Ligand Effects on Dirhodium(II) Carbene Reactivities. Highly Effective Switching between Competitive Carbenoid Transformations

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Abstract: Carboxylate and carboxamide ligands of dirhodium(II) catalysts control chemoselectivity in competitive metal carbene transformations of diazo compounds. For competitive intramolecular cyclopropanation versus intramolecular aromatic substitution with 1-diazo-3-aryl-5-hexen-2-ones, use of $Rh_2(OAc)_4$ results in the products from both transformations in nearly equal amounts, but dirhodium(II) perfluorobutyrate ($Rh_2(pfb)_4$) provides only the aromatic substitution product while dirhodium(II) caprolactamate ($Rh_2(cap)_4$) gives only the cyclopropanation product. Similar results are obtained from dirhodium(II) catalysts in competitive intramolecular cyclopropanation versus tertiary C–H insertion, aromatic cycloaddition versus C–H insertion, cyclopropanation versus aromatic cycloaddition, and C–H insertion versus aromatic substitution. The order of reactivity for metal carbenes generated from $Rh_2(pfb)_4$ is aromatic substitution > tertiary C–H insertion > cyclopropanation ~aromatic cycloaddition > secondary C–H insertion, and the rate differences between them are as much as 100-fold. For $Rh_2(cap)_4$ the order of reactivity is cyclopropanation > tertiary C–H insertion > secondary C–H insertion > aromatic cycloaddition with aromatic substitution not observed as a competing process for the diazo compounds examined. Control of chemoselectivity through charge and/or frontier molecular orbital properties of the intermediate metal carbene has been evaluated. Competitive product formation from dirhodium(II) caprolactamate catalyzed reactions of *N*-*tert*-butyl-*N*-benzyldiazoacetoacetamide is temperature dependent over a narrow 15-deg range. The effect of carbene substituents other than the ligated dirhodium(II) on chemoselectivity is described and discussed.

The use of dirhodium(II) acetate and related carboxylates to form metal carbenes from diazo carbonyl compounds affords an entry into a broad spectrum of chemical transformations,[1-3] including cyclopropanation,[4] carbon–hydrogen insertion,[5] ylide generation,[6] and aromatic cycloaddition.[7] Product yields are high in reactions with model substrates, and significant regio- and/or stereocontrol can be achieved.[8-12] However, the use of these catalysts for targeted outcomes in complex systems capable of more than one carbenoid transformation is limited by the paucity of information on chemoselectivity.[13-15] The relative reactivities of free carbenes in competition reactions are directly attributed to the "philicity" of the carbene;[16] by analogy, control of metal carbene electrophilicity should induce high selectivity in competition experiments.

The dirhodium(II) framework is amenable to ligand exchange with a large number of bridging ligands[17,18] that could substantially increase or decrease electron density at the rhodium nucleus relative to that of dirhodium(II) acetate. The extent of control that can be achieved is illustrated by the use of dirhodium(II) acetamidate ($Rh_2(acam)_4$), which exhibits exceptional stereocontrol for the *trans* isomer in intermolecular cyclopropanation reactions.[9] Extraordinary regiocontrol of intramolecular C–H insertion reactions of diazoacetate esters[19] and cyclopropanation reactions of unsymmetrical dienes[9] has also been observed with

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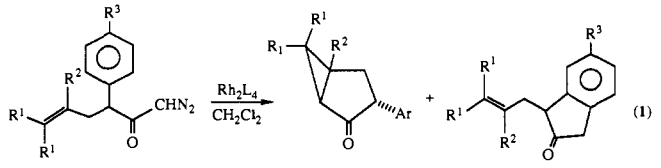
this catalyst. Equilibrium associations of dirhodium(II) butanoate with Lewis bases such as acetonitrile suggest that the Lewis acidity of this rhodium species is 2 orders of magnitude less than that for dirhodium(II) perfluorobutyrate ($Rh_2(pfb)_4$).[20] Although the latter compound is highly reactive toward diazocarbonyl compounds, little or no regio- or stereocontrol is provided through its use in metal carbene transformations.[9,19] We have previously reported preliminary results which demonstrated that remarkably high chemoselectivity can be achieved over a broad spectrum of carbene transformations by simply changing the dirhodium(II) ligands.[21] We now report extensive studies which define the extent of their chemoselectivity and describe our rationale for the virtually complete switch in selectivity from reactions performed with $Rh_2(cap)_4$ or $Rh_2(acam)_4$ to those performed with $Rh_2(pfb)_4$.

Results and Discussion

Intramolecular metal carbene reactions catalyzed by dirhodium(II) carboxylates generally exhibit an overwhelming preference for five-membered-ring formation.[1-3,5] Exceptions are known,[22] but they can be attributed to steric factors or to electronic stabilization of the center at which four- or six-membered-ring formation occurs. We have synthesized representative diazo carbonyl compounds that possess two potentially reactive centers for five-membered-ring formation upon generation of the intermediate metal carbenes. In virtually all cases, changing the ligand from perfluorobutyrate to acetamidate (or caprolactamate) turns one competitive pathway "*off*" and the other "*on*".

Cyclopropanation versus Aromatic Substitution. Addition of diazo ketone **1a** (eq 1; R^1 = H, R^2 = Me, R^3 = H) to a refluxing



