the π bonding in the P-N and Se-N systems is important in stabilizing the low-energy conformer. This π bonding together with the electrostatic interaction is responsible for the high stability of the tub structure.

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Electronic and Steric Control in Carbon-Hydrogen Insertion Reactions of Diazoacetoacetates Catalyzed by Dirhodium(II) Carboxylates and Carboxamides

Michael P. Doyle,* Larry J. Westrum, Wendelmoed N. E. Wolthuis, Marjorie M. See, William P. Boone, Vahid Bagheri, and Matthew M. Pearson

Contribution from the Department of Chemistry, Trinity University, San Antonio, Texas 78212.
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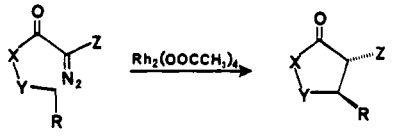
Abstract: Carboxylate and carboxamide ligands on dirhodium(II) catalysts can provide enormous regiocontrol in carbon-hydrogen insertion reactions of diazoacetate esters. Whereas 2,3,4-trimethyl-3-pentyl diazoacetoacetate (**1**) forms γ-lactone products from insertion into primary and tertiary C-H bonds in a statistical distribution (61:39) with dirhodium(II) tetrakis(perfluorobutyrate), only tertiary C-H insertion is observed with dirhodium(II) tetraacetamide. Similar results are obtained with 2-methyl-2-octyl diazoacetoacetate (**3**), where competition for insertion exists between secondary and primary C-H bonds and electronic factors govern regioselection. However, with 2-methyl-3-isopropyl-3-heptyl diazoacetoacetate (**2**) and 2-methyl-1-phenyl-2-propyl diazoacetoacetate (**4**), product distributions from C-H insertion are invariant with the dirhodium(II) ligands; insertion into a secondary C-H bond is favored over tertiary C-H insertion with **2** (95:5), and insertion into a primary C-H bond is preferred to benzylic secondary C-H insertion with **4** (70:30). In such cases, which are amenable to analyses by MM2 calculations, regioselectivity is determined by conformational preferences for which C-H insertion selectivity can be as random as that found with **2** and **4**. When only one C-H bond site is available for insertion to form a five-membered ring product, only one γ-lactone is observed from reactions catalyzed by dirhodium(II) tetraacetate, and that product is not necessarily the one predicted by presumed electronic preferences.

The development of dirhodium(II) catalysts for intramolecular carbon-hydrogen insertion reactions of diazo carbonyl compounds has been a significant synthetic achievement.[1,2] β-Keto-α-diazo esters, phosphonates, and sulfones have been employed for the construction of cyclopentanone derivatives (eq 1: X = Y = CH_2;



(1)

Z = COOEt, $PO(OR)_2$, SO_2Ar),[3-6] diazoacetates and diazoacetoacetates form γ-lactones (eq 1: X = O; Y = CH_2; Z = H, $COCH_3$),[7] 3-alkoxy-1-diazoacetates provide access to 2(3*H*)-dihydrofuranones (eq 1, X = CH_2, Y = O, Z = H),[8] and diazomalonate esters are reported to produce either or both γ-lactones and β-lactones.[9] These reactions occur in moderate to high yield and, ordinarily, with an overwhelming preference for the formation of a five-membered ring. There are, however, notable exceptions to five-membered ring formation, especially in reactions of diazo amides[10] and of sterically constrained systems,[11,12] that limit predictability for these constructions.

Regiocontrol in carbon-hydrogen insertion reactions is one of the major advantages attributed to the use of rhodium(II) acetate as the catalyst.[2] For reactions involving five-membered ring formation, there is general agreement that insertion into a tertiary C-H bond is favored over insertion into a secondary C-H bond, and primary C-H insertion, when observed, is the least favorable.[7,13,14] Surprisingly, for what is commonly regarded to be an electrophilic transformation, allylic or benzylic C-H bonds are reported to be less reactive than secondary C-H bonds for insertion,[13] although, more recently, allylic C-H insertion has been shown to be greatly preferred to nonallylic secondary C-H in-

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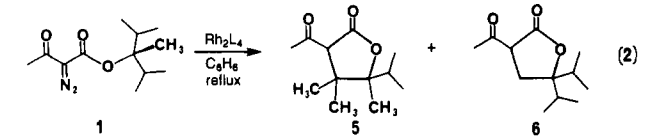
sertion.[12] We recently described preliminary results for C–H insertion reactions of diazoacetate and diazoacetoacetate esters that resulted in the production of γ-lactones in high yield and with a high degree of regiocontrol.[7] In that report we presented examples of the dependence of regioselectivity on the carboxylate or carboxamide ligand of the dirhodium(II) catalyst. We now report detailed investigations that demonstrate the unique capabilities of rhodium(II) carboxylates and carboxamides to modify regiocontrol in C–H insertion reactions and that identify the electronic and steric factors that control regioselectivity.

Results

Diazoacetoacetates **1–4**, designed to offer the intermediate metal carbene two different sites for C–H insertion, were selected to evaluate regioselectivity in reactions catalyzed by dirhodium(II) carboxylates and carboxamides. These diazo compounds were prepared from the corresponding alcohols by condensation with diketene[15] followed by diazo transfer.[16] Reactions took place in refluxing benzene and, with one exception, γ-lactones were the sole products from C–H insertion. With diazoacetoacetate **1**, competition exists for tertiary versus primary C–H insertion (eq 2), and with **2**, competition is between tertiary and secondary C–H



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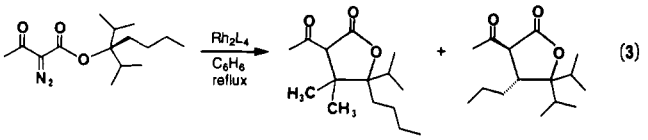

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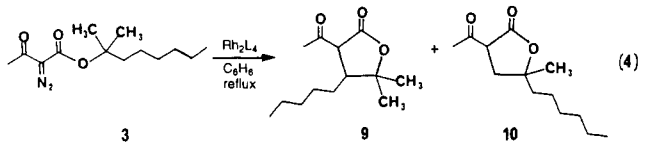
insertion (eq 3). Insertion products can arise from reaction with secondary and primary C–H bonds in **3** (eq 4), and for **4**, com-



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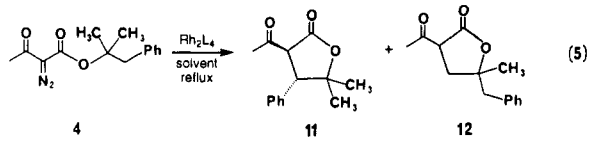
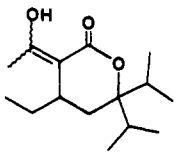


(5)

petition exists between primary and benzylic secondary C–H insertion (eq 5). Table I reports the yields of these products and the regioselectivity for C–H insertion as a function of the dirhodium(II) catalyst. The identity of these products and their stereochemistry were determined by spectroscopic analyses. Lactones **8**, **9**, and **11** were identified as the trans isomers by their characteristic NMR coupling constants; although the exact stereochemistry of the others (**5**, **10**, and **12**) remains uncertain, only one product having the assigned structure was identified for **5** and **12** through both GC and NMR analyses. The catalysts chosen to exemplify the influence of the dirhodium(II) ligand on regioselectivity included rhodium(II) perfluorobutyrate (Rh_2(pfb)$_4$), rhodium(II) acetate ($Rh_2(OAc)_4$), and either rhodium(II) acetamide ($Rh_2(acam)_4$) or the more soluble rhodium(II) caprolactam ($Rh_2(cap)_4$). Previous reports of reactivity/stereoselectivity for catalytic cyclopropanation,[17,18] of selectivity for β-lactam formation resulting from C–H insertion reactions of diazoacetamides,[10a] and of chemoselectivity in catalytic carbenoid reactions[19] suggested that decreased electron withdrawal by dirhodium(II) ligands (acam, cap < OAc < pfb) lowered reactivity but increased selectivity, and the same outcome was expected for C–H insertion reactions of diazoacetoacetates.

