalysts with the ultimate goal of broadening the scope of the vinylogous reactivity and achieving enantioselective variants of this chemistry.

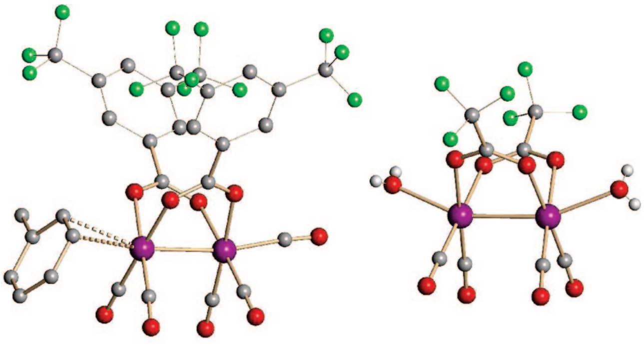

IX **X**

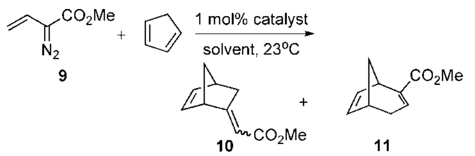
Figure 3. Molecular view of compounds **IX** and **X**.

Experimental Section

General Procedures. All synthetic reactions and manipulations with diruthenium(I,I) complexes were carried out under a dry dinitrogen atmosphere using standard Schlenk techniques. Sublimation–deposition procedures were performed in small evacuated (ca. 10^{-2} Torr) glass ampules (ca. 7 cm long with an o.d. of 1.1 cm), which were placed in electric furnaces having a small temperature gradient along the length of the tube. $Ru_3(CO)_{12}$ was obtained from Strem. 2,3,4-Trifluorobenzoic, $(2,3,4\text{-}F)_3C_6H_2COOH$, 2,4,6-trifluorobenzoic, $(2,4,6\text{-}F)_3C_6H_2COOH$, and pentafluorobenzoic, C_6F_5-COOH, acids were purchased from SynQuest Fluorochemicals and used as received. All other materials were purchased from Aldrich or Acros and used without further purification unless stated.

All catalytic reactions were conducted in flame-dried glassware under an inert Ar atmosphere. Reagents were used as received from commercial suppliers. Dichloromethane was purified by passage

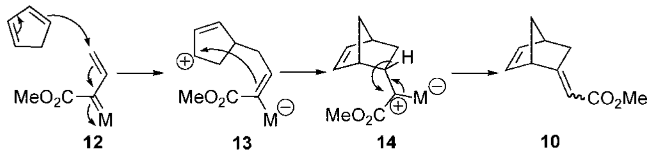
Scheme 8. Vinylogous Reactivity in Reaction with Cyclopentadiene



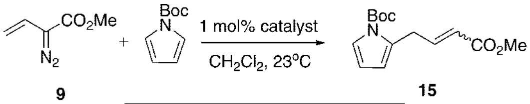
Conditions	**10:11** ratio	*Z*/*E* ratio of **10**	Yield, %
I/CH_2Cl_2	>98:2	2:1	54
II/CH_2Cl_2	>98:2	2:1	37
VI/CH_2Cl_2	>98:2	2.4:1	40
$Rh_2(OAc)_4/CH_2Cl_2$ [a]	33:67	2.5:1	81
$Rh_2(OPiv)_4$/pentane [a]	2:98	0.8:1	86
$Rh_2(TFA)_4/CH_2Cl_2$ [a]	68:32	1.1:1	60

[a] Values from the literature.[15]

Scheme 9. Proposed Reaction Mechanism



Scheme 10. Vinylogous Reactivity in Reaction with *N*-Boc pyrrole



Catalyst	*Z*:*E* ratio	Yield, %
I	11:1	57
II	13:1	45
VI	25:1	54

through a bed of activated A2 alumina (Grubbs type solvent purifier) and then degassed by bubbling Ar through the solvent for 15−20 min prior to use. *N*-Boc pyrrole was distilled before use. Styrene was filtered through a plug of silica before use. Methyl phenyldiazoacetate (**7**) and methyl phenylvinyldiazoacetate (**4**) were synthesized according to literature procedures.[34] Thin-layer chromatography (TLC) was performed on aluminum-backed plates precoated with silica (0.25 mm, 60F-254), which were developed using UV fluorescence (254 nm) and phosphomolybdenic acid. Column chromatography was carried out on Merck silica gel 60 (230−400 mesh).