1a: $R^1 = R^3$ = H, R^2 = Me 2 3

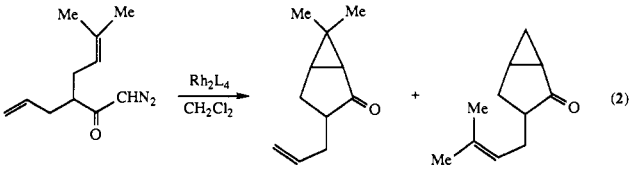
1b: R^1 = H, R^2 = Me, R^3 = OMe

1c: R^1 = Me, $R^2 = R^3$ = H

1d: $R^1 = R^2 = R^3$ = H

solution of $Rh_2(OAc)_4$ in dichloromethane resulted in the formation of nearly equal amounts of products derived from intramolecular cyclopropanation (**2a**, 48%) and aromatic C–H insertion (**3a**, 52%). In contrast to this result, only **2a** was produced with $Rh_2(cap)_4$ used as the catalyst, whereas $Rh_2(pfb)_4$ afforded **3a** exclusively. This extraordinary selectivity is virtually independent of substituents placed on the aromatic ring or on the carbon–carbon double bond (Table I). Minor variations in product distributions from $Rh_2(OAc)_4$-catalyzed reactions are evident, but in each case, decomposition of the diazo carbonyl reactant with $Rh_2(pfb)_4$ produced the aromatic substitution product exclusively, and only cyclopropanation was found from reactions catalyzed by $Rh_2(cap)_4$. Ikegami and co-workers recently reported that dirhodium(II) triphenylacetate produced **3d** from **1d** exclusively (83% yield).[15] This result could be attributed to the steric bulk of the triphenylmethyl group, but electronic preference for aromatic substitution is a more likely explanation (*vide infra*).

Aromatic substitution reactions of diazo carbonyl compounds catalyzed by $Rh_2(OAc)_4$ are facile processes[1,2,23,24] and have been described by others as aromatic C–H insertion reactions.[10c,25] However, the influence of ring substituents on the reactivity/selectivity in these reactions is better accounted for by invoking electrophilic addition of the metal-bound carbene followed by 1,2-hydride migration to complete the overall substitution process.[26] Cyclopropanation is generally thought to involve simultaneous bond formation to both carbon atoms of the carbon–carbon double bond without significant charge build-up,[1-4] and this mechanism is consistent with the relative absence of substituent effects from the carbon–carbon double bond on metal carbene selectivity. Further evidence for the virtual absence of electronic influences from the carbon–carbon double bond on selectivity is seen in product distributions from competitive cyclopropanation of mono- and trisubstituted C=C bonds in **4** (eq 2). Meaningful increases in stereoselectivity, but not



4	yield, %	5 (cis/trans)	6
$Rh_2(OAc)_4$	92	54 (2.3)	46
$Rh_2(pfb)_4$	98	48 (2.4)	52
$Rh_2(cap)_4$	91	45 (5.8)	55

regioselectivity, are observed when the catalyst is changed from $Rh_2(pfb)_4$ to $Rh_2(OAc)_4$ to $Rh_2(cap)_4$. The origin of the exceptional chemoselectivity reported in Table I, but absent in eq 2, can be attributed to the passage of the metal carbene from highly electrophilic, in the case of $Rh_2(pfb)_4$, to weakly electrophilic, in the case of $Rh_2(cap)_4$.[27]

To address the significant changes in catalyst selectivities as the ligand is changed from perfluorobutyrate to acetamide, we performed calculations on a methylene bound to the dirhodium(II) catalyst ($RhL_4Rh{=}CH_2$) to determine the charge on the carbene carbon and the HOMO/LUMO associated with each dirhodium(II) carbene. For these calculations, trifluoroacetate (tfa) was substituted for perfluorobutyrate. Zindo calculations of methylene-bound dirhodium(II) complexes ($RhL_4Rh{=}CH_2$) reveal an increasing order in charge localization at the carbene carbon when the dirhodium(II) ligands are changed from acetamidate (0.090) to trifluoroacetate (0.117), but the positive charge at the carbene carbon (0.088) with acetate ligands for

Table I. Competition between Cyclopropanation and Aromatic Substitution in Rh_2L_4-Catalyzed Reactions of Diazo Ketones **1**[a]

compd	R^1	R^2	R^3	Rh_2L_4	isolated yield, %	rel yield, % 2	rel yield, % 3
a	H	Me	H	$Rh_2(OAc)_4$	92	48	52
				$Rh_2(pfb)_4$	86	0	100
				$Rh_2(cap)_4$	75	100	0
b	H	Me	OCH_3	$Rh_2(OAc)_4$	83	60	40
				$Rh_2(pfb)_4$	80	0	100
				$Rh_2(cap)_4$	80	100	0
c	Me	H	H	$Rh_2(OAc)_4$	88	45	55
				$Rh_2)pfb)_4$	82	0	100
				$Rh_2(cap)_4$	97	100	0
d	H	H	H	$Rh_2(OAc)_4$	99	67	33
				$Rh_2(pfb)_4$	95	0	100
				$Rh_2(cap)_4$	72	100	0

[a] Reactions were performed in refluxing dichloromethane.

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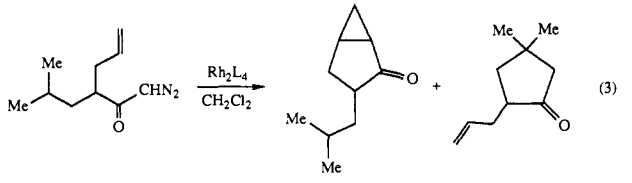
Table II. Charge and HOMO and LUMO Energies Calculated for the Hypothetical $RhL_4Rh{=}CH_2$

L	charge[a]	HOMO, eV[b]	LUMO, eV[b]
trifluoroacetate	0.117	−10.888	−9.300
acetate	0.088	−10.884	−9.292
acetamidate	0.090	−10.784	−9.364

[a] Zindo calculations. [b] Extended Hückel calculations. Trends in differences for HOMO–LUMO energies from Zindo calculations are the same.

dirhodium(II) is virtually the same as that for the acetamidate-ligated dirhodium(II) carbene. Although these values are small in comparison with those for the methyl (0.525) and ethyl (0.450) cations, the increase in charge localization from acetamidate- to trifluoroacetate-ligated dirhodium(II) is consistent with increasing electrophilicity of the bound carbene. In contrast, calculations of the HOMO and LUMO show large differences between $Rh(OAc)_4Rh{=}CH_2$ and $Rh(acam)_4Rh{=}CH_2$, but only minor differences are observed for $Rh(tfa)_4Rh{=}CH_2$ and $Rh(OAc)_4Rh{=}CH_2$ (Table II). These results are consistent with the experimental data. The large differences in chemical behavior between $Rh_2(tfa)_4$ and $Rh_2(acam)_4$ can be attributed to the large differences in charge and frontier orbital properties, while the intermediate behavior of $Rh_2(OAc)_4$ may result from its contrasting charge or frontier orbital properties, where experimental results serve as an indicator of the relative importance of charge and frontier orbital control.