δ-Lactone **13** was formed in competition with **7** and **8** in Rh_2(pfb)$_4$-catalyzed reactions of **2** (18%), but **13** either was not produced or was a trace component (<1%) when either $Rh_2(OAc)_4$ or $Rh_2(cap)_4$ was the catalyst. Thermal decomposition of **2** at

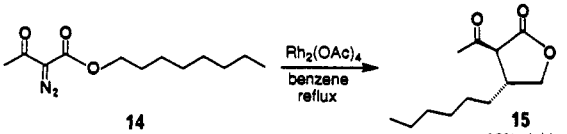


13

200 °C in the absence of dirhodium(II) resulted in the production of both **8** and **13** (~1:1) but not **7**. Both enol stereoisomers of **13** were evident (64:36). The δ-lactone from C–H insertion into an isopropyl methyl group was not formed. The production of six-membered ring products in dirhodium(II)-catalyzed reactions has been observed only rarely,[11,12] and the present example sets an upper limit to this competition in lactone generation from intramolecular C–H insertion reactions of acyclic diazoacetoacetates.

The dependence of regioselection on the dirhodium(II) catalyst in C–H insertion reactions is pronounced. The strong electron-withdrawing capabilities of the perfluorobutyrate ligand[20] provide, with the exception of reactions with **2** and **4**, insertion products that are almost a statistical accounting of the number of primary, secondary, or tertiary C–H bonds. With $Rh_2(acam)_4$ or $Rh_2(cap)_4$, on the other hand, the product from insertion into the more electron-rich C–H bond is expected to dominate, but this is observed only with **1** and **3**. With diazoacetoacetate **2**, the product from insertion into a secondary C–H bond is favored over that from tertiary C–H bond insertion by a factor of >20. In addition, primary C–H bond insertion resulting through dinitrogen extrusion from **4** competes effectively with benzylic secondary C–H insertion. Obviously, regioselectivity in these insertion reactions cannot be attributed solely to electronic factors, at least for **2** and **4**, which do not follow the order tertiary > secondary > primary and are not responsive to the electronic influence of the catalyst. Also, as suggested in Table I for Rh_2(pfb)$_4$- and $Rh_2(OAc)_4$-catalyzed reactions of **4**, temperature and solvent have a negligible influence on regioselectivity.

When only one C–H bond site is available for insertion to form a five-membered ring product, only one γ-lactone is observed from reactions catalyzed by $Rh_2(OAc)_4$. Thus, for example, **14** and **16** are transformed to γ-lactones **15** and **17**, respectively, in high yield (eqs 6 and 7) without the formation of detectable amounts



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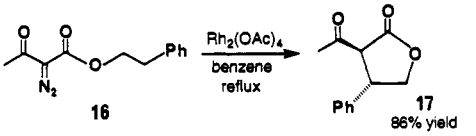

(7)

of β- or δ-lactones. However, structurally more complex diazo-

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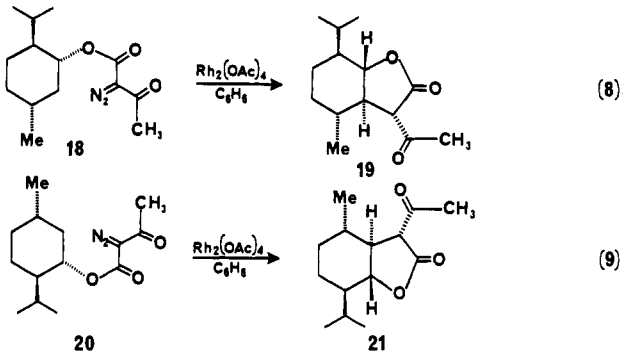
Table I. Product Yields of γ-Lactones Formed From Diazoacetoacetates as a Function of Catalyst and Conditions[a]

diazo substrate	catalyst	solvent	temp, °C	isolated yield, %	relative yield, %	
1	$Rh_2(pfb)_4$	C_6H_6	80	61	39 (**5**)	61 (**6**)
	$Rh_2(OAc)_4$	C_6H_6	80	97	90 (**5**)	10 (**6**)
	$Rh_2(acam)_4$[b]	C_6H_6	80	89	>99 (**5**)	<1 (**6**)
2	$Rh_2(pfb)_4$	C_6H_6	80	74[c]	5 (**7**)	95 (**8**)
	$Rh_2(OAc)_4$	C_6H_6	80	88	3 (**7**)	97 (**8**)
	$Rh_2(cap)_4$	C_6H_6	80	79	4 (**7**)	96 (**8**)
3	$Rh_2(pfb)_4$	C_6H_6	80	75	34 (**9**)	66 (**10**)[d]
	$Rh_2(OAc)_4$	C_6H_6	80	84	75 (**9**)	25 (**10**)[d]
	$Rh_2(cap)_4$	C_6H_6	80	80	92 (**9**)	8 (**10**)[d]
4	$Rh_2(pfb)_4$	C_6H_6	80	31[e]	26 (**11**)	74 (**12**)
	$Rh_2(pfb)_4$	$(ClCH_2)_2$	83	61	29 (**11**)	71 (**12**)
	$Rh_2(OAc)_4$	C_6H_6	80	84	29 (**11**)	71 (**12**)
	$Rh_2(OAc)_4$	CH_2Cl_2	40	56	36 (**11**)	64 (**12**)
	$Rh_2(cap)_4$	C_6H_6	80	71	30 (**11**)	70 (**12**)

[a] Reactions were generally performed on a 1.0-mmol scale with 1.0 mol % catalyst. Relative product yields were independent of the scale of reactants, concentration, and mol % catalyst. [b] Identical results were obtained with $Rh_2(cap)_4$. [c] Includes δ-lactone **13**: relative yields are 6% **7**, 76% **8**, and 18% **13**. [d] Formed as a 1:1 mixture of geometrical isomers. [e] Lower yield due to electrophilic aromatic cycloaddition of the carbene to the solvent benzene.

acetates can also lead to single products, as in the production of **19** or **21** (eqs 8 and 9) from *l*-(1*S*,2*R*,5*S*)-(+)- or *d*-



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(1*R*,2*S*,5*R*)-(−)-menthyl diazoacetoacetate (**18** or **20**). Bicyclic lactones **19** and **21** were formed in >80% isolated yield by insertion into a secondary C–H bond without evidence of other insertion products. Their trans ring fusion and acetyl group stereochemistry were established by NMR coupling constants for H-5 and H-3 (10.7 and 12.4 Hz, respectively). Identical results were obtained with $Rh_2(acam)_4$ as the catalyst.

Discussion

Dirhodium(II) catalysts are exceptionally effective for C–H insertion reactions of diazoacetoacetate esters. The high yields obtained from these reactions, especially for the construction of highly substituted products, and the specificity for C–H bond insertion four atoms removed from the carbene carbon suggest the versatility of this catalytic metal carbene transformation for the synthesis of γ-lactones. As exemplified by the formation of single stereoisomers for each product, these insertion reactions also occur with an exceptional degree of stereocontrol.

The influence of dirhodium(II) ligands on chemoselectivity has recently been demonstrated in competitive transformations where $Rh_2(pfb)_4$ provides exceptional selectivity for one reaction pathway and $Rh_2(cap)_4$ gives equally high selectivity for the competing pathway.[19] More limited changes in dirhodium(II) ligands have also been reported to afford chemoselection.[21] Cyclopropanation stereoselectivity and regioselectivity is also influenced by dirhodium(II) ligands, being significantly enhanced by the use of $Rh_2(acam)_4$.[17,18] For C–H insertion reactions, the effectiveness of catalyst ligands on regiocontrol is amply demonstrated by the results obtained for reactions described in eqs 2 and 4.

The influence of the dirhodium(II) catalyst on the formation of **5** and **6** from **1** (eq 2) exemplifies the extent of regiocontrol that can be achieved through ligand variation. With $Rh_2(pfb)_4$, their product ratio (**5**:**6** = 39:61) is almost exactly that of a predicted statistical product distribution based on the number of carbon–hydrogen bonds of each type (tertiary:primary) that are available for insertion. Use of $Rh_2(OAc)_4$ brings that ratio to 90:10, suggesting a 13-fold higher reactivity for tertiary C–H insertion than for primary C–H insertion beyond a statistical preference, and $Rh_2(acam)_4$ provides a further increase in the product ratio to 99:1, suggesting a 150-fold difference in reactivity. The influence of catalyst ligand on regioselectivity demonstrates that, at least for reactions with $Rh_2(OAc)_4$ and $Rh_2(acam)_4$ or $Rh_2(cap)_4$, C–H insertion occurs from the intermediate metal carbene rather than from a free carbene. Furthermore, the increased regioselectivity suggests a tighter transition state for insertion reactions catalyzed by $Rh_2(acam)_4$ or $Rh_2(cap)_4$ rather than by $Rh_2(OAc)_4$.