Instruments. For characterization of metal catalysts the NMR spectra were recorded on a Varian Gemini spectrometer at 300 MHz for ^1H and 282 MHz for ^{19}F at 22 °C using $SiMe_4$ and $CFCl_3$ as internal standards. The infrared spectra were obtained using KBr pellets on a Nicolet Magna 550 FTIR spectrometer. Elemental analyses were performed by Canadian Microanalytical Service, Delta, BC, Canada.

For characterization of products of catalytic reactions the ^1H NMR spectra were recorded on either a 400 or 500 MHz Varian Inova, and ^{13}C NMR at 75 MHz with the sample solvent being $CDCl_3$ unless otherwise noted. Tetramethylsilane was used as an internal reference standard. All coupling constants were rounded to the nearest half-integer. Mass spectral determinations were carried out by GC-MS (EI) and LC-MS (ESI) in the Instrument Center, Department of Chemistry, University at Buffalo.

Preparation of Metal Catalysts. Preparation of [$Ru_2(O_2C$-(2,3,4-F)$_3C_6H_2)_2(CO)_5$] (IV). The title compound was obtained in a melt reaction between $Ru_3(CO)_{12}$ (0.020 g, 0.03 mmol) and (2,3,4-F)$_3C_6H_2COOH$ (0.038 g, 0.22 mmol). Starting materials were loaded in an ampule, which was then placed in a sand bath at 150 °C. A brown melt was formed instantly, but reaction was allowed to proceed for a total of 30 min. After that, the ampule was sealed and excess of unreacted acid was removed by sublimation at 90 °C for 3 days. The resulting yellow crude powder was collected in an ampule and placed in a furnace at 125 °C. First pale yellow crystals of **IV** appeared in the cold zone after 4 days, but only in a month their yield achieved 50%. Anal. Calcd for $C_{38}H_8F_{12}O_{18}Ru_4$: C, 32.93; O, 20.80; H, 0.58. Found: C, 32.96; O, 21.21; H, 0.77. IR (KBr, cm^{-1}): 3094(sh), 2105(s), 2050(s), 2017(s), 1998(s), 1960(s), 1948(s), 1634(m), 1615(w), 1569(s), 1550(m), 1514(m), 1487(w), 1475(m), 1412(s), 1321(sh), 1284(m), 1240(w), 11445(sh), 1047(m), 955(m), 829(sh), 814(m), 778(m), 726(w), 713(w), 693(w), 644(m), 568(w), 524(w), 506(w). ^1H NMR ($CDCl_3$, 22 °C): δ 7.67, 7.05 (C-H_{arom}) with an integrated ratio of 1:1, respectively. ^{19}F NMR ($CDCl_3$, 22 °C): δ −129.75, −132.34, −160.92.

Preparation of [$Ru_2(O_2C(2,4,6\text{-}F)_3C_6H_2)_2(CO)_5$] (V). The title compound was obtained in a melt reaction between $Ru_3(CO)_{12}$ (0.120 g, 0.19 mmol) and (2,4,6-F)$_3C_6H_2COOH$ (0.165 g, 0.94 mmol). Starting materials were loaded in an ampule, which was then placed in a sand bath at 154 °C. A red melt was formed instantly, but reaction was allowed to proceed for a total of 20 min. After that, the ampule was sealed and excess unreacted acid was removed by sublimation at 120 °C for 5 days. The resulting orange crude powder was collected in an ampule and placed in a furnace at 163 °C. First yellow crystals of **V** appeared in the cold zone after 1 day. After 4 days the yield is 30%. Anal. Calcd for $C_{38}H_8F_{12}O_{18}Ru_4$: C, 32.93; O, 20.80; H, 0.58. Found: C, 32.51; O, 21.10; H, 0.69. IR (KBr, cm^{-1}): 3113(sh), 3091(sh), 2108(s), 2048(s), 2025(s), 2007(s), 1987(sh), 1948(s), 1695(w), 1660(w), 1643(s), 1617(sh), 1603(s), 1585(s), 1553(m), 1535(w), 1500(w), 1484(w), 1442(w), 1419(s), 1409(s), 1350(m), 1172(w), 1144(m), 1121(s), 1041(m), 998(m), 854(sh), 844(m), 783(w), 751(w), 733(w), 663(w), 626(m), 573(w), 522(w), 512(w). ^1H NMR ($CDCl_3$, 22 °C): δ 6.68 (C-H_{arom}). ^{19}F NMR ($CDCl_3$, 22 °C): δ −103.47, −107.45.

