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Metal Carbene-Directed Intramolecular Vinylogous Reactions of Vinyldiazoacetates

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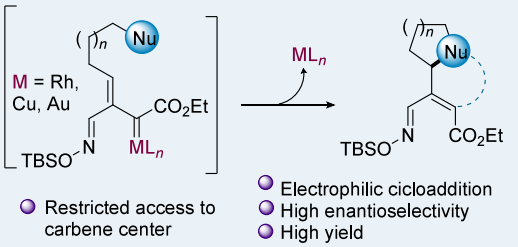
ABSTRACT: Intramolecular addition reactions of electrophilic metallovinylcarbenes with nucleophiles that do not have access to the carbene center undergo addition to the vinylogous position, forming products that rely on subsequent transformations of vinylmetal intermediates. Catalytic addition to a carbon-carbon double bond elicits the formation of an intermediate carbocation whose proton loss causes protodemetalation of the vinylmetal intermediate. Addition to the azido group results in the formation of aliphatic 1,2,3-triazines by [3 + 3]-cycloaddition. Catalytic intramolecular reactions with a carbamate nucleophile yield a carbonyl ylide whose loss of isobutylene produces oximidovinyl-oxazolidinone esters with high enantioselectivity. Comparisons are made between rhodium, copper, gold, and silver catalysts



KEYWORDS: *intramolecular reactions, vinyldiazo compounds, metallovinylcarbenes, electrophilic addition, catalysis*

INTRODUCTION

That a reaction center can relay its electronic influence to a distant point in the molecule when these two sites are connected by conjugated unsaturated linkages has long been identified as a guiding principle in organic chemistry,[1] and its applications in a nucleophile relay for aldol and Michael reactions, among others, have been numerous.[2] Electrophilic vinylogous reactions have been much less represented.[3] Metallovinylcarbenes have two electrophilic sites suitable for association with nucleophiles, the carbene carbon and the vinylogous carbon, and their juxtaposition has made possible [3 + *n*]-cycloaddition reactions, which are a relatively recent development in metal carbene chemistry.[4] In these reactions, the nucleophilic center of the reacting dipole undergoes addition to the electrophilic vinylogous carbon of the metallovinylcarbene to generate a metal−vinyl adduct whose polarity allows electrophilic addition to the original carbene carbon that releases the metal species for further catalytic activity (Scheme 1a). The success of [3 + *n*]-cycloaddition transformations is dependent on the ability of a compatible electrophile to effect the elimination of the catalyst. Gold vinylcarbenes are well regarded for their ability to undergo highly selective electrophilic addition to a carbon−carbon double bond at the vinylogous carbenic center,[5] but dirhodium(II) and copper(I) vinylcarbenes are not, and there is only one example with dirhodium(II) catalysts of a vinylogous addition in 1,4-N-H insertion with hydrazones (Scheme 1b).[6]

Catalytic intramolecular reactions of diazo compounds in which the reacting nucleophile has access to the carbene carbon have a rich history in chemical synthesis,[7] but what would be the reaction outcome with vinyldiazo compounds if the reacting nucleophile did not have access to the carbene carbon but could approach its vinylogous position (Scheme 1c)? To answer this question requires the design of vinyldiazo compounds in which the reacting nucleophile is linked to the carbon−carbon double bond on the side opposite the diazo carbon. Access to such compounds has recently become available in the synthesis of oximidovinyldiazoacetates from 5-substituted-4-carboxylato-1,2,3-triazine 1-oxides[8] via treatment with a catalytic amount of mild base.[9] The oximidovinyldiazoacetate is formed as the *Z*-isomer with the substituent group trans to the diazo carbon. We now report the development of successful intramolecular vinylogous reactions of metallovinylcarbenes with remote nucleophilic sites, including the ability of chiral catalysts to effect enantiocontrol at the remote center.