Similar results have been obtained for the formation of **9** and **10** from **3** (eq 4). Here competition is between secondary and primary C–H insertion, and relative reactivities also vary with the dirhodium(II) ligand: $Rh_2(pfb)_4$ (1.5), $Rh_2(OAc)_4$ (9), and $Rh_2(cap)_4$ (34). However, the major products from catalytic reactions of both **2** and **4** (eqs 3 and 5) are those for which insertion has occurred at the electronically disfavored C–H bond, and there is little or no variation in the product distribution with changes in the dirhodium(II) ligand. The same apparent inversion of electronic preference is seen in the production of **19** and **21**, although in these cases insertion takes place into the equatorial C–H bond, which is only possible in the direction that yields the secondary C–H insertion product.

Metal carbene reactions catalyzed by dirhodium(II) carboxylates and carboxamides are electrophilic in character, resembling those of a metal–stabilized carbocation more than those of a metal carbene.[18,22,23] As established by Taber,[3a] C–H insertion occurs with retention of configuration at the carbon–hydrogen bond undergoing insertion. In addition, the high degree of enantioselectivity that is achieved in these reactions with chiral dirhodium(II) carboxamides[24] and, to a lesser extent, from diazo ketones with homochiral rhodium(II) carboxylates[6,25] suggests that the integrity of the ligands on the dirhodium framework remains intact during the insertion process. On the basis of these considerations, the mechanism depicted in Scheme I provides a suitable rationale for the C–H insertion process. Overlap of the metal carbene's p-orbital with the σ-orbital of the reacting C–H bond initiates the process in which C–C and C–H bond formation with the carbene carbon proceeds as the ligated metal dissociates.

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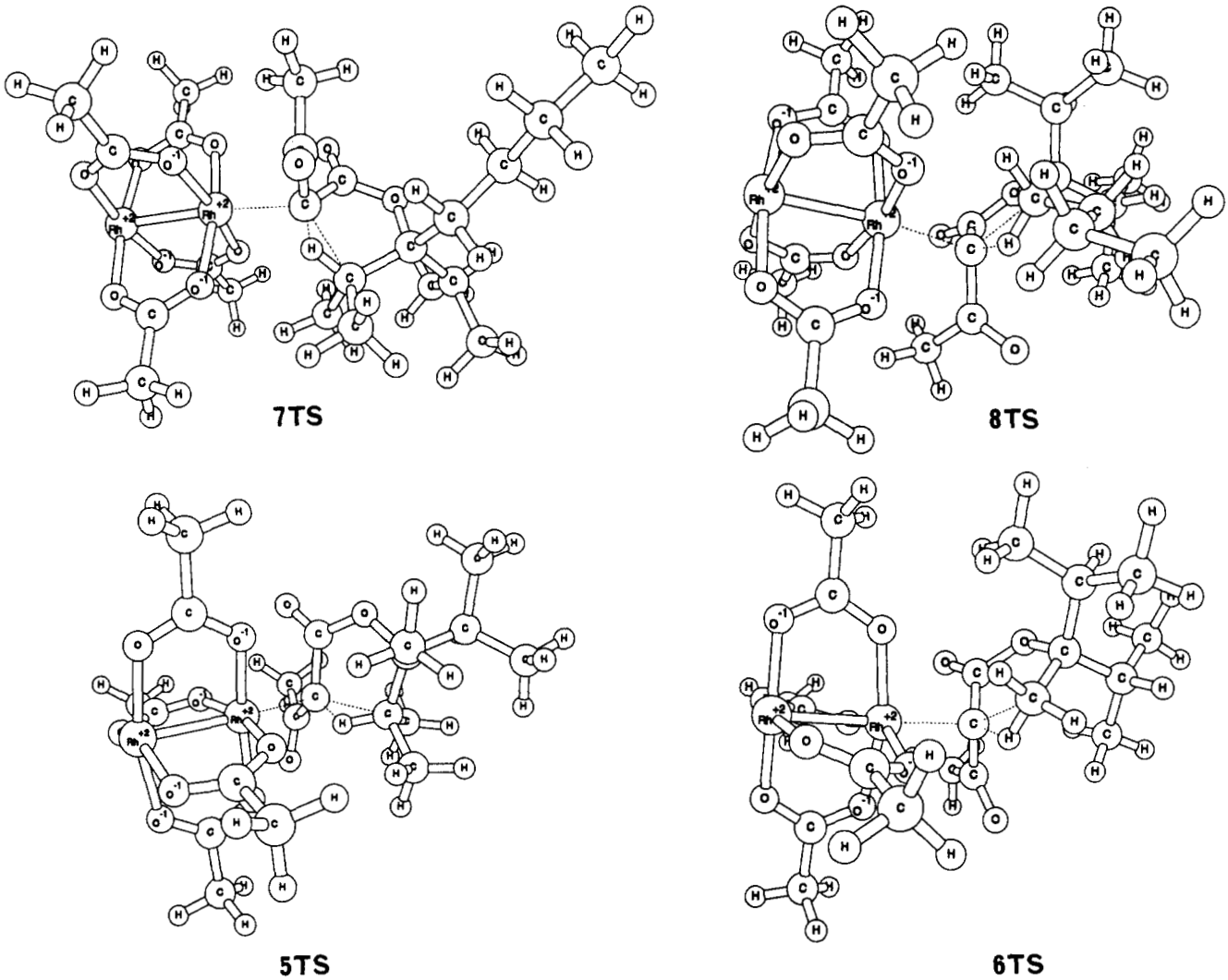
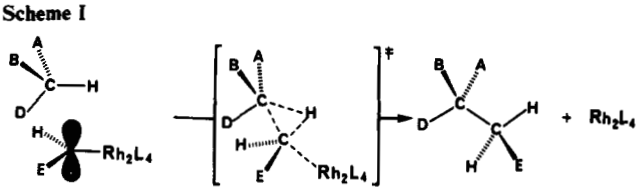


Figure 1. Minimum-energy structures (MM2) of pseudo-transition states (TS) for C–H insertion from $Rh_2(OAc)_4$-catalyzed reactions of **1** and **2** that result in **5**,**6** and **7**,**8**, respectively.

Scheme I



According to this model, increased electron withdrawal by the ligand from the metal increases the electrophilicity of the carbene and causes bond formation to take place at a greater distance from the reacting C–H bond (earlier transition state) with resulting lower selectivity. Decreased electron withdrawal, as occurs with carboxamide ligands, leads to a later transition state and greater selectivity. Carbene substituents whose electron donation or electron withdrawal affect carbene electrophilicity (e.g. H, COOR, COR, SO_2R, and CH_3)[10,21,26] also influence selectivity.

The absence of any significant influence by the catalyst on regioselectivity for C–H insertion in reactions of either **2** or **4** and the formation of their electronically disfavored insertion products suggest that the factors responsible for regioselection in these cases have a minimal electronic input. Molecular mechanics calculations using an augmented version of the MM2 force fields that accommodate octahedrally disposed nuclei (CAChe system) on the proposed transition states for C–H insertion with $Rh_2(OAc)_4$ leading to **7** and **8** (eq 3) estimate methylene C–H insertion to be favored over methine C–H insertion by 4.6 kcal/mol (Figure 1, **7TS** and **8TS**). In contrast, methyl C–H insertion is favored over methine C–H insertion in the transition states leading to **6** and **5** (eq 2), respectively, by 5.4 kcal/mol (Figure 1, **6TS** and **5TS**). Similarly, **8** is calculated (MM2) to be more stable than **7** by 3.21 kcal/mol whereas **6** is more stable than **5** by 4.84 kcal/mol, both in agreement with the calculated differences in transition-state energies. δ-Lactone **13** is less stable than γ-lactone **8** by 2.89 kcal/mol. These energy differences reflect the degree of steric crowding by alkyl substituents of the developing or product lactones.[27] The electronic preference for tertiary C–H insertion over primary C–H insertion (**5** vs **6**) must obviously be factored into the data observed for dirhodium(II)-catalyzed reactions of **1**, and here it is evident that this preference is greatest for $Rh_2(acam)_4$ or $Rh_2(cap)_4$ (estimated from transition-state energy differences to be 8.1 kcal/mol) and least for $Rh_2(pfb)_4$ (estimated to be 5.2 kcal/mol). However, a similar argument about electronic preferences cannot be made for dirhodium(II)-catalyzed reactions of **2**.