Preparation of [$Ru_2(O_2CC_6F_5)_2(CO)_5$] (VI). The title compound was obtained in a melt reaction between $Ru_3(CO)_{12}$ (0.020 g, 0.03 mmol) and C_6F_5COOH (0.036 g, 0.17 mmol). Starting materials were loaded in an ampule, which was then placed in a sand bath at 120 °C. A bright orange melt was formed instantly, but reaction was allowed to proceed for a total of 35 min. After that, the ampule was sealed and excess unreacted acid was removed by sublimation at 90 °C for 5 days. The resulting orange crude powder was collected in an ampule and placed in a furnace at 145 °C for a week (yield 70%). Anal. Calcd for $C_{38}F_{20}O_{18}Ru_4$: C, 29.83; O, 18.84. Found: C, 30.03; O, 18.46. IR (KBr, cm^{-1}): 2107(s), 2043(s), 2022(s), 2016(s), 1956(s), 1646(m), 1598(s), 1575(sh), 1525(m), 1501(m), 1489(m), 1471(w), 1435(m), 1409(s), 1302(w), 1124(w), 1112(w), 1008(m), 993(m), 950(w), 889(m), 782(m), 771(m). ^{19}F NMR ($CDCl_3$, 22 °C): δ −139.52, −161.06.

Preparation of [$Ru_2(O_2C(3,5\text{-}CF_3)_2C_6H_3)_2(CO)_4$] (VIII). The title compound can be synthesized following the same procedure as for [$Ru_2(O_2C(3,5\text{-}CF_3)_2C_6H_3)_2(CO)_5$][28] but using higher temperatures and longer reaction times. Thus, conducting a melt reaction at 170−180 °C for 40 min and subliming the crude powder at 180 °C would quantitatively produce the title product in 70% yield. A tiny amount of dichroic red crystals of [$Ru_2(O_2C(3,5\text{-}CF_3)_2C_6H_3)_2(CO)_5$] and yellow crystals of [$Ru_2(O_2C(3,5\text{-}CF_3)_2C_6H_3)_2(CO)_6$] are separated in the gas-phase sublimation procedure. Single crystals of **VIII** suitable for X-ray data collection were obtained in a transport reaction when [$Ru_2(O_2C(3,5\text{-}CF_3)_2C_6H_3)_2(CO)_5$] (**III**) (0.019 g, 0.01 mmol) was cosublimed with dibenzocorannulene, $C_{28}H_{14}$ (0.002 g, 0.006 mmol), at 180 °C. The crystal growth took 3 weeks and the title product appeared with ca. 20% yield. IR (KBr, cm^{-1}): 3099(w), 2060(s), 2014(s), 1979(s), 1957(m), 1627(m), 1539(s), 1469(w), 1456(m), 1429(m), 1342(s),

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(34) Davies, H. M. L.; Panaro, S. A. *Tetrahedron* **2000**, *56*, 4871–4880.

1325(sh), 1279(s), 1188(m), 1155(sh), 1137(s), 1130(m), 915(m), 847(m), 789(m), 768(m), 710(m), 682(m). ^1H NMR ($(CD_3)_2CO$, 22 °C): δ 8.47, 8.22 ($C\text{-}H_{arom}$) with an integrated ratio of 2:1. ^{19}F NMR ($CDCl_3$, 22 °C): δ −62.41.

Preparation of [$Ru_2(O_2C(3,5\text{-}CF_3)_2C_6H_3)_2(CO)_5\cdot(C_6H_5CH_3)$] (IX). [$Ru_2(O_2CCF_3)_2(CO)_5$] (**I**) (0.035 g, 0.06 mmol) was dissolved in 10 mL of toluene. The yellow solution was filtered to a round-bottom flask, which was then connected to a tube with a pre-evacuated mineral oil. Orange crystals of **IX** appeared in 1 day in 80−90% yield.