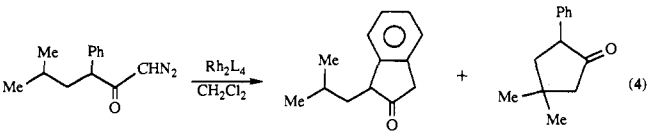
Cyclopropanation versus Carbon–Hydrogen Insertion. Competition between cyclopropanation and insertion into a tertiary C–H bond provides another example of ligand effectiveness in controlling chemoselectivity in dirhodium(II)-catalyzed metal carbene reactions. Addition of diazo ketone **7** to a refluxing solution of dichloromethane containing the dirhodium(II) catalyst produced both the cyclopropanation product **8** and the C–H insertion product **9** with $Rh_2(OAc)_4$, but only **8** was formed with $Rh_2(cap)_4$. Catalysis by $Rh_2(pfb)_4$, on the other hand, resulted in the exclusive formation of the insertion product **9** (eq 3). This



7	yield, %	8	9
$Rh_2(OAc)_4$	97	44	56
$Rh_2(pfb)_4$	56	0	100
$Rh_2(cap)_4$	76	100	0

selectivity is surprising in view of the order for functional group nucleophilicity which places a C=C bond at a significantly higher level of reactivity than a C—H bond. However, free carbene reactivities for a C=C bond and tertiary C—H bond (with PhCCl)[28] only differ by a factor of 6.5 ($k_{1\text{-hexene}}/k_{\text{cumene}}$). Other carbenes may, in fact, exhibit a reverse order of reactivity that favors insertion into a tertiary C—H bond over addition to a monosubstituted C=C bond. That $Rh_2(pfb)_4$ favors C—H insertion over cyclopropanation, like its promotion of aromatic substitution over cyclopropanation, suggests that a major contributor to this selectivity is the increased electrophilicity at the carbene center.

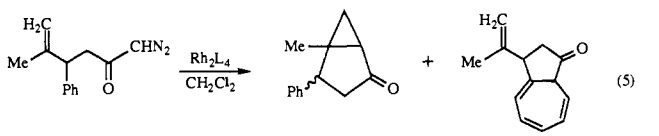
Carbon–Hydrogen Insertion versus Aromatic Substitution. The apparent similarities in factors that promote aromatic substitution and C–H insertion led us to investigate their competition from diazo ketone **10** (eq 4). The exclusive formation of the aromatic



10	yield, %	11	12
$Rh_2(OAc)_4$	96	65	35
$Rh_2(pfb)_4$	96	100	0
$Rh_2(cap)_4$	64	59	41

substitution product **11** from the $Rh_2(pfb)_4$-catalyzed decomposition of **10**, combined with data from eqs 1 and 3, identifies the order of reactivity of $Rh_2(pfb)_4$-generated metal carbenes as aromatic substitution > tertiary C–H insertion > cyclopropanation.[10c] Aromatic substitution is also the exclusive transformation in reactions of the diazo keto ester analog of **10** ($RCOCN_2COOMe$) with rhodium(II) triphenylacetate.[15] On the other hand, $Rh_2(cap)_4$ exhibits similar reactivities of its bound carbene toward both tertiary C–H insertion and aromatic substitution. The results from $Rh_2(OAc)_4$ in this and previous examples demonstrate that chemoselectivity with this catalyst lies between the two extremes of $Rh_2(pfb)_4$ and $Rh_2(cap)_4$. The similarity in results from $Rh_2(cap)_4$- and $Rh_2(OAc)_4$-catalyzed reactions in eq 4 suggests that charge control is the principal determinant of selectivity.

Cyclopropanation versus Aromatic Cycloaddition. The process whereby carbenes or metal carbenes add to an aromatic ring is commonly described as a cycloaddition reaction that forms a norcaradiene intermediate which rearranges to a cycloheptatriene.[1,2,7,29] Aromatic cycloaddition reactions are expected to be similar to cyclopropanation reactions of a C=C bond, and competition between them should differ only in the reactivities of the aromatic ring and the C=C bond toward a metal carbene intermediate. Addition of diazo ketone **13** (eq 5) to a refluxing



13	yield, %	14 (cis/trans)	15
$Rh_2(OAc)_4$	99	53 (3.5)	47
$Rh_2(pfb)_4$	100	35 (2.5)	65
$Rh_2(cap)_4$	100	100 (3.0)	0

solution of dichloromethane containing $Rh_2(OAc)_4$ resulted in the formation of nearly equal amounts of products from cyclopropanation (**14**) and aromatic cycloaddition (**15**). With $Rh_2(cap)_4$ as the catalyst, however, only **14** was produced, while $Rh_2(pbf)_4$ enhanced the relative yield of **15**. Stereoselectivity for formation of **14**, like that for **5** (eq 2), favored the *cis* isomer. Clearly there are differences between cycloaddition to a C=C bond and cycloaddition to an aromatic ring, and these differences are subject to the catalyst employed with selectivity consistent with frontier orbital control. In all cases examined (eqs 1, 3, and 5), $Rh_2(cap)_4$ exhibits exceptional selectivity toward carbene addition to an aliphatic C=C bond.