For systems in which each of the possible sites for insertion can present a C–H bond to the carbene center with equal probability for C–H insertion, electronic influences from substituents on the

(26) Stork, G.; Nakatani, K. *Tetrahedron Lett.* **1988**, *29*, 2283.

(27) The crowding of the two isopropyl groups, particularly 1,3-methyl interactions in **7TS**, was of concern to one of the reviewers and prompted us to evaluate energy versus dihedral angle for their universe of conformational isomers. Although no lower energy conformer than that described for **7TS** was found, one of nearly the same energy (+0.3 kcal/mol for 180° vs 60° with Me–(CHMe-CR)–$CHMe_2$) was found, and the barrier to interconversion of these two conformers was approximately 10 kcal/mol.

reacting C–H bond will influence regioselectivity. In such cases, the preference tertiary > secondary > primary is expected,[2] and decreasing the electrophilicity of the metal carbene by changing the dirhodium(II) ligands from perfluorobutyrate to carboxamide magnifies this selectivity.[14,15] However, when the possible sites for insertion cannot present their C–H bonds to the carbene center with equal probability for C–H insertion, regioselectivity is governed more by conformational preference than by electronic preference. In such cases, selectivity for insertion into primary, secondary, or tertiary C–H bonds can be as random as that observed with **2** and **4**, and decreasing the electrophilicity of the metal carbene should have little effect on selectivity.

The case of **4** (eq 5) is instructive. According to results obtained with **3** from eq 4, $Rh_2(cap)_4$ provides a 34-fold rate enhancement for insertion into a secondary C–H position relative to insertion into a primary C–H position (**9**/**10**). In contrast, with the same catalyst applied to **4**, **12** is preferred over **11** by 7:3 in actual relative yield and is formed with approximately equal probability when the number of possible C–H sites for insertion is taken into account. Thus insertion into the benzylic secondary C–H site is approximately 30 times less than expected if the phenyl substituent is assumed not to modify benzylic C–H reactivity. This suggests that of the two conformations for insertion, that leading to **11** is less populated than the one resulting in **12** by a comparable factor.

These same considerations are applicable to other competitive insertion reactions.[10-14,19,26] Only when the product ratio is responsive to electronic influences from the ligands of the catalyst, as is evident in this investigation, can a conclusion be drawn regarding electronic influences on reactivity by substituents of a C–H bond.

Experimental Section

Proton NMR spectra were obtained from a 300-MHz spectrometer, and ^{13}C NMR spectra were recorded at 75 MHz. Mass spectra were obtained from a quadripole instrument at an ionizing voltage of 70 eV. Infrared spectra were recorded on a FT instrument having a resolution of ±1 cm^{-1}. Melting points are uncorrected. Microanalyses were performed at Texas Analytical Laboratories, Inc. $Rh_2(pfb)_4$[28] and $Rh_2(acam)_4$[18] were prepared by acetate displacement from stock $Rh_2(OAc)_4$, which was synthesized from rhodium(III) chloride hydrate.[29]

Rhodium(II) Caprolactam. In a Soxhlet extraction apparatus, rhodium(II) acetate (0.490 g, 1.11 mmol) and caprolactam (2.560 g, 22.62 mmol) in freshly distilled chlorobenzene were refluxed under a nitrogen atmosphere. The Soxhlet extractor thimble was charged with oven-dried Na_2CO_3 and sand in a 3:1 ratio. The reaction was monitored by HPLC using a μ-Bondapak-CN column with 0.3% CH_3CN in methanol as the eluent, and analysis showed that ligand substitution was >98% complete after 17 h. Chlorobenzene was then removed under reduced pressure, leaving a purple solid. A column was prepared with 17 g of reverse-phase silica (CN-Bakerbond) and the reaction mixture was loaded on the silica with methanol. A blue band eluted with the methanol. Collection of the blue band, followed by evaporation of methanol yielded 0.485 g of a blue solid that was pure by HPLC (0.74 mmol, 67% yield). Anal. Calcd for $C_{24}H_{40}N_4O_4Rh_2$: C, 44.05; H, 6.16; N, 8.56. Found: C, 43.83; H, 6.28; N, 8.50.

2,3,4-Trimethyl-3-pentyl Diazoacetoacetate (1). 2,3,4-Trimethyl-3-pentyl 3-oxobutanoate[18] (6.40 g, 29.9 mmol) was dissolved in 50 mL of anhydrous acetonitrile containing triethylamine (3.64 g, 36.0 mmol), and a solution of methanesulfonyl azide (4.48 g, 37.0 mmol) in 40 mL of acetonitrile was added dropwise to the stirred solution over 20 min. The resulting yellow solution was maintained at room temperature for 4 h and then diluted by addition of water. The aqueous acetonitrile solution was washed with three 50-mL portions of ether, and the combined ether solution was washed with 50 mL of a saturated sodium chloride solution, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The resulting oil was purified by column chromatography on silica gel using 97:3 hexane/ethyl acetate as the eluent to yield 5.42 g of a bright-yellow oil (22.6 mmol, 76% yield). Bp: 110 °C (0.05 Torr). ^1H NMR ($CDCl_3$): δ 2.45 (s, 3 H), 2.31 (hept, J = 6.8 Hz, 2 H), 1.49 (s, 3 H), 0.98 (d, J = 6.8 Hz, 6 H), and 0.97 (d, J = 6.8 Hz, 6 H). IR (thin film): 2127 (C=N_2), 1710 (C=O), and 1659 (C=O) cm^{-1}. Anal. Calcd for $C_{12}H_{20}N_2O_3$: C, 59.98; H, 8.39; N, 11.65. Found: C, 59.78; H, 8.48; N, 11.56.

Catalytic Dinitrogen Extrusion from 2,3,4-Trimethyl-3-pentyl Diazoacetoacetate. A mixture of the diazo compound (0.220 g, 0.92 mmol) and 1.0 mol % of the dirhodium(II) catalyst in 10 mL of anhydrous benzene was heated at reflux for 12 h. The resulting solution was passed through a short plug of neutral alumina to remove the catalyst with further elution by CH_2Cl_2. The solvent was removed under reduced pressure, and the residue was weighed (0.189 g) and analyzed by spectroscopy and GC. The product from decomposition by $Rh_2(acam)_4$ was further purified by Kugelrohr distillation. ***trans*-3-Acetyl-4,4,5-trimethyl-5-isopropyldihydro-2(3*H*)-furanone (5)**: Bp: 140 °C (0.1 Torr). ^1H NMR ($CDCl_3$): δ 11.76 (s, enol form, 15%), 3.45 (s, keto form, 85%), 2.38 (s, CH_3CO of keto form), 2.36 (s, CH_3CO of enol form), 2.23 (hept, J = 6.7 Hz, C*H*Me_2 of enol form), 2.21 (hept, J = 6.9 Hz, C*H*Me_2 of keto form), 1.31, 1.24, and 1.13 (s, three Me of keto form), 1.33, 1.22, and 1.19 (s, three Me of enol form), 1.06 and 0.95 (d, J = 6.9 Hz, CH*Me*$_2$ of keto form), and 1.05 and 0.98 (d, J = 6.7 Hz, CH*Me*$_2$ of enol form). Mass spectrum, *m/e* (relative abundance): 212 (M, 1), 197 (3), 169 (10), 127 (11), 98 (25), 83 (100), and 55 (22). IR (thin film): 1765 (C=O) and 1706 (C=O) cm^{-1}. Anal. Calcd for $C_{12}H_{20}O_3$: C, 67.89; H, 9.50. Found: C, 67.95; H, 9.51. **3-Acetyl-5,5-diisopropyldihydro-2-(3*H*)-furanone (6)**: ^1H NMR ($CDCl_3$): δ 3.75 (dd, J = 11.3, 8.4 Hz, 1 H), 2.76 (dd, J = 14.2, 8.4 Hz, 1 H), 2.48 (s, 3 H), 2.18–2.02 (m, 2 H), 1.90 (dd, J = 14.2, 11.3 Hz, 1 H), 0.96 (d, J = 6.7 Hz, 3 H), 0.94 (d, J = 6.7 Hz), 0.89 (d, J = 6.9 Hz, 3 H), and 0.87 (d, J = 6.9 Hz, 3 H). Mass spectrum, *m/e* (relative abundance): 212 (M, 4), 170 (14), 169 (100), 127 (78), 125 (20), 109 (37), 99 (26), 98 (16), 83 (46), 71 (53), 55 (69). IR (thin film): 1762 (C=O) and 1726 (C=O) cm^{-1}. Anal. Calcd for $C_{12}H_{20}O_3$: C, 67.89; H, 9.50. Found: C, 67.81; H, 9.58.