Preparation of [$Ru_2(O_2CCF_3)_2(CO)_4\cdot(H_2O)_2$] (X). [$Ru_2(O_2CCF_3)_2(CO)_4$] (**VII**) (0.050 g, 0.09 mmol) was dissolved in 2 mL of toluene, followed by the addition of several drops of water. The red-colored solution was filtered to a clean round-bottom flask, which was then connected to a tube with a pre-evacuated mineral oil. Orange crystals of **X** appeared after 1 month in 80−90% yield.

X-ray Crystallographic Study. X-ray crystal data and refinement details for **IV**: $C_{38}H_8F_{12}O_{18}Ru_4$, fw = 1384.72, yellow block, 0.23 × 0.06 × 0.05 mm, monoclinic $P2_1/n$, $a = 10.3336(5)$ Å, $b = 11.8386(6)$ Å, $c = 18.0531(10)$ Å, $\beta = 106.042(1)°$, $V = 2122.53(19)$ Å^3, $Z = 2$, $D_c = 2.167$ g·cm^{-3}, $\mu = 1.527$ mm^{-1}, $T = 173(2)$ K, $\theta_{max} = 28.27°$. For **V**: $C_{38}H_8F_{12}O_{18}Ru_4$, fw = 1384.72, yellow block, 0.07 × 0.06 × 0.05 mm, monoclinic $P2_1/n$, $a = 10.2883(5)$ Å, $b = 15.4363(8)$ Å, $c = 14.0317(7)$ Å, $\beta = 110.340(1)°$, $V = 2089.47(18)$ Å^3, $Z = 2$, $D_c = 2.201$ g·cm^{-3}, $\mu = 1.551$ mm^{-1}, $T = 173(2)$ K, $\theta_{max} = 28.26°$. For **VI**: $C_{38}F_{20}O_{18}Ru_4$, fw = 1528.66, yellow block, 0.10 × 0.09 × 0.08 mm, triclinic $P1$, $a = 9.6158(10)$ Å, $b = 10.5643(11)$ Å, $c = 11.7591(12)$ Å, $\alpha = 112.876(1)°$, $\beta = 95.196(2)°$, $\gamma = 91.192(2)°$, $V = 1094.0(2)$ Å^3, $Z = 1$, $D_c = 2.320$ g·cm^{-3}, $\mu = 1.518$ mm^{-1}, $T = 173(2)$ K, $\theta_{max} = 25.00°$. For **VIII**: $C_{22}H_6F_{12}O_8Ru_2$, fw = 828.41, orange needle, 0.13 × 0.05 × 0.02 mm, triclinic $P1$, $a = 9.6393(7)$ Å, $b = 11.3055(8)$ Å, $c = 14.1228(10)$ Å, $\alpha = 72.102(1)°$, $\beta = 73.861(1)°$, $\gamma = 67.004(1)°$, $V = 1326.11(16)$ Å^3, $Z = 2$, $D_c = 2.075$ g·cm^{-3}, $\mu = 1.269$ mm^{-1}, $T = 173(2)$ K, $\theta_{max} = 24.99°$. For **IX**: $C_{30}H_{14}F_{12}O_9Ru_2$, fw = 948.55, orange plate, 0.11 × 0.08 × 0.04 mm, triclinic $P1$, $a = 11.5905(7)$ Å, $b = 11.9241(7)$ Å, $c = 13.0024(8)$ Å, $\alpha = 76.263(1)°$, $\beta = 73.727(1)°$, $\gamma = 77.817(1)°$, $V = 1655.44(17)$ Å^3, $Z = 2$, $D_c = 1.903$ g·cm^{-3}, $\mu = 1.032$ mm^{-1}, $T = 173(2)$ K, $\theta_{max} = 28.15°$. For **X**: $C_8H_4F_6O_{10}Ru_2$, fw = 576.25, orange block, 0.25 × 0.10 × 0.07 mm, monoclinic $P2_1/c$, $a = 12.6491(5)$ Å, $b = 8.7326(3)$ Å, $c = 13.6260(5)$ Å, $\beta = 99.274(1)°$, $V = 1485.45(9)$ Å^3, $Z = 4$, $D_c = 2.577$ g·cm^{-3}, $\mu = 2.157$ mm^{-1}, $T = 173(2)$ K, $\theta_{max} = 28.28°$. Bruker SMART APEX CCD-based X-ray diffractometer system, Mo Kα radiation ($\lambda = 0.71073$ Å). Data were