The location of the functional group that is designed to react with the metal carbene is critical. Aromatic cycloaddition and substitution reactions generally require placement of the aromatic ring so as to form a five-membered-ring product,[1,2,30] as do C–H insertion reactions.[1,2,10,22] In the case of diazo ketone **16**, aromatic cycloaddition should form a disfavored bicyclo[5.4.0]-undecatrieneone, and C–H insertion should form a favored cyclopentanone product. However, neither is observed. Instead,

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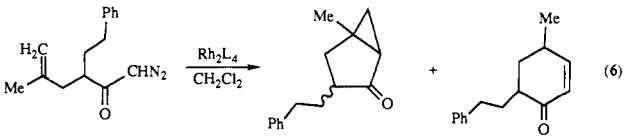
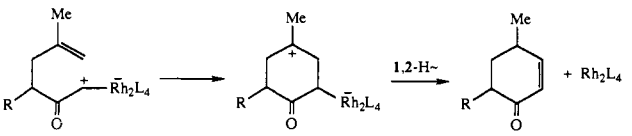


16	yield, %	17 (isomer ratio)	18
$Rh_2(OAc)_4$	53	87 (1.0)	13
$Rh_2(pfb)_4$	39	72 (0.56)	28
$Rh_2(cap)_4$	61	100 (4.6)	0

(6)

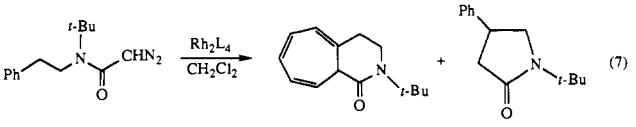
reaction with the C=C bond occurs exclusively (eq 6). The formation of **18**, a byproduct of cyclopropanation favored with catalysis by $Rh_2(pfb)_4$, can be rationalized by electrophilic addition of the metal carbene to form a tertiary carbocation intermediate followed by 1,2-hydride transfer to the cationic center with concurrent dissociation of the dirhodium(II) catalyst (Scheme I;

Scheme I



R = $PhCH_2CH_2$). Consistent with this mechanism, the relative yield of **18** increases with increasing electrophilicity of the catalyst. Alonso has reported cationic rearrangement byproducts from intermolecular cyclopropanation reactions that are consistent with Scheme I,[31] and the well-known "*apparent*" allylic C–H insertion transformation from reactions of diazomalonates with alkenes,[1] originally reported by Wenkert,[32] also fits this description.

Carbon–Hydrogen Insertion versus Aromatic Cycloaddition. Competition between carbon–hydrogen insertion and aromatic cycloaddition was investigated with two systems in which one of the reactive functional groups was offset one atom from optimal (six-versus five-membered-ring formation or five-versus four-membered-ring formation). With diazoacetamide **19**, for example, production of **20** (eq 7) requires cycloaddition to form a

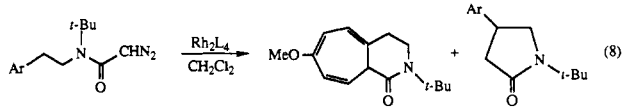


19	yield, %	20	21
$Rh_2(OAc)_4$	85	68	32
$Rh_2(pfb)_4$	80	95	5
$Rh_2(cap)_4$	82	3	97
$Rh_2(acam)_4$	80	23	77

(7)

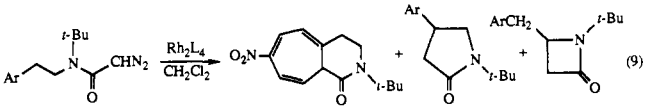
six-membered-ring fused norcaradiene that rearranges to **20**, whereas carbon–hydrogen insertion produces the preferred five-membered-ring γ-lactam **21**. Consistent with results from eq 5, $Rh_2(cap)_4$ provided γ-lactam **21** to the virtual absence of **20**, but $Rh_2(acam)_4$, like $Rh_2(OAc)_4$, gave a mixture of the two products. With $Rh_2(pfb)_4$, compound **20** was formed nearly exclusively. No insertion into the *tert*-butyl group was observed.

The effect of aromatic ring substitution on this competition is surprising. Substitution at the para position by a methoxy group gives virtually the same results as substitution by hydrogen at the same position (eq 8; Ar = *p*-$MeOC_6H_4$). Yet a *p*-NO_2 substituent effectively limits cycloaddition to the aromatic ring and, in fact, supports formation of the previously absent strained β-lactam **28** (eq 9; Ar = *p*-$NO_2C_6H_4$). The *p*-MeO substituent obviously has an effect parallel with that of *p*-H on aromatic cycloaddition and insertion into the benzylic C–H position. In contrast, a *p*-NO_2 substituent inhibits aromatic cycloaddition more than benzylic



22	yield, %	23	24
$Rh_2(OAc)_4$	90	76	24
$Rh_2(pfb)_4$	93	93	7
$Rh_2(cap)_4$	81	14	86
$Rh_2(acam)_4$	80	36	64

(8)

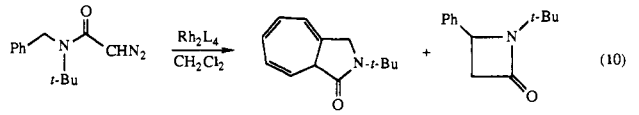


25	yield, %	26	27	28
$Rh_2(OAc)_4$	80	8	77	15
$Rh_2(pfb)_4$	92	27	60	13
$Rh_2(acam)_4$	92	0	97	3

(9)

C–H insertion but, even here, deactivation of C–H insertion at the benzylic position is suggested by the formation of **28**.