2-Methyl-3-isopropyl-3-heptyl Diazoacetoacetate (2). Diazo transfer from methanesulfonyl azide (9.68 g, 80.0 mmol) to 2-methyl-3-isopropyl-3-heptyl 3-oxobutanoate[15] (17.92 g, 70.0 mmol) was effected with the use of triethylamine (8.08 g, 79.9 mmol) in 60 mL of acetonitrile at 40 °C (12 h). The title compound was isolated and purified as described for **1** (17.80 g, 62.7 mmol, 90% yield). ^1H NMR ($CDCl_3$): δ 2.46 (s, 3 H), 2.44 (hept, J = 7.0 Hz, 2 H), 2.00–1.97 (m, 2 H), 1.40–1.22 (m, 4 H), 1.03 (d, J = 7.0 Hz, 6 H), 1.01 (d, J = 7.0 Hz, 6 H), and 0.92 (t, J = 6.9 Hz, 3 H). IR (thin film): 2128 (C=N_2), 1715 (C=O), and 1661 (C=O) cm^{-1}. Anal. Calcd for $C_{15}H_{26}O_3N_2$: C, 63.80; H, 9.28; N, 9.92. Found: C, 64.02; H, 9.33; N, 9.88.

Catalytic Dinitrogen Extrusion from 2-Methyl-3-isopropyl-3-heptyl Diazoacetoacetate. The diazo compound (0.282 g, 1.00 mmol) in 4.0 mL of anhydrous benzene was added over a 4-h period to 1.0 mol % (10.8 mg) of dirhodium(II) perfluorobutyrate in 6.0 mL of anhydrous benzene that was heated at reflux. The solvent was removed under reduced pressure, and the residue was distilled by Kugelrohr to give 0.213 g of residue. **3-Acetyl-5-*n*-butyl-4,4-dimethyl-5-isopropyldihydro-2(3*H*)-furanone (7)**: Compound coeluted with **8** and was evident in the NMR spectrum of reaction mixture only by δ 3.45 (s, COC*H*CO), 1.30 and 1.23 (s, *gem*-Me_2), and 1.05 (d, J = 6.9 Hz, CH*Me*$_2$). The assignment of structure **7** was based primarily on mass spectral fragmentation which corresponded to that for the structurally analogous **5**. Mass spectrum, *m/e* (relative abundance): 254 (1.5, M), 239 (4), 212 (2), 211 (14), 193 (4), 169 (6), 167 (6), 151 (6), 126 (14), 98 (42), 85 (10), 83 (100), 69 (21), 55 (30). ***trans*-3-Acetyl-5,5-diisopropyl-4-*n*-propyldihydro-2-(3*H*)-furanone (8)**: ^1H NMR ($CDCl_3$): δ 3.53 (d, J = 10.4 Hz, 1 H), 3.31 (ddd, J = 10.4, 7.7, 5.5 Hz, 1 H), 2.45 (s, 3 H), 2.35 (hept, J = 6.9 Hz, 1 H), 2.15 (hept, J = 6.7 Hz, 1 H), 1.53–1.44 (m, 2 H), 1.24–1.02 (m, 2 H), 1.00 (d, J = 6.7 Hz, 3 H), 0.96 (d, J = 6.7 Hz, 3 H), 0.95 (d, J = 6.9 Hz, 3 H), 0.92 (d, J = 6.9 Hz, 3 H), and 0.91 (t, J = 7.0 Hz, 3 H). ^{13}C NMR ($CDCl_3$): δ 200.7, 171.8, 92.9 (C-5), 61.7 (C-3), 37.6, 33.9, 33.1, 30.9, 30.4, 22.3, 18.9, 17.4, 16.5, and 14.2. Mass spectrum *m/e* (relative abundance): 254 (0.2, M), 212 (15), 211 (100), 193 (16), 169 (51), 167 (39), 165 (16), 151 (71), 123 (30), 109 (20), 97 (80), 83 (22), 81 (25), 71 (43), 69 (30), 55 (89). IR (thin film): 1768 (C=O) and 1727 (C=O) cm^{-1}. Anal. Calcd for $C_{15}H_{26}O_3$: C, 70.83; H, 10.30. Found: C, 70.67; H, 10.36. **3-Acetyl-4-ethyl-6,6-diisopropyldihydro-2-(3*H*)-pyranone (13)**: ^1H NMR (C_6D_6): mixture of isomers, δ 14.89 and 14.86 (s, 1 H, enol), 1.93 and 1.79 (hept, J = 6.9 Hz, 1 H, C*H*Me_2), 1.84–1.67 (m, 2 H), 1.64 and 1.63 (s, 3 H), 1.55–1.44 (m, 2 H), 1.37–1.05 (m, 5 H), 0.97 and 0.92 (d, J = 6.9 Hz, 3 H), 0.84 and 0.67 (d, J = 7.0 Hz, 3 H), 0.84 and 0.80 (t, J = 6.8 Hz, 3 H), and 0.70 and 0.64 (d, J = 6.8 Hz, 3 H). ^{13}C NMR ($CDCl_3$): mixture of isomers, δ 175.3 and 175.1, 173.0 and 172.9, 92.6 and 92.3, 88.9 and 88.8, 33.4 and 33.0, 31.8 and 31.7, 31.6 and 31.5, 28.5 and 27.8, 25.8 and 25.6, 23.5 and 23.4, 18.8 and 18.4, 17.7 and 17.1, 16.8 and 16.1, and 14.0 and 13.9. Mass spectrum, *m/e* (relative abundance): 254 (1.4, M), 211 (20), 197 (16), 167 (8), 152 (11), 141 (22), 140 (14), 139 (16), 127 (16), 126 (22), 115 (14), 111 (17), 109 (17), 98 (27), 97 (52), 85 (27), 83 (71), 71 (17),

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70 (18), 69 (57), 57 (28), 55 (100). IR (CCl_4): 3448 (br, O—H), 3264 (s, O—H), 1641 (C=O), and 1613 (C=C) cm^{-1}. Anal. Calcd for $C_{15}H_{26}O_3$: C, 70.83; H, 10.30. Found: C, 70.78; H, 10.35.

2-Methyl-2-octyl Diazoacetoacetate (3). To a solution of 2-methyl-2-octanol (4.50 g, 31.3 mmol), prepared by the addition of methylmagnesium iodide to 2-octanone, and anhydrous sodium acetate (0.026 g, 0.31 mmol) in 20 mL of anhydrous acetonitrile in an ice bath was added 2.89 g of diketene (34 mmol) in 10 mL of acetonitrile over a 30-min period. After stirring for 30 min, the solution was heated at reflux for 1 h. The resulting solution was cooled, combined with 50 mL of ether, and extracted three times with 50-mL portions of saturated aqueous sodium chloride. After drying the ether solution over anhydrous $MgSO_4$, the solvent was removed under reduced pressure to yield 7.06 g of a brown oil, which after distillation, bp 96–100 °C at 0.2 Torr, gave 2-methyl-2-octyl acetoacetate in 81% yield. ^1H NMR ($CDCl_3$) of the keto form: δ 3.35 (s, 2 H), 2.26 (s, 3 H), 1.85–1.70 (m, 2 H), 1.45 (s, 6 H), 1.40–1.20 (m, 8 H), and 0.88 (t, J = 6.8 Hz, 3 H).