corrected for absorption effects using the empirical methods SADABS (minimum/maximum apparent transmissions are 0.7203/0.9276, 0.8992/0.9265, 0.8630/0.8882, 0.8524/0.9751, 0.8949/0.9599, and 0.6147/0.8637 for **IV**, **V**, **VI**, **VIII**, **IX**, and **X**, respectively). All non-hydrogen atoms were refined anisotropically, except for disordered carbon and fluorine atoms of four CF_3 groups in **VIII**, three CF_3 groups in **IX**, and one CF_3 group in **X**, for which disorder was modeled over three rotational orientations. Hydrogen atoms in **IV**−**VI** and **X** were found in the difference Fourier map and refined independently, while their refinement in **VIII** and **IX** was mixed. For **IV** full-matrix least-squares refinement on F^2 converged at $R_1 = 0.0207$ and $wR_2 = 0.0502$ for 341 parameters and 4770 reflections with $I > 2\sigma(I)$ ($R_1 = 0.0221$, $wR_2 = 0.0507$ for 4997 unique reflections) and a goodness of fit of 1.111. Final difference map is between +0.430 and −0.542 e/Å^3. For **V** full-matrix least-squares refinement on F^2 converged at $R_1 = 0.0219$ and $wR_2 = 0.0532$ for 341 parameters and 4455 reflections with $I > 2\sigma(I)$ ($R_1 = 0.0254$, $wR_2 = 0.0546$ for 4920 unique reflections) and a goodness of fit of 1.048. Final difference map is between +0.489 and −0.349 e/Å^3. For **VI** full-matrix least-squares refinement on F^2 converged at $R_1 = 0.0438$ and $wR_2 = 0.1130$ for 361 parameters and 3410 reflections with $I > 2\sigma(I)$ ($R_1 = 0.0475$, $wR_2 = 0.1169$ for 3796 unique reflections) and a goodness of fit of 1.061. Final difference map is between +1.870 and −1.474 e/Å^3. For **VIII** full-matrix least-squares refinement on F^2 converged at $R_1 = 0.0461$ and $wR_2 = 0.1003$ for 433 parameters and 3548 reflections with $I > 2\sigma(I)$ ($R_1 = 0.0673$, $wR_2 = 0.1095$ for 4623 unique reflections) and a goodness of fit of 1.023. Final difference map is between +1.102 and −0.626 e/Å^3. For **IX** full-matrix least-squares refinement on F^2 converged at $R_1 = 0.0441$ and $wR_2 = 0.1035$ for 550 parameters and 5533 reflections with $I > 2\sigma(I)$ ($R_1 = 0.0654$, $wR_2 = 0.1155$ for 7438 unique reflections) and a goodness of fit of 1.007. Final difference map is between +1.024 and −0.711 e/Å^3. For **X** full-matrix least-squares refinement on F^2 converged at $R_1 = 0.0177$ and $wR_2 = 0.0444$ for 261 parameters and 3376 reflections with $I > 2\sigma(I)$ ($R_1 = 0.0183$, $wR_2 = 0.0449$ for 3475 unique reflections) and a goodness of fit of 1.075. Final difference map is between +0.527 and −0.622 e/Å^3.