METHODS AND MATERIALS

Access to a remote carbon−carbon double bond was achieved in the construction of chiral nonracemic oximidovinyldiazoacetate **2** derived from (*S*)-(−)-citronellal. Treatment of **2** with a catalytic amount of rhodium acetate produced two identifiable products (**3** and **4**) whose structural frameworks and stereochemistry were determined by spectrometric

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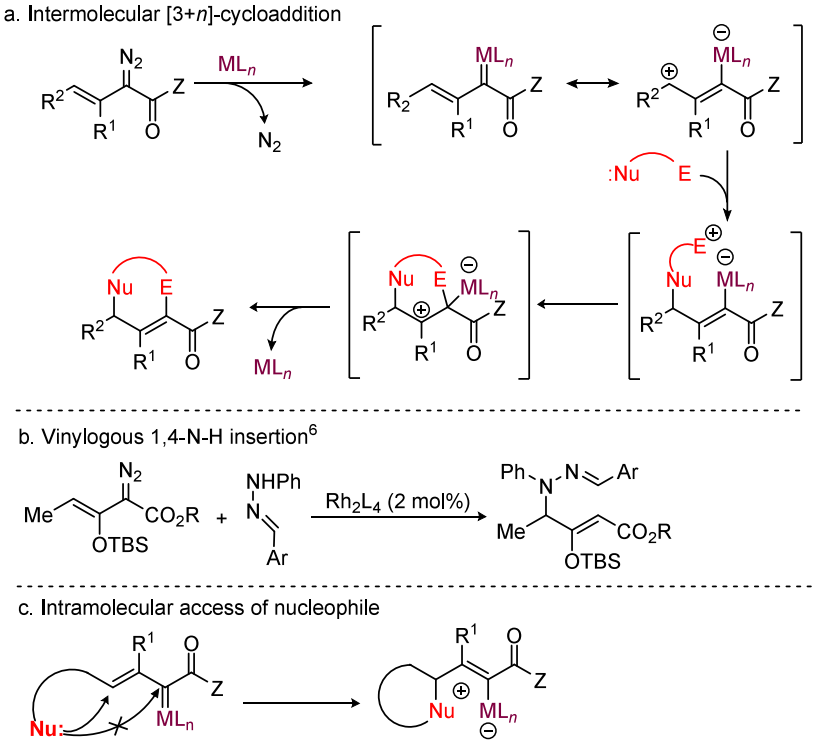
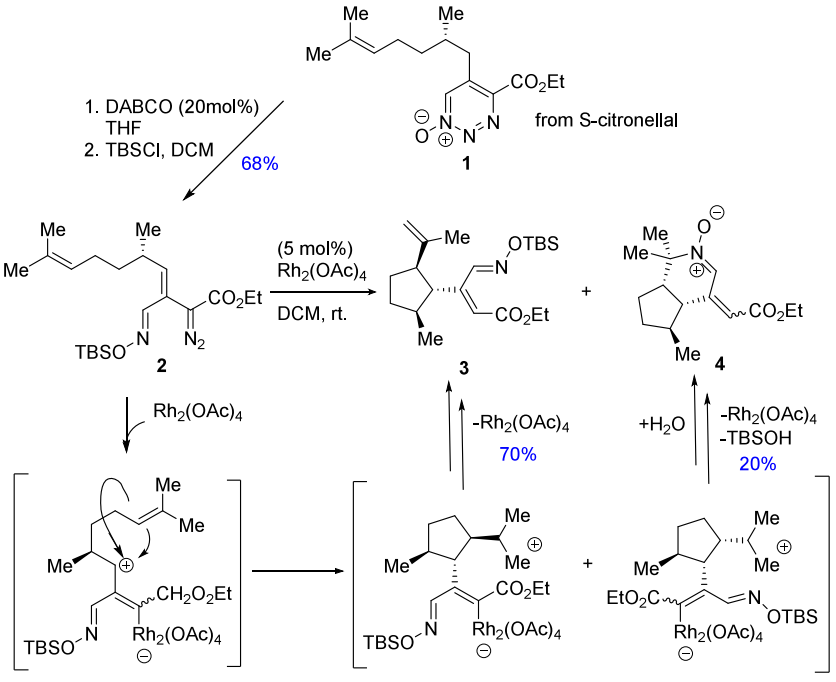
Scheme 1. Electrophilic Vinylogous Reactions of Vinyldiazo Compounds[a]



[a](a) [3 + *n*]-cycloaddition. (b) Vinylogous N-H-insertion. (c) This report: controlled access to the vinylogous position.