To the acetoacetate (7.00 g, 3.07 mmol) and triethylamine (3.72 g, 36.8 mmol) dissolved in 30 mL of anhydrous acetonitrile was added 4.46 g (36.8 mmol) of methanesulfonyl azide in 30 mL of acetonitrile dropwise over 45 min. The resulting solution was stirred at room temperature for 1 h, during which time the color of the solution became red-brown, and then combined with 50 mL of ether, extracted with two 50-mL portions of saturated aqueous sodium chloride, and then dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure, and the resulting deep-yellow oil was purified by column chromatography on silica gel using 95:5 hexane/ethyl acetate as the eluent to yield 4.76 g (18.7 mmol, 61% yield) of the title compound. ^1H NMR ($CDCl_3$): δ 2.45 (s, 3 H), 1.82–1.74 (m, 2 H), 1.50 (s, 6 H), 1.38–1.20 (m, 8 H), and 0.88 (t, J = 7.0 Hz, 3 H). IR (thin film): 2136 (C=N_2), 1716 (C=O), and 1662 (C=O) cm^{-1}. Anal. Calcd for $C_{13}H_{22}N_2O_3$: C, 61.36; H, 8.74; N, 11.01. Found: C, 61.13; H, 8.81; N, 10.92.

Catalytic Dinitrogen Extrusion from 2-Methyl-2-octyl Diazoacetoacetate. To 1.0 mol % of the dirhodium(II) catalyst, based on diazo compound, in 10 mL of refluxing anhydrous benzene was added 0.260 g (1.02 mmol) of 2-methyl-2-octyl diazoacetoacetate in 3.0 mL of benzene by syringe pump over a 6-h period. The resulting solution was passed through a short plug of neutral alumina, which was eluted with CH_2Cl_2. Removal of the solvent under reduced pressure left a residue (0.181 g, 0.80 mmol) that was analyzed by spectroscopy and GC. ***trans*-3-Acetyl-5,5-dimethyl-4-*n*-pentyldihydro-2(3*H*)-furanone (9)**: ^1H NMR ($CDCl_3$): δ 3.47 (d, J = 11.4 Hz, 1 H), 2.79 (ddd, J = 11.4, 8.3, 6.2 Hz, 1 H), 2.44 (s, 3 H), 1.49 (s, 3 H), 1.49–1.05 (m, 8 H), 1.28 (s, 3 H), and 0.88 (t, J = 6.6 Hz, 3 H). Mass spectrum, *m/e* (relative abundance): 226 (M, 1), 211 (5), 184 (12), 169 (8), 155 (23), 125 (55), 114 (27), 113 (31), 111 (27), 97 (18), 96 (26), 69 (54), 55 (100). IR (thin film): 1766 (C=O) and 1720 (C=O) cm^{-1}. Anal. Calcd for $C_{13}H_{22}O_3$: C, 68.99; H, 9.80. Found: C, 68.60; H, 9.72. **3-Acetyl-5-*n*-hexyl-5-methyldihydro-2(3*H*)-furanone (10)**: ^1H NMR ($CDCl_3$) of two geometrical isomers: δ 3.88–3.79 (m, 1 H), 2.70–2.55 (m, 1 H), 2.47 (s, 3 H), 2.16–1.96 (m, 1 H), 1.80–1.60 (m, 2 H), 1.45 (s, 3 H), 1.45–1.20 (m, 8 H), and 0.89 (t, J = Hz, 3 H). Individual isomers (1:1 mixture) exhibit absorptions at δ 3.85 (dd, J = 9.8, 9.6 Hz) and 3.82 (dd, J = 10.1, 7.7 Hz), 2.66 (dd, J = 13.5, 9.8 Hz) and 2.58 (dd, J = 13.5, 7.7 Hz), and 2.12 (dd, J = 13.5 Hz, J = 13.5, 10.1 Hz) and 2.00 (dd, J = 13,5, 9.6 Hz). IR (thin film): 1750 (C=O) and 1720 (C=O) cm^{-1}. Mass spectrum, *m/e* (relative abundance): 226 (3, M), 211 (3), 184 (10), 141 (100), 124 (14), 114 (24), 113 (11), 99 (66), 97 (30), 95 (22), 69 (24), 55 (65). Anal. Calcd for $C_{13}H_{22}O_3$: C, 68.99, H, 9.80. Found: C, 68.85; H, 9.87.

2-Methyl-1-phenyl-2-propyl Diazoacetoacetate (4). To a solution of 2-methyl-1-phenyl-2-propanol (6.01 g, 40.0 mmol) and anhydrous sodium acetate (0.050 g, 0.62 mmol) was added 5.5 mL of diketene (5.0 g, 60 mmol) dropwise over a 10-min period. The solution was then heated at 80 °C for 2 h, after which the light-brown liquid was cooled. Purification by column chromatography on silica gel (50:50 ethyl acetate/hexane) gave 8.81 g of a light-orange oil. ^1H NMR ($CDCl_3$): δ 7.35–7.15 (m, 5 H), 3.50 (s, 2 H), 3.06 (s, 2 H), 2.19 (s, 3 H), and 1.48 (s, 3 H). The 2-methyl-1-phenyl-2-propyl acetoacetate collected from this procedure (37.6 mmol, 94% yield) was subjected to diazo transfer with mesyl azide as previously described for the synthesis of **1**, and the resulting orange liquid was purified by column chromatography on silica gel using 10% ethyl acetate/90% hexane as the eluent to give a light-yellow oil that crystallized on standing. This solid was dissolved in ether; the resulting solution was washed with aqueous lithium hydroxide and saturated aqueous sodium chloride solutions and dried over anhydrous $MgSO_4$, and the solvent was evaporated to provide 5.42 g of a yellow solid (20.7 mmol, 55% yield). Recrystallization from hexane afforded **4**, mp 48.5 °C, as an off-white solid. ^1H NMR ($CDCl_3$): δ 7.35–7.12 (m, 5 H), 3.09 (s, 2 H), 2.43 (s, 3 H), and 1.55 (s, 3 H). IR (thin film): 2141 (C=N_2), 1707 (C=O), and 1649 (C=O) cm^{-1}. Anal. Calcd for $C_{14}H_{16}N_2O_3$: C, 64.60; H, 6.20; N, 10.76. Found: C, 64.53; H, 6.28; N, 10.80.

Catalytic Dinitrogen Extrusion from 2-Methyl-1-phenyl-2-propyl Diazoacetoacetate. To 1.2 mol % of the dirhodium(II) catalyst, based on diazo compound, in 25 mL of refluxing anhydrous benzene was added 0.263 g (1.00 mmol) of **4** in 10 mL of benzene by syringe pump over a 6-h period. The resulting solution was passed through a short plug of silica to remove the catalyst, and the silica was rinsed with CH_2Cl_2. Solvent removal under reduced pressure produced a pale-orange oil, which was weighed and then analyzed by spectroscopy and GC. Separation of the reaction components was achieved chromatographically on silica gel with 3% ethyl acetate/97% hexane as the eluent. ***trans*-3-Acetyl-4-phenyl-5,5-dimethyldihydro-2(3*H*)-furanone (11)**: ^1H NMR ($CDCl_3$): δ 7.40–7.10 (m, 5 H), 4.24 (d, J = 11.5 Hz, 1 H), 4.01 (d, J = 11.5 Hz, 1 H), 2.44 (s, 3 H), 1.56 (s, 3 H), and 1.09 (s, 3 H). Mass spectrum *m/e* (relative abundance): 232 (2.5, M), 189 (12), 174 (25), 146 (33), 145 (47), 131 (100), 103 (28), 91 (13), 77 (21), 51 (12). IR (thin film): 1762 (C=O) and 1722 (C=O) cm^{-1}. Anal. Calcd for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94. Found: C, 72.30; H, 7.06. **3-Acetyl-5-benzyl-5-methyldihydro-2(3*H*)-furanone (12)**: ^1H NMR ($CDCl_3$): δ 7.38–7.20 (m, 5 H), 3.80 (t, J = 8.8 Hz, 1 H, keto form), 3.06 (d, J = 14.0 Hz, 1 H, enol form), 3.02–2.90 (m, 2 H), 2.93 (dd, J = 13.4, 8.9 Hz, 1 H, keto form), 2.82 (d, J = 14.0 Hz, 1 H, enol form), 2.78 (dd, J = 13.5, 8.8 Hz, 1 H, keto form), 2.55 (dd, J = 13.5, 8.8 Hz, 1 H, keto form), 2.37 (s, 3 H, keto form), 2.31 (s, 3 H, enol form), 1.99 (dd, J = 13.2, 9.8 Hz, 1 H, keto form), 1.51 (s, 3 H, enol form), and 1.38 (s, 3 H, keto form). Mass spectrum, *m/e* (relative abundance): 233 (0.6, M + 1), 232 (3.8, M), 214 (11), 141 (100), 99 (93), 97 (30), 91 (49), 65 (24), 55 (24). IR (thin film): 1766 (C=O) and 1722 (C=O) cm^{-1}. Anal. Calcd for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94. Found: C, 72.23; H, 7.04.