N-Benzyldiazoacetamides have previously been reported to undergo aromatic cycloaddition exclusively in nearly quantitative yield in reactions catalyzed by $Rh_2(OAc)_4$, $Rh_2(acam)_4$, and $Rh_2(pfb)_4$.[7b] These reactions were repeated with *N*-benzyl-*N*-*tert*-butyldiazoacetamide (**29**) at room temperature in dichloromethane with the same results: virtually complete aromatic cycloaddition using $Rh_2(OAc)_4$, $Rh_2(acam)_4$, and $Rh_2(cap)_4$. However, when **29** was treated with $Rh_2(cap)_4$ in refluxing dichloromethane, the products from aromatic cycloaddition (**30**) and benzylic C–H insertion (**31**) were formed in equal amounts (eq 10). No significant increase in **31** occurred when the catalytic



29	yield, %	30	31
$Rh_2(OAc)_4$(25°C)	98	>99	<1
$Rh_2(cap)_4$(25°C)	97	98	2
$Rh_2(cap)_4$(40°C)	99	50	50
Rh_2(5S-MEPY)$_4$	96	30	70

(10)

reaction was performed in refluxing dichloroethane. This unprecedented influence of a 15-deg change in temperature on chemoselectivity can be attributed to restricted rotation of the phenyl substituent around the benzylic carbon–nitrogen bond.[33] No significant change in the ratio of **31** to **30** occurred when the catalytic reaction was carried out at 83 °C in refluxing 1,2-dichloroethane (**30**/**31** = 45/55). With $Rh_2(OAc)_4$ at 40 °C, aromatic cycloaddition was the sole reaction process. Use of dirhodium(II) tetrakis[methyl 2-pyrrolidone-5(*R*)-carboxylate-(1–)] ($Rh_2(5R\text{-MEPY})_4$)[34] increased the relative yield of **31** to 70% at 40 °C, and this change suggests that chemoselectivities beyond those obtained with $Rh_2(cap)_4$ can be achieved by further elaborations of ligands for dirhodium(II).[35] The enantiomeric excess obtained for **31** with the use of $Rh_2(5R\text{-MEPY})_4$ was 40%, but that for **30** was not determined.

Competition and Catalyst Ligand Electron Withdrawal. The composite results demonstrate that for diazo ketones and diazoacetamides the order of reactivity for metal carbenes generated from $Rh_2(pfb)_4$ is aromatic substitution > tertiary C–H

(31) (a) Alonso, M. E.; Fernandez, R. *Tetrahedron* **1989**, *45*, 3313. (b) Alonso, M. E.; del Carmen Garcia, M. *J. Org. Chem.* **1985**, *50*, 988.

(32) Wenkert, E.; Alonso, M. E.; Buckwalter, B. L.; Sanchez, E. L. *J. Am. Chem. Soc.* **1983**, *105*, 2021.

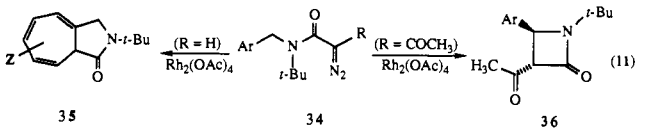
(33) For a review of the effect of conformational changes on reactivity see: Seeman, J. I. *Chem. Rev.* **1983**, *83*, 83.

(34) (a) Doyle, M. P.; Brandes, B. D.; Kazala, A. P.; Pieters, R. J.; Jarstfer, M. B.; Watkins, L. M.; Eagle, C. T. *Tetrahedron Lett.* **1990**, *31*, 6613. (b) Doyle, M. P.; Pieters, R. J.; Martin, S. F.; Austin, R. E.; Oalmann, C. J.; Müller, P. *J. Am. Chem. Soc.* **1991**, *113*, 1423. (c) Doyle, M. P.; van Oeveren, A.; Westrum, L. J.; Protopopova, M. N.; Clayton, T. W., Jr. *J. Am. Chem. Soc.* **1991**, *113*, 8982.

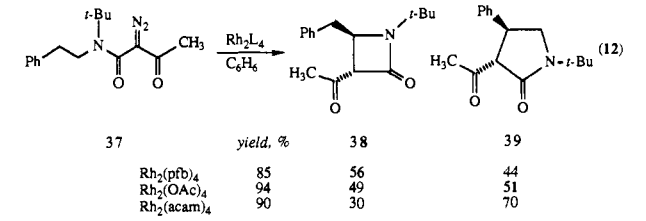
(35) An example of this ligand control on regioselectivity in C–H insertion reactions of diazoacetamides was recently reported: Doyle, M. P.; Protopopova, M. N.; Winchester, W. R.; Daniel, K. L. *Tetrahedron Lett.* **1992**, *33*, 7819.

insertion > cyclopropanation ~ aromatic cycloaddition > secondary C–H insertion and that the rate differences are as much as 100-fold. For $Rh_2(cap)_4$, the order of reactivity appears to be cyclopropanation > aromatic C–H substitution > tertiary C–H insertion > secondary C–H insertion > aromatic cycloaddition. Aromatic substitution was not competitive with cyclopropanation for $Rh_2(cap)_4$-catalyzed reactions of the diazo compounds that are reported in eq 1. We can conclude that it is now possible to conduct a specific metal carbene transformation by selecting the dirhodium(II) catalyst whose ligand constitution favors that particular transformation. Results with $Rh_2(OAc)_4$ normally fall between those from $Rh_2(cap)_4$- and $Rh_2(pfb)_4$-catalyzed reactions except in the competition between intramolecular cyclopropanation of a monosubstituted and a trisubstituted C=C bond (eq 2). Intermolecular competition reactions for cyclopropanation of trisubstituted versus monosubstituted C=C bonds was expected to lead to ratio of 1.5 for the $Rh_2(OAc)_4$-catalyzed reactions.[4a] Chemoselectivity in dirhodium(II)-catalyzed reactions appears to be governed by more than electrophilicity of the carbene carbon (charge control), and in certain competition reactions, frontier orbital interactions may provide a greater relative contribution to overall selectivity.