Scheme 2. Electrophilic Addition to a C═C from the Vinylogous Position of a Metallovinylcarbene



analyses to be those from electrophilic addition to the carbon−carbon double bond from the vinylogous carbon position (Scheme 2). Production of **3** suggests sufficient electrophilic character at the vinylogous center to undergo addition to the remote carbon−carbon double bond from the bottom side of the carbon−carbon double bond, providing the syn relationship between the cyclopentyl methyl and isopropyl cation groups; elimination of a proton coupled with protonolysis of the vinyl−rhodium completes the process. The production of **3** is complimentary, involving capture by the oxime nitrogen of the carbocation initially formed by vinylogous addition to the remote carbon−carbon double bond from the top side of the carbon−carbon double bond providing the anti relationship between the cyclopentyl methyl and isopropyl cation groups; displacement of the TBS group by trace water and subsequent protonolysis of the vinyl−rhodium bond results in the

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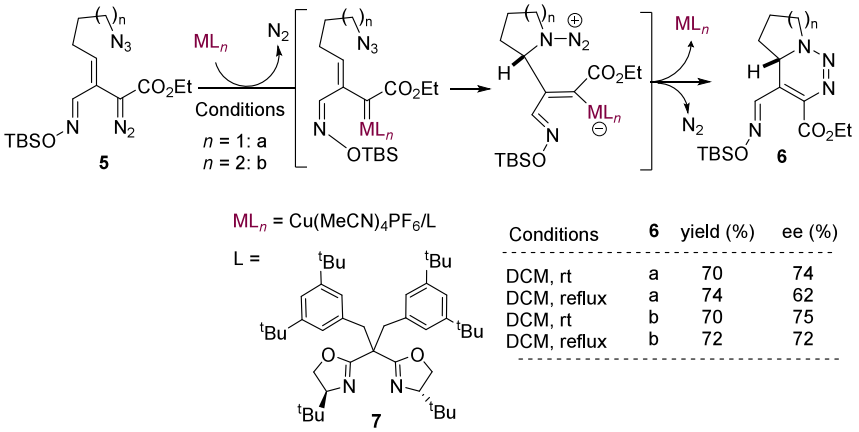
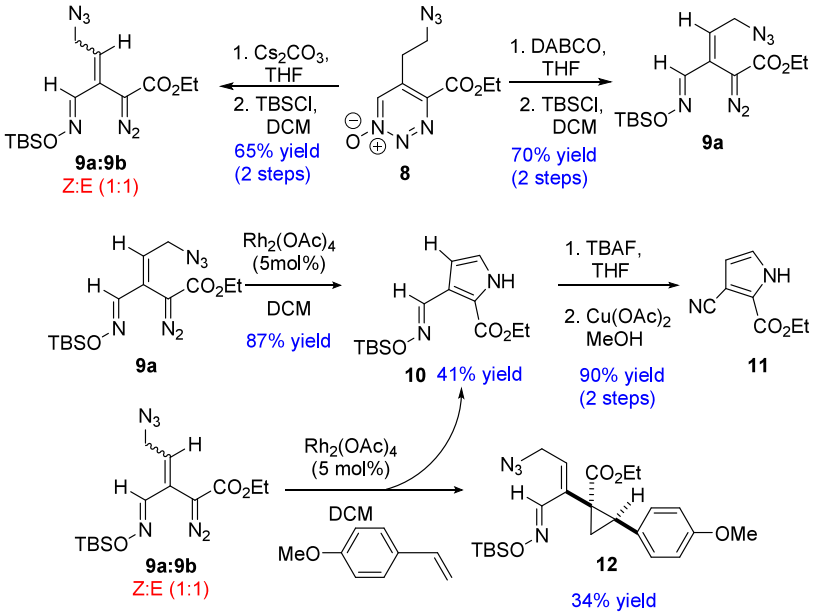
Scheme 3. Electrophilic Intramolecular [3 + 3]-Cycloaddition of Terminal Azides with Metallovinylcarbenes