1-Octyl Diazoacetoacetate (14). To a solution of 1-octanol (6.43 g, 49.3 mmol) and anhydrous sodium acetate (0.043 g, 0.5 mmol) in 30 mL of refluxing anhydrous acetonitrile was added 5.04 g of diketene (60.0 mmol) in 20 mL of acetonitrile dropwise over a period of 15 min. After heating at reflux for 90 min, the solution was cooled, combined with 50 mL of ether, and extracted three times with 50-mL portions of saturated aqueous sodium chloride. After the ether solution was dried over anhydrous $MgSO_4$, the solvent was removed under reduced pressure, and the residue was distilled to yield 9.10 g (42.5 mmol, 86% yield) of a colorless oil. Bp: 102–108 °C at 0.2 Torr. ^1H NMR ($CDCl_3$): δ 4.13 (t, J = 6.8 Hz, 2 H), 3.44 (s, 2 H), 2.27 (s, 3 H), 1.70–1.55 (m, 2 H), 1.40–1.20 (m, 10 H), and 0.88 (t, J = 7.1 Hz, 3 H).

To the acetoacetate (8.87 g, 41.4 mmol) and triethylamine (5.1 g, 50 mmol) dissolved in 50 mL of anhydrous acetonitrile was added 6.14 g (50.7 mmol) of methanesulfonyl azide in 40 mL of acetonitrile dropwise over 15 min. The resulting solution was stirred at room temperature for 7.5 h, during which time the color of the solution became golden yellow, and then combined with 50 mL of ether, extracted with three 50-mL portions of saturated aqueous sodium chloride, and then dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure, and the resulting deep-yellow oil was purified by column chromatography on silica gel using 97:3 hexane/ethyl acetate as the eluent to yield 9.73 g (40.5 mmol, 98% yield) of the title compound. ^1H NMR ($CDCl_3$): δ 4.23 (t, J = 7.0 Hz, 2 H), 2.47 (s, 3 H), 1.68 (quin, J = 6.8 Hz, 2 H), 1.42–1.18 (m, 10 H), and 0.87 (t, J = 7.0 Hz, 3 H). IR (thin film): 2138 (C=N_2), 1720 (C=O), and 1662 (C=O) cm^{-1}. Anal. Calcd for $C_{12}H_{20}N_2O_3$: C, 59.98; H, 8.39; N, 11.65. Found: C, 59.81; H, 8.45; N, 11.60.

Catalytic Dinitrogen Extrusion from 1-Octyl Diazoacetoacetate. To 1.0 mol % of dirhodium(II) acetate, based on diazo compound, in 6.0 mL of refluxing anhydrous benzene was added 0.238 g (0.99 mmol) of 1-octyl diazoacetoacetate in 4.0 mL of benzene by syringe pump over a 4-h period. The resulting solution was passed through a short plug of neutral alumina to remove the catalyst, and the alumina was washed with CH_2Cl_2. The solvent was removed under reduced pressure, and the residue was weighed (0.194 g, 0.92 mmol, 92% yield) and analyzed by spectroscopy and GC. Only one C–H insertion product was formed. Identical results were obtained with $Rh_2(acam)_4$ (85% yield). ***trans*-3-Acetyl-4-*n*-hexyldihydro-2(3*H*)-furanone (15)**: Bp: 130 °C (0.1 Torr). ^1H NMR ($CDCl_3$) of keto form: δ 4.45 (dd, J = 8.8, 7.8 Hz, 1 H), 3.90 (dd, J = 8.8, 7.6 Hz, 1 H), 3.35 (d, J = 8.1 Hz, 1 H), 3.03 (sex, J = 7.1 Hz, 1 H), 2.43 (s, 3 H), 1.60–1.40 (m, 2 H), 1.40–1.20 (m, 8 H), and 0.88 (t, J = 7.0 Hz, 3 H). Mass spectrum, *m/e* (relative abundance): 212 (M, 1), 127 (41), 111 (25), 110 (15), 108 (11), 85 (100), 81 (11), 69 (27), and 55 (31). IR (thin film): 1774 (C=O) and 1720 (C=O) cm^{-1}. Anal. Calcd for $C_{12}H_{20}O_3$: C, 67.86; H, 9.52. Found: C, 67.78; H, 9.57.

2-Phenyl-1-ethyl diazoacetoacetate (16) was prepared as described for 1-octyl diazoacetoacetate in 72% yield from 2-phenethanol. Mp: 39–40 °C. ^1H NMR ($CDCl_3$): δ 7.36–7.18 (m, 5 H), 4.45 (t, J = 7.0 Hz, 2

H), 3.00 (t, J = 7.0 Hz, 2 H), and 2.43 (s, 3 H). IR (KBr): 2144 (C=N_2), 1718 (C=O), and 1651 (C=O) cm^{-1}. Anal. Calcd for $C_{12}H_{12}O_3N_2$: C, 62.06; H, 5.21; N, 12.06. Found: C, 62.36; H, 5.22; N, 12.01.

Catalytic Dinitrogen Extrusion from 2-Phenyl-1-ethyl Diazoacetoacetate. To 1.0 mol % of dirhodium(II) acetate, based on diazo compound, in 10 mL of refluxing anhydrous benzene was added 0.238 g (1.03 mmol) of 2-phenyl-1-ethyl diazoacetoacetate in 3.0 mL of benzene by syringe pump over a 5-h period. The resulting solution was passed through a short plug of neutral alumina to remove the catalyst, and the alumina was washed with CH_2Cl_2. The solvent was removed under reduced pressure, and the residue was weighed and analyzed by spectroscopy and GC. Distillation afforded 0.180 g of a colorless liquid identified as ***trans*-3-acetyl-4-phenyldihydro-2(3*H*)-furanone (17**, 86% yield): Bp 120 °C (0.4 Torr), lit[30] bp 130–145 °C (2 Torr). ^{1}H NMR ($CDCl_3$): δ 11.84 (s, OH of enol), 7.40–7.18 (m, 5 H), 5.15 (dd, J = 10.4, 8.3 Hz, 1 H of enol, 15%), 4.76–4.63 (m, 1 H), 4.35–4.18 (m, 2 H), 3.82 (d, J = 8.3 Hz, 1 H of keto form, 85%), 3.81 (dd, J = 10.4, 7.5 Hz, 1 H of enol, 15%), 3.17 (dd, J = 6.1, 3.0 Hz, 1 H of enol), 2.44 (s, 3 H, keto form), 2.43 (s, 3 H, enol), and 2.27 (s, 3 H, enol).