Catalytic Reactions. Cyclopropanations. Reactions at 23 °C: To a rigorously dried round flask was added the diruthenium(I,I) catalyst (1 mol %) dissolved in CH_2Cl_2(1 mL). Styrene (0.25−0.3 mL, 2.1−2.6 mmol, 10 equiv) was added and the solution stirred at room temperature for a few minutes under Ar to ensure complete catalyst dissolution. Diazoacetate **7** (0.035 g, 0.2 mmol, 1 equiv) was dissolved in CH_2Cl_2 (3 mL) and added to the reaction over 3 h via syringe pump, and the solution was then allowed to stir overnight at room temperature. The mixture was then concentrated *in vacuo*. Reactions at 40 °C: To a rigorously dried round flask was added the diruthenium(I,I) catalyst (1 mol %) dissolved in CH_2Cl_2 (2 mL) under Ar atmosphere. Styrene (0.3 mL, 2.6 mmol, 13 equiv) was added, and the solution was heated to reflux. Methyl phenyldiazoacetate **7** (0.035 g, 0.2 mmol, 1 equiv) was dissolved in dry CH_2Cl_2 (3 mL) and added to the reaction mixture with a syringe pump at the top of the reflux condenser over 3 h. The solution was then allowed to stir for 2−5 h at reflux until all diazo compound was decomposed (monitored by TLC). The mixture was cooled to room temperature, concentrated *in vacuo*, analyzed by crude ^1H NMR spectroscopy, and purified by flash column chromatography (SiO_2, 10% Et_2O/pentane) to afford a white solid. Data for *Z*-**8**: ^1H NMR (400 MHz, $CDCl_3$): δ 7.11−7.09 (m, 3H), 7.03−7.00 (m, 5H), 6.76−6.74 (m, 2H), 3.63 (s, 3H), 3.11 (dd, 1H, J = 7.0, 9.5 Hz), 2.13 (dd, 1H, J = 5.0, 9.5 Hz), 1.86 (dd, 1H, J = 5.0, 7.0 Hz). The spectroscopic data are consistent with the previously reported results.[35]

O−H Insertions. The diruthenium catalyst (0.007 g, 0.004 mmol, 1 mol %) was added to a rigorously dried round-bottom flask purged with Ar. Anhydrous methanol (1 mL) was added to dissolve the catalyst. Methyl phenylvinyldiazoacetate **4** (0.4 mmol, 1 equiv) was dissolved in anhydrous methanol (3 mL) and added to the reaction mixture over 3 h via syringe pump. The reaction mixture was allowed to stir at room temperature under argon for 24 h, concentrated *in vacuo*, and then analyzed by crude ^1H NMR spectroscopy. Purification by flash column chromatography (SiO_2, 10% Et_2O/petroleum ether to 50% diethylether/petroleum ether gradient) resulted in a colorless oil. Reaction with **I** with 0.2 mmol of **4**: *Z*-**6**:*E*-**6**:**5a**:**5b** = 75:11:14:0 (0.022 g, 0.109 mmol, 45% yield); reaction with **II**: *Z*-**6**:*E*-**6**:**5a**:**5b** = 67:15:18:0 (0.022 g, 0.107 mmol, 26% yield); reaction with **III**: *Z*-**6**:*E*-**6**:**5a**:**5b** = 62:18:20:0 (0.027 g, 0.132 mmol, 28% yield). Data for *Z*-**6**: ^1H NMR (500 MHz, $CDCl_3$): δ 7.47−7.28 (m, 5H), 6.32 (dd, J = 11.5, 9 Hz, 1H), 5.97 (d, J = 9 Hz, 1H), 5.87 (d, J = 11.5 Hz, 1H), 3.75 (s, 3H), 3.34 (s, 3H). Data for *E*-**6**: ^1HNMR (500 MHz, $CDCl_3$): δ 7.44−7.29 (m, 5H), 6.97 (dd, J = 6, 15.5 Hz, 1H), 6.10 (d, J = 15.5 Hz, 1H), 4.78 (d, J = 6 Hz, 1H), 3.72 (s, 3H), 3.33 (s, 3H). Data for **5a**,**b**: ^1H NMR (500 MHz, $CDCl_3$): δ 7.41−7.28 (m, 5H), 6.77 (d, J = 15.5, 1H), 6.20 (dd, J = 7, 15.5, 1H), 4.43 (d, J = 7, 1H), 3.79 (s,

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[35] Thompson, J. L.; Davies, H. M. L. *J. Am. Chem. Soc.* **2007**, *129*, 6090–6091.