The influence of carbene substituents other than the ligated metal on chemoselectivity is demonstrated by results obtained from the dirhodium(II)-catalyzed decomposition of **34**. When R = H, only aromatic cycloaddition occurs with $Rh_2(OAc)_4$ catalysis,[7b] but when R = $COCH_3$, only C–H insertion is observed (eq 11: e.g., Z = H, Br, MeO).[36] A similar dramatic influence



of diazo carbon substituents (CH_3CO versus COOMe) on chemoselectivity for $Rh_2(OAc)_4$-catalyzed aromatic substitution versus C–H insertion was recently reported by Wee and co-workers.[14] With diazoacetoacetamide **37**, the analog of **19** (eq 7), β-lactam formation competes with the production of the γ-lactam (eq 12), but the product from aromatic cycloaddition



is completely absent. In this example, the dirhodium(II) ligands have a less dramatic influence on product selectivity than does the replacement of H by CH_3CO on the carbene carbon. The acetyl group completely shuts down aromatic cycloaddition, even with $Rh_2(pfb)_4$ catalysis. Moreover, as the caalyst is changed from $Rh_2(acam)_4$ to $Rh_2(pfb)_4$, C–H insertion becomes more dependent on neighboring heteroatom stabilization (e.g., from the amide nitrogen) in the transition state (for β-lactam formation).[8]

We have attributed the absence of aromatic cycloaddition in reactions of **34** (R = $COCH_3$) to conformational influences of the acetyl group which inhibit approach of the phenyl group to the carbene center,[36] and the same explanation can be offered for the absence of aromatic cycloaddition in the catalytic decomposition of **37**. However, Wee has suggested that the nature of the substituent, implying its electronic effect, rather than steric influences, dictates chemoselectivity in examples such as these.[14] This latter argument has credibility, but it requires acceptance of the fact that COMe and COOMe carbene carbon substituents lead to different products in selected cases even though the electronic difference between them is quite small.[37]

In conclusion, changes in the ligands on dirhodium(II) provide a switch that can turn one competitive transformation "on" and another "off". Although $Rh_2(OAc)_4$ is most often used to evaluate the feasibility of metal carbene transformations, chemoselectivity with this catalyst generally falls between those of $Rh_2(pfb)_4$ and $Rh_2(cap)_4$. Either charge or HOMO/LUMO control or both may be operating in these transformations, and with certain substrates, conformational effects may play a dominant role in product formation. Ongoing investigations will further clarify the controlling factors in dirhodium(II)-catalyzed reactions with additional examples that amplify the degree to which selectivity can be achieved.

Experimental Section

Melting points are uncorrected. Mass spectra were determined at an ionizing voltage of 70 eV. Proton NMR spectra were obtained from a 300-MHz spectrometer, and ^{13}C NMR spectra were recorded at 75 MHz. Infrared spectra were recorded on a dispersive instrument with a resolution of ±2 cm^{-1}. Microanalyses were performed at Atlanta Microlabs, Atlanta, GA, or at Texas Analytical Laboratories, Inc., Stafford, TX. $Rh_2(pfb)_4$,[20a] $Rh_2(acam)_4$,[9] and $Rh_2(cap)_4$[19a] were prepared by acetate displacement from stock $Rh_2(OAc)_4$ which was synthesized from rhodium(III) chloride hydrate.[38] Methanesulfonyl azide was prepared from mesyl chloride and sodium azide.[39] Unless otherwise noted, all reactions were performed in oven-dried glassware under an atmosphere of extradry nitrogen. Solutions were evaporated under reduced pressure with a rotatory evaporator, and the residue was chromatographed on a silica gel column using an ethyl acetate/hexane mixture as the eluent, unless specified otherwise.

Preparation and Transition Metal Catalyzed Decomposition of 1-Diazo-3-phenyl-5-methyl-5-hexen-2-one (1a). To a solution containing 4.9 g (33 mmol) of diisopropylamine in 100 mL of THF was added 29 mL (47 mmol) of a 1.6 M *n*-butyllithium solution dropwise at –78 °C, and the mixture was allowed to warm to 0 °C for 1.5 h. The light yellow solution was cooled to –78 °C and treated with 3.0 g (22 mmol) of phenylacetic acid, and the mixture was allowed to warm to 0 °C for 2 h. The mixture was cooled to –78 °C and treated with 6.0 g (33 mmol) of 1-iodo-2-methyl-2-propene, and the resulting mixture was allowed to warm to room temperature for 3 h, after which 10 mL of water was added at 0 °C. The product was extracted with 0.5 M KOH, washed with ether, acidified to pH 2, and extracted again with ether. The resulting organic layer was washed with water and brine and dried over Na_2SO_4. The solution was concentrated under reduced pressure to give 2.8 g (66%) of chromatographically pure 4-methyl-2-phenyl-4-pentenoic acid as a pale yellow oil: IR (neat) 1709, 1651, 1285 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.77 (s, 3H), 2.51 (dd, 1H, *J* = 14.7 and 8.8 Hz), 2.89 (dd, 1H, *J* = 14.7 and 6.6 Hz), 3.87 (dd, 1H, *J* = 8.8 and 6.6 Hz), 4.78 (s, 1H), 4.81 (s, 1H), 7.24–7.42 (m, 5H), 11.48 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 22.5, 40.7, 49.9, 112.4, 127.5, 128.0, 128.6, 138.0, 142.1, 180.1.

To a solution containing 0.85 g (4.5 mmol) of 4-methyl-2-phenyl-4-pentenoic acid and 0.46 mL (6.0 mmol) of methyl chloroformate in 100 mL of ether was added 0.70 mL (5.0 mmol) of Et_3N. The resulting white suspension was stirred at room temperature for 1 h. The precipitated triethylamine hydrochloride was removed by filtration, and the resulting clear solution was immediately treated with 20 mmol of freshly prepared diazomethane at 0 °C. The mixture was allowed to warm to room temperature overnight, and the excess diazomethane was removed under reduced pressure. The resulting yellow oil was chromatographed on a silica gel column to give 0.83 g (75%) of 1-diazo-5-methyl-3-phenyl-5-hexen-2-one (**1a**) as a yellow oil: IR (neat) 1790, 1643 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.69 (s, 3H), 2.43 (dd, 1H, *J* = 14.8 and 7.5 Hz), 2.90 (dd, 1H, *J* = 14.8 and 7.5 Hz), 3.65–3.75 (m, 1H), 4.64 (s, 1H),

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4.71 (s, 1H), 5.16 (s 1H), 7.20–7.35 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 22.6, 40.0, 54.7, 55.2, 112.1, 127.3, 128.0, 128.7, 138.9, 142.6, 194.3.