***l*-(−)-Menthyl Diazoacetoacetate (18).** To a solution of *l*-menthol (7.88 g, 50.5 mmol) and 0.044 g of anhydrous sodium acetate in 30 mL of refluxing anhydrous acetonitrile was added 5.01 g of diketene (59.6 mmol) in 20 mL of acetonitrile dropwise over a 10-min period. The orange-red solution was maintained at reflux with stirring for 90 min, then cooled, diluted with 50 mL of ether, and extracted three times with 50-mL portions of saturated aqueous sodium chloride. After the ether solution was dried over anhydrous $MgSO_4$, the solvent was removed under reduced pressure, and the red residue was distilled to yield 10.5 g (43.8 mmol, 87% yield) of a colorless oil. Bp: 95–102 °C at 0.1 Torr. ^{1}H NMR ($CDCl_3$): δ 4.74 (dt, J = 10.8, 4.4 Hz, 1 H), 3.43 (s, 2 H), 2.26 (s, 3 H), 2.10–1.96 (m, 1 H), 1.87 (dquin, J = 6.9, 2.7 Hz, 1 H), 1.74–1.62 (m, 2 H), 1.58–1.32 (m, 3 H), 1.14–0.96 (m, 2 H), 0.91 (d, J = 6.5 Hz, 3 H), 0.89 (d, J = 7.0 Hz, 3 H), and 0.77 (d, J = 6.9 Hz, 3 H).

To the acetoacetate (6.90 g, 28.8 mmol) and triethylamine (3.34 g, 33 mmol) dissolved in 50 mL of anhydrous acetonitrile was added 4.02 g (33.2 mmol) of methanesulfonyl azide in 40 mL of acetonitrile dropwise over 15 min. The resulting solution was stirred at room temperature for 10 h, during which time the color of the solution became golden yellow. The reaction solution was diluted with 50 mL of ether and extracted with three 50-mL portions of saturated aqueous sodium chloride which were then washed with 50 mL of ether, and the combined ether solution was dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure, and the resulting deep-yellow oil was purified by column chromatography on silica gel using 97:3 hexane/ethyl acetate as the eluent to provide 7.05 g (26.5 mmol, 92% yield) of the light-yellow title compound. ^{1}H NMR ($CDCl_3$): δ 4.82 (dt, J = 10.9, 4.4 Hz, 1 H), 2.48 (s, 3 H), 2.10–2.02 (m, 1 H), 1.84 (dquin, J = 7.0, 2.7 Hz, 1 H), 1.76–1.65 (m, 2 H), 1.60–1.32 (m, 3 H), 1.18–0.98 (m, 2 H), 0.92 (d, J = 6.5 Hz, 3 H), 0.91 (d, J = 7.0 Hz, 3 H), and 0.80 (d, J = 6.9 Hz, 3 H). IR (thin film): 2139 (C=N_2), 1712 (C=O), and 1662 (C=O) cm^{-1}. $[\alpha]^{25}_D$ = −88.7° (c = 2.15, $CHCl_3$). Anal. Calcd for $C_{14}H_{22}N_2O_3$: C, 63.18; H, 8.33; N, 10.52. Found: C, 63.26; H, 8.38; N, 10.61.

Catalytic Dinitrogen Extrusion from *l*-(−)-Menthyl Diazoacetoacetate. To 1.0 mol % of dirhodium(II) acetate, based on diazo compound, in 10 mL of refluxing anhydrous benzene was added 0.268 g (1.01 mmol) of *l*-(−)-menthyl diazoacetoacetate in 3.0 mL of benzene by syringe pump over a 6-h period. The resulting solution was passed through a short plug of neutral alumina, and the alumina was washed with CH_2Cl_2. The solvent was removed under reduced pressure, and the resulting solid residue was recrystallized from pentane to yield 0.193 g of a white solid (0.81 mmol, 80% yield) identified as **(−)-(1*S*,4*S*,5*R*,6*S*,9*R*)-4-acetyl-6-methyl-9-isopropyl-2-oxabicyclo[4.3.0]nonan-3-one (19)**: Mp: 98–99 °C. ^{1}H NMR ($CDCl_3$): δ 3.72 (t, J = 10.7 Hz, 1 H), 3.44 (d, J = 12.4 Hz, 1 H), 2.41 (s, 3 H), 2.31 (dt, J = 12.4, 10.7, 10.7 Hz, 1 H), 2.00–1.88 (m, 1 H), 1.84–1.62 (m, 3 H), 1.58–1.38 (m, 1 H), 1.23–1.00 (m, 2 H), 0.95 (d, J = 7.0 Hz, 3 H), 0.89 (d, J = 7.0 Hz, 3 H), and 0.82 (d, J = 6.6 Hz, 3 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 202.0, 172.5, 84.5, 58.7, 52.2, 46.6, 35.4, 34.4, 30.6, 28.6, 25.0, 19.8, 19.7, and 17.8. IR (KBr): $[\alpha]^{24}_D$ = −33.4° (c = 0.59, $CHCl_3$). Anal. Calcd for $C_{14}H_{22}O_3$: C, 70.55; H, 9.31. Found: C, 70.38; H, 9.40.

Catalytic Dinitrogen Extrusion from *d*-(+)-Menthyl Diazoacetoacetate (20). *d*-(+)-Menthyl diazoacetoacetate was prepared from *d*-(+)-menthol in 85% overall yield by a procedure identical to that used for the synthesis of its enantiomer: $[\alpha]^{25}_D$ = +88.7° (c = 2.27, $CHCl_3$). Anal. Calcd for $C_{14}H_{22}N_2O_3$: C, 63.18; H, 8.33; N, 10.52. Found: C, 63.31; H, 8.52; N, 10.50. To 0.017 g of $Rh_2(OAc)_4$ (0.038 mmol, 1.0 mol %) in 20 mL of refluxing benzene was added 1.00 g (3.76 mmol) of *d*-(+)-menthyl diazoacetoacetate in 5.0 mL of benzene by syringe pump over a 6-h period. The resulting solution was passed through a short plug of neutral alumina, and the alumina was washed with 30 mL of CH_2Cl_2. The solvent was removed under reduced pressure, and the resulting solid residue was recrystallized from pentane to yield 0.780 g of white needles (3.28 mmol, 87% yield) identified as **(+)-(1*R*,4*R*,5*S*,6*R*,9*S*)-4-acetyl-6-methyl-9-isopropyl-2-oxabicyclo[4.3.0]nonan-3-one (21)**: Mp: 98 °C. $[\alpha]^{26}_D$ = +33.2° (c = 1.08, $CHCl_3$). Anal. Calcd for $C_{14}H_{22}O_3$: C, 70.55; H, 9.31. Found: C, 70.59; H, 9.27.

Molecular Mechanics Calculations. Structure minimization was accomplished using the molecular dynamics and molecular mechanics packages provided in the Tektronics CAChe System, Version 2.8. CAChe uses an augmented version of Allinger's MM2 force field whereby force field parameters are estimated for cases not explicitly addressed by MM2 (i.e., octahedrally disposed nuclei).

Transition-state structures of rhodium carbenoid carbon–hydrogen insertion reactions are difficult to define precisely, in part due to the large number of degrees of freedom present and in part due to the absence of data regarding the synchronicity of bond breaking and bond forming. Therefore, pseudo-transition-state structures were assembled on the basis of several assumptions. The carbene carbon and the carbon involved in C–H insertion were defined as sp^3, and the rhodium–carbenoid, carbenoid–hydrogen, and carbenoid–carbon bonds were defined as weak bonds having force constants of about one-fifth that of a C–C bond.

Structures were first minimized using molecular mechanics, and the resulting structures were then submitted to molecular dynamics simulation, where a trajectory for each structure was generated. The molecular dynamics calculations provide one means of determining a global minimum by sampling the full energy surface. The initial velocities of each atom were based upon an internally generated random number, and the molecule was then subjected to a simulated heating to 800 K. Data were acquired with a sampling period of 10 ps in 1.0-fs intervals, and a trajectory was saved every 20 fs. The five lowest energy trajectories were each submitted to MM2 using conjugate gradient minimization, and the lowest energy structure was taken. Optimization of the five lowest energy trajectories was expected to provide the lowest energy conformer. Nevertheless, in order to evaluate the influence of 1,3-methyl interactions from the two isopropyl groups in **7TS** (Figure 1), calculations of energy versus dihedral angle were performed; although a second minimum was observed, it was no lower in energy than that reported for **7TS**.

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