Conditions	6	yield (%)	ee (%)
DCM, rt	a	70	74
DCM, reflux	a	74	62
DCM, rt	b	70	75
DCM, reflux	b	72	72

Scheme 4. Divergent Reactions with Isomeric Azidoethyl Derivatives 9a and 9b



formation of TBS-OH and **4** (*Z*:*E* = 6:1). Even with rigorous exclusion of water from the solvent, however, compound **4** continued to be formed. These products were also obtained with *rac*-**2**, but attempts to effect enantiocontrol in the formation of **3** or **4** with chiral dirhodium carboxylate or copper(I)−Box catalysts (see the Supporting Information) gave less than 5% *ee*. The structures of **3** and **4** were determined by spectral analyses, especially including 2D spectral methods, and TBS−OH was detected in amounts comparable to that of **4**.

With access to oximidovinyldiazoacetates from 5-substituted-4-carboxylato-1,2,3-triazine 1-oxides, we were able to produce additional oximidovinyldiazoacetates with other remote functionalities trans to the diazo carbon. One of these placed a terminal azido group four and five carbon positions from the vinylogous carbon of the vinyldiazoacetate (**5a** and **5b**, respectively). Treatment of these diazo compounds with catalytic rhodium acetate resulted in a rapid reaction accompanying the extrusion of dinitrogen that formed bicyclic aliphatic 1,2,3-triazines **6a** (86% yield) and **6b** (90% yield). These reactions apparently occur by nucleophilic attack from the internal nitrogen of the azide at the vinylogous position of the metallovinylcarbene with concurrent or subsequent diazonium ion induced release of the catalyst (Scheme 3). Performed with different chiral dirhodium(II) and copper(I)/Box catalysts, this transformation occurred in good yields with catalyst-dependent levels of enantioselectivity. Catalyst screening (see the Supporting Information) showed that dirhodium(II) catalysts had higher reactivity, resulting in a lower reaction time (3.5 h), but they provided lower stereocontrol (45% *ee* maximum), whereas copper(I) hexafluorophosphate in combination with chiral SaBOX ligands showed superior enantioselectivity, providing **6** in up to 74% *ee* with SABOX ligand **7**, albeit with reaction times of 9 h. The fused 1,6-dihydro-1,2,3-triazines were obtained with good yields and a relatively high enantioselectivity.

Aliphatic 1,2,3-triazines are quite rare,[10] and those with a bridgehead nitrogen, like that of **6**, are even more limited. An intramolecular [3 + 3]-cycloaddition between a pendant azide and an allyl alcohol derived allylic cation has been reported,[11] but their yields were modest.

Unexpectedly, the 1,2,3-triazine 1-oxide having an azidoethyl group at the 5-position **8** underwent the base-catalyzed rearrangement to oximidovinyldiazoacetate **9a** in which the