A solution containing 0.20 g (0.94 mmol) of α-diazo ketone **1** in 50 mL of CH_2Cl_2 was treated with 7 mg of rhodium(II) caprolactamate. The mixture was allowed to stir at 45 °C for 1 h and was then concentrated under reduced pressure. Chromatography of the resulting oil on silica gel gave 5-methyl-3-phenylbicyclo[3.1.0]hexan-2-one (**2a**) (75%) as a light yellow oil: IR (neat) 1725, 1603, 1165 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.21 (dd, 1H, J = 8.8 and 4.6 Hz), 1.37 (dd, 1H, J = 4.6 and 3.1 Hz), 1.41 (s, 3H), 1.80 (dd, , J = 8.8 and 3.1 Hz), 2.14 (dd, 1H, J = 12.2 and 11.0 Hz), 2.59 (dd, 1H, J = 12.2 and 8.9 Hz), 3.38 (dd, 1H, J = 11.0 and 8.9 Hz), 7.10–7.39 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.0, 21.4, 27.7, 34.3, 38.3, 49.3, 126.3, 127.9, 128.2, 137.7, 212.4; HRMS calcd for $C_{13}H_{14}O$ 186.1044, found 186.1040.

A solution containing 0.10 g (0.47 mmol) of α-diazo ketone **1a** in 50 mL of CH_2Cl_2 was treated with 5 mg of rhodium(II) perfluorobutyrate. The mixture was allowed to stir at room temperature for 30 min and was then concentrated under reduced pressure. Chromatography of the resulting oil on silica gel gave 1,3-dihydro-1-(2-methyl-2-propenyl)-2*H*-inden-2-one (**3a**) (86%) as a clear oil: IR (neat) 1752, 1665, 1480 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.75 (s, 3H), 2.40 (dd, 1H, J = 14.4 and 4.9 Hz), 2.70 (dd, 1H, J = 14.4 and 8.6 Hz), 3.55–3.63 (m, 3H), 4.72 (s, 1H), 4.85 (s, 1H), 7.24–7.32 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 22.2, 39.7, 42.9, 50.8, 113.3, 124.6, 125.0, 127.1, 127.3, 136.4, 141.8, 142.2, 217.1; HRMS calcd for $C_{13}H_{14}O$ 186.1045, found 186.1044.

A solution containing 10 mg (0.07 mmol) of α-diazo ketone **1** in 10 mL of CH_2Cl_2 was treated with 2 mg of rhodium(II) acetate, and the mixture was allowed to stir at room temperature for 1 h. The solution was concentrated under reduced pressure to give two compounds whose spectral and physical properties were identical to those described above for **2a** (44%) and **3a** (48%).

Preparation and Transition Metal Catalyzed Decomposition of 1-Diazo-5-methyl-3-(*p*-methoxyphenyl)-5-hexen-2-one (1b). To a solution containing 5.9 g (40 mmol) of diisopropylamine in 10 mL of THF was added 28 mL (45 mmol) of a 1.6 M *n*-butyllithium solution dropwise at –78 °C, and the mixture was allowed to warm to 0 °C for 1 h. The light yellow solution was cooled to –78 °C and treated with 3.3 g (20 mmol) of (*p*-methoxyphenyl)acetic acid. The mixture was allowed to warm to 0 °C for 1.5 h, after which it was cooled to –78 °C and treated with 4.5 g (25 mmol) of 1-iodo-2-methyl-2-propene. The resulting mixture was warmed to room temperature for 1 h, after which 10 mL of water was added at 0 °C. The product was extracted with 0.5 M KOH, washed with ether, acidified to pH 2, and extracted again with ether. The resulting organic layer was washed with water and brine and dried over $MgSO_4$. The solution was concentrated under reduced pressure to give 3.2 g (72%) of 4-methyl-2-(*p*-methoxyphenyl)-4-pentenoic acid as a pale yellow oil: IR (neat) 1696, 1454, 1259, 773 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.71 (s, 3H), 2.43 (dd, 1H, J = 14.6 and 6.9 Hz), 2.80 (dd, 1H, J = 14.6 and 8.7 Hz), 3.58–3.88 (m, 1H), 3.78 (s, 3H), 4.71 (s, 1H), 4.75 (s, 1H), 6.86 (d, 2H, J = 8.7 Hz), 7.26 (d, 2H, J = 8.7 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 22.4, 40.6, 48.9, 55.1, 112.3, 113.9, 128.9, 130.0, 142.1, 158.8, 180.8.

To a solution containing 1.0 g (4.5 mmol) of 4-methyl-2-(*p*-methoxyphenyl)-4-pentenoic acid and 0.43 mL (5.7 mmol) of methyl chloroformate in 150 mL of ether was added 0.64 mL (4.5 mmol) of triethylamine. The resulting white suspension was treated as previously described for **1a** with eventual immediate addition of 80 mmol of freshly prepared diazomethane at 0 °C. The mixture was allowed to warm to room temperature overnight, and the excess diazomethane was removed under reduced pressure. The resulting yellow oil was chromatographed on a silica gel column to give 0.79 g (76%) of 1-diazo-5-methyl-3-(*p*-methoxyphenyl)-5-hexen-2-one (**1b**) as a yellow oil: IR (neat) 2107, 1717, 1642 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.65 (s, 3H), 2.39 (dd, 1H, J = 14.5 and 3 Hz), 2.80 (dd, 1H, J = 14.5 and 7.0), 3.53–3.66 (m, 1H), 3.75 (s, 3H), 4.61 (s, 1H), 4.69 (s, 1H), 5.11 (s, 1H), 6.83 (d, 2H, J = 9 Hz), 7.14 (d, 2H, J = 9 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 22.5, 39.9, 54.3, 55.0, 61.1, 112.0, 114.0, 128.9, 130.8, 142.6, 158.7, 194.6.