3H), 3.46 (s, 3H). The spectroscopic data are consistent with the previously reported results.[18]

Reaction with Cyclopentadiene. The diruthenium catalyst (0.002 mmol, 1 mol %) was added to a rigorously dried round-bottom flask, and cyclopentadiene (0.33 g, 5.0 mmol, 20 equiv) and CH_2Cl_2 (2 mL) were added under an Ar atmosphere. Vinyldiazoacetate **9** (0.032 g, 0.25 mmol, 1 equiv) was dissolved in CH_2Cl_2 (3 mL) and added to the reaction mixture over 2 h with a syringe pump. The mixture was then stirred for a further 9−12 h at room temperature until complete consumption of the diazo compound. The solvent was removed *in vacuo* and the crude residue analyzed by ^{1}H NMR. Purification by flash column chromatography (SiO_2, 10% Et_2O/pentane) resulted in *cis/trans*-**10** as a colorless oil. With catalyst **I** (22 mg, 0.13 mmol, 54%): 2:1 isomer ratio; catalyst **II** (15.0 mg, 0.09 mmol, 37%): 2:1 isomer ratio; catalyst **VI** (16.4 mg, 0.10 mmol, 40%): 2.4:1 isomer ratio. Data for **10**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.28 (dd, $J = 3.0$, 5.5 Hz, 1H), 6.00 (dd, $J = 3.0$, 5.5 Hz, 1H), 5.92 (s, 1H), 3.67 (s, 3H), 3.32 (m, 1H), 3.08 (m, 1H), 2.57 (dm, 1H), 2.34 (dm, 1H), 1.70−1.67 (m, 1H), 1.47 (d, $J = 8.0$ Hz, 1H). The spectroscopic data are consistent with the previously reported results.[15]

Reaction with *N*-Boc Pyrrole. The diruthenium catalyst (0.002 mmol, 1 mol %) was dissolved in dry CH_2Cl_2 (2 mL) under Ar atmosphere, and *N*-Boc pyrrole (20 equiv) was added. Vinyldiazoacetate **9** (0.25 mmol, 1 equiv) was dissolved in dry CH_2Cl_2 (3 mL) and added to the reaction mixture over 2 h with a syringe pump. After the addition was complete the reaction was stirred at rt for a further 9–12 h, concentrated *in vacuo*, and analyzed by crude ^{1}H NMR. Purification by flash column chromatography (10% Et_2O/pentane) resulted in **15** as a colorless oil. Catalyst **I** (37.6 mg, 0.14 mmol, 57%): 11:1 *cis/trans*-ratio; catalyst **II** (30 mg, 0.11 mmol, 45%): 13:1 *cis/trans* ratio; catalyst **VI** (35.6 mg, 0.13 mmol, 54%): 25:1 *cis/trans* ratio. Data for *cis*-**15**: TLC (10% Et_2O/pentane): $R_f = 0.39$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.21 (m, 1H), 6.43 (dt, 1H, $J_L = 11.5$ Hz, J_S=7.0 Hz), 6.08 (t, 1H, $J = 3.0$ Hz), 6.01 (m, 1H), 5.87 (m, 1H), 5.85 (m, 1H), 4.24 (d, 2H, $J = 11.0$ Hz), 3.73 (s, 3H), 1.59 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.6, 149.4, 147.0, 132.6, 121.2, 119.5, 112.0, 110.1, 83.7, 51.1, 28.7, 28.0. IR (film, cm^{-1}): 2981(m), 1741(s), 1724(s), 1644(m), 1493(m), 1438(m), 1397(m), 1371(m), 1338(s), 1318(s), 1236(m), 1172(s), 1124(s), 1064(m). MS (ESI): *m/z* (rel. int.) 288 (31), 266 (100), 210 (17), 166 (46). HRMS (ESI): *m/z* calcd for [$C_{14}H_{19}O_4N$ + Na] 288.1206; found [M + Na] 288.1208.

Acknowledgment. M.P. thanks the Donors of the American Chemical Society Petroleum Research Fund (PRF #42910-AC3) and the National Science Foundation Career Award (NSF-0546945) for partial support of this work, and the National Science Foundation funding of the NMR spectrometer (CHE-0342660) at the University at Albany. H.M.L.D. thanks the National Science Foundation (CHE-0350536 and CHE-0750273) for support of this work.

Supporting Information Available: Four CIF files providing crystallographic data for compounds IV-VI, and VIII. This material is available free of charge via the Internet at http://pubs.acs.org.

OM700888F