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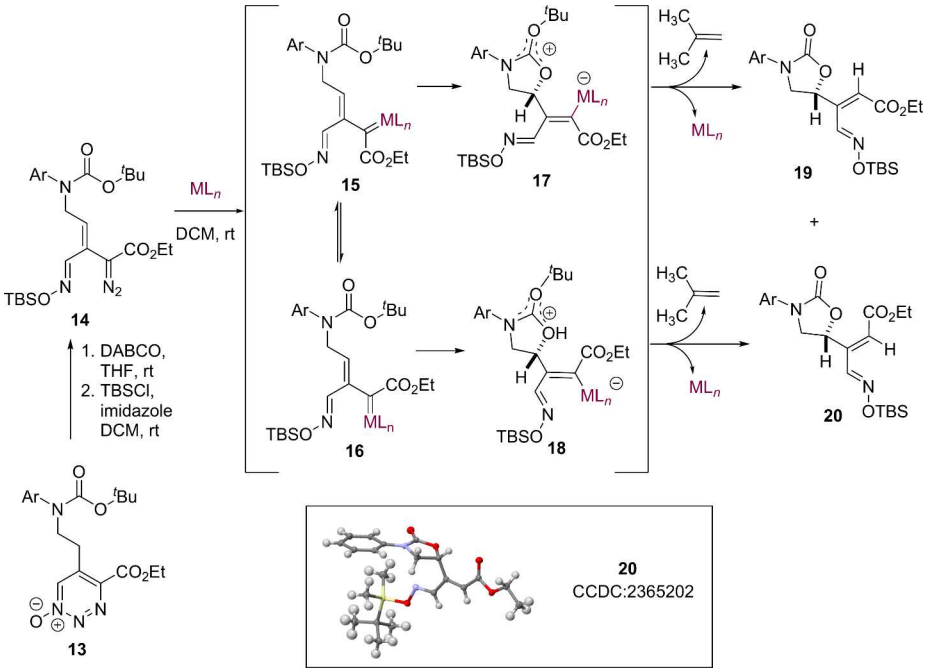
Scheme 5. Electrophilic Vinylogous Intramolecular Cyclization of *N*-Phenylcarbamate 14



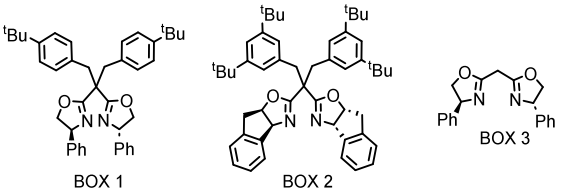
azidomethyl group was in the *Z*-configuration, placing the azido group in close proximity to the diazo carbon (Scheme 4). Treatment with catalytic $Rh_2(OAc)_4$ resulted in the formation of pyrrole **10** in 87% yield whose oximido group was converted into nitrile **11** with catalytic cupric acetate.[12] Access to the *E*-isomer of **9b** was partially achieved when Cs_2CO_3 was used as the base instead of DABCO. Treatment of the *E*/*Z* mixture with $Rh_2(OAc)_4$ in the presence of 3.0 equiv of 4-methoxystyrene rapidly formed the product from intermolecular cyclopropanation (**12b**), leaving **9a** intact initially, but after an extended time **9a** was fully converted to **10**. Consistent with the stereochemical outcome of other intermolecular cyclopropanation reactions with vinyldiazoacetates,[7] only the *Z*-diastereoisomer of **12** was formed.

Having established remote cycloaddition with terminal azides, we directed our attention to carbamates whose nucleophilic carbonyl oxygen might be suitable to react at the vinylogous carbon of the intermediate metallovinylcarbene to produce a carbonyl ylide.[13] The reactants, **14**, were prepared from 1,2,3-triazine-1-oxides **13** with a *tert*-butyl-*N*-arylcarbamate attachment. Both nitrogen substituents could possibly serve as nucleophiles for the vinylogous electrophilic center of the intermediate metal carbene (the amide carbonyl for ylide formation and the aryl group for Friedel−Crafts-type electrophilic aromatic substitution).[14] To probe these pathways, treatment of **14** with catalytic $Rh_2(OAc)_4$ revealed that only products from carbonyl ylide formation were obtained, yielding isomeric oxazolidinones **19** and **20** in 45% and 25% yields, respectively (Scheme 5). The structure of **19** was confirmed by spectral analyses, and the structure of **20** was determined by X-ray crystallography[15] (from catalysis by Rh_2(*S*-BTPCP)$_4$). The overall process requires the loss of isobutylene, which was also detected as a reaction product.

With the assumption that protodemetalation occurs with retention of configuration,[16] the formation of **19** and **20** implies that the two conformational isomers of the intermediate metal carbene (**15** and **16**) are responsible, and the **19:20** ratio dependence on the catalyst ligand (Table 1) is consistent with this interpretation. Enantioselectivities imparted by transition metal catalysts having chiral ligands afforded another dimension in understanding stereochemical control of the remote catalyst. These reactions occurred in

Table 1. Influence of Catalyst on 19:20 Product Ratio and Enantioselectivities[a]

Ligand =



entry	catalyst	ligand[f]	total yield (%)[d]	**19:20** ratio	*ee* **19** (%)[g]	*ee* **20** (%)[g]
1	$Rh_2(OAc)_4$[b]		71	65:35		
2	$Rh_2(TPA)_4$[c]		80	93:7		
3	AuJP/AgOTf[d]		76	82: 18		
4	Rh_2(*S*-DOSP)$_4$[c]		82	67: 33	−21	17
5	Rh_2(*S*-BTPCP)$_4$[c]		85	45: 55	84	65
6	Rh_2(*S*-PTA)$_4$[c]		87	66: 34	−33	−11
7	Rh_2(*S*-PTTL)$_4$[c]		92	97:3	91	31
8	Rh_2(*S*-PTAD)$_4$[c]		89	96:4	74	57
9	$Cu(MeCN)_4PF_6$[e]	BOX1	83	28:72	−27	−4
10	$Cu(MeCN)_4PF_6$[e]	BOX2	76	49:51	−57	13
11	$Cu(MeCN)_4PF_6$[e]	BOX3	74	51:49	−6	<1
12	$AgPF_6$[e]	BOX2	78	86:14	−32	−14

[a]Reaction conditions: a solution of 0.050 mmol of **14** in 0.5 mL of DCM was added to a solution of catalyst, ligand, and 4 Å MS (25 mg) in 0.5 mL of DCM over 3 h at rt under N_2. [b]2 mol % $Rh_2(OAc)_4$ was used. [c]1.0 mol % catalyst was used. [d]5.0 mol % AuJP (i.e., Au(MeCN)(JohnPhos)SbF_6) and 4.0 mol % AgOTf were used. [e]5.0 mol % catalyst was used. [f]Isolated yield. [g]The *ee* values were determined by chiral HPLC analysis (Chiralpak AS-H column).

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good to excellent combined yields, and formation of the two geometrical isomers is observed in each case. The highest level of stereocontrol was achieved with the use of the Hashimoto *S*-PTTL ligand on dirhodium[17] that produced **19** as the major product (>20:1 **19**:**20**) with 91% *ee*. Comparative results with rhodium(II) acetate and triphenylacetate (TPA) suggest that the **19**:**20** ratio is strongly influenced by steric factors, but a similar influence is not evident with Box ligands on copper(I). Enantioselectivities for **19** are higher than those for **20**, which is consistent with the closer approach of the ligated metal to the vinylogous carbene center in **19**. However, the dominant enantiomer is not the same with the same configuration of chiral dirhodium(II) ligands, suggesting a greater complexity for enantiocontrol with these catalysts than previously understood,[7] and a similar variation in dominant isomer occurs in reactions with **5a** (see the Supporting Information). With the *p*-MeOPh analogue of **14** the corresponding products were formed in excellent yield (86%) and enantioselectivity, in which the *E*-isomer prevailed (*E*:*Z* = 97:3) with 91% *ee* for the *E*-isomer and 42% *ee* for the *Z*-isomer from the reaction catalyzed by Rh_2(*S*-PTTL)$_4$.

CONCLUSION

Transition metal catalyzed vinylogous reactions of vinyldiazoacetates are robust when access to the metal carbene center is inhibited. Intramolecular nucleophilic reactions with the carbon-carbon double bond, the azide functional group, and the carbonyl group of a carbamate occur to give cyclic alkane, 1,2,3-triazine, and oxazolidinone products in good yields. Although the pendant catalyst is remote from the site of nucleophilic attack, asymmetric induction from the use of chiral dirhodium(II) or copper(I) catalysts can be high.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.4c05839.

Experimental procedures and instrumental analyses, including ^{1}H NMR and ^{13}C NMR for all new products, 2D spectra and HPLC-DAD chromatograms for reaction optimization and enantioselective reactions, diastereomers, ORTEP diagram, crystal data (PDF)

Compound **20** (CIF)

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Notes

The authors declare no competing financial interest.

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