A solution containing 0.13 g (0.54 mmol) of α-diazo ketone **1b** in 60 mL of CH_2Cl_2 was treated with 5 mg of rhodium(II) caprolactamate. The mixture was allowed to stir at 45 °C for 1 h and was then concentrated under reduced pressure. Chromatography of the resulting oil on silica gel gave 5-methyl-3-(*p*-methoxyphenyl)bicyclo[3.1.0]hexan-2-one (**2b**) (80%) as a yellow oil: IR (neat) 1726, 1613, 1515 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.17–1.22 (m, 1H), 1.34–1.37 (m, 1H), 1.40 (s, 3H), 1.77 (dd, 1H, J = 8.9 and 2.8 Hz), 2.08 (dd, 1H, J = 12.5 and 12.2 Hz), 2.56 (dd, 1H, J = 12.2 and 7.7 Hz), 3.47 (dd, 1H, J = 12.5 and 7.7 Hz), 3.77 (s, 3H), 6.86 (d, 2H, J = 8.7 Hz), 7.03 (d, 2H, J = 8.7 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.5, 21.9, 28.1, 34.6, 38.8, 49,0, 55.1, 113.9, 129.6, 130.1, 158.4, 213.3; HRMS calcd for $C_{14}H_{16}O_2$ 216.1150, found 216.1151.

A solution containing 0.20 g (0.82 mmol) of α-diazo ketone **1b** in 80 mL of CH_2Cl_2 was treated with 5 mg of rhodium(II) perfluorobutyrate. The mixture was allowed to stir at room temperature for 30 min and was then concentrated under reduced pressure. Chromatography of the resulting oil on silica gel gave 1,3-dihydro-1-(2-methyl-2-propenyl)-6-methoxy-2*H*-inden-2-one (**3b**) (80%) as a clear oil: IR (neat) 1750, 1650, 1252 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.73 (s, 3H), 2.33 (dd, 1H, J = 14.2 and 8.7 Hz), 2.66 (dd, 1H, J = 14.2 and 4.2 Hz), 3.43–3.59 (m, 3H), 3.79 (s, 3H), 4.69 (s, 1H), 4.83 (s, 1H), 6.78–6.83 (m, 2H), 7.18–7.24 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 22.2, 29.6, 40.0, 43.2, 50.2, 55.2, 109.8, 113.3, 125.9, 133.8, 137.7, 142.2, 159.0, 217.3; HRMS calcd for $C_{14}H_{16}O_2$ 216.1151, found 216.1150.

A solution containing 0.15 g (0.61 mmol) of α-diazo ketone **1b** in 50 mL of CH_2Cl_2 was treated with 5 mg of rhodium(II) acetate and allowed to stir at room temperature for 1 h. The solution was concentrated under reduced pressure to give two compounds whose spectral and physical properties were identical to those described above for **2b** (50%) and **3b** (33%).

Preparation and Transition Metal Catalyzed Decomposition of 1-Diazo-3-phenyl-6-methyl-5-hepten-2-one (1c). To a solution containing 2.2 g (15 mmol) of diisopropylamine in 50 mL of THF was added 10 mL (16 mmol) of a 1.6 M *n*-butyllilthium solution dropwise at –78 °C, and the mixture was allowed to warm to 0 °C for 1.5 h. The light yellow solution was cooled to –78 °C and treated with 1.0 g (7.3 mmol) of phenylacetic acid, and the mixture was warmed to 0 °C for 2 h. The solution was then cooled to –78 °C and treated with 1.6 g (11 mmol) of 4-bromo-2-methyl-2-butene, and the mixture was stirred for 3 h, after which 3 mL of water was added at 0 °C. The product was extracted with 0.5 M KOH, washed with ether, acidified to pH 2, and reextracted with ether. The organic layer was washed with brine and water and dried over Na_2SO_4. The solution was concentrated under reduced pressure to give 1.3 g (83%) of 5-methyl-2-phenyl-4-hexenoic acid as a pale yellow oil: IR (neat) 1707, 1601, 1290 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.62 (s, 3H), 1.69 (s, 3H), 2.51 (dt, 1H, J = 14.5 and 7.4 Hz), 2.83 (dt, 1H, J = 14.5 and 7.4 Hz), 3.61 (t, 1H, J = 7.4 Hz), 5.11 (t, 1H, J = 7.4 Hz), 7.24–7.44 (m, 5H), 11.83 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 17.7, 25.6, 31.7, 51.8, 120.5, 127.3, 128.0, 128.5, 134.2, 138.2, 180.4.

To a solution containing 1.0 g (4.9 mmol) of 5-methyl-2-phenyl-4-hexenoic acid and 0.46 mL (5.9 mmol) of methyl chloroformate in 100 mL of ether was added 0.7 mL (4.9 mmol) of triethylamine. The resulting white suspension was treated as previously described for **1a** with eventual immediate addition of 20 mmol of freshly prepared diazomethane at 0 °C, and the mixture was then allowed to warm to room temperature overnight. The excess diazomethane was removed under reduced pressure. The resulting yellow oil was chromatographed on a silica gel column to give 0.59 g (50%) of 1-diazo-6-methyl-3-phenyl-5-hepten-2-one (**1c**) as a yellow oil: IR (neat) 2105, 1733, 1642 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.54 (s, 3H), 1.62 (s, 3H), 2.42 (dt, 1H, J = 14.6 and 7.3 Hz), 2.80 (dt, 1H, J = 14.6 and 7.3 Hz), 3.44 (t, 1H, J = 7.3 Hz), 5.00 (t, 1H, J = 7.3 Hz), 5.11 (s, 1H), 7.20–7.40 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 17.7, 25.6, 31.3, 54.6, 57.5, 121.0, 127.1, 128.0, 128.6, 133.6, 139.1, 194.7.

A solution containing 0.10 g (0.44 mmol) of α-diazo ketone **1c** in 50 mL of CH_2Cl_2 was treated with 5 mg of rhodium(II) caprolactamate. The mixture was allowed to stir at 45 °C for 1 h and was then concentrated under reduced pressure. Filtration of the reaction mixture through a silica plug using ether as the eluent give 6,6-dimethyl-3-phenylbicyclo-[3.1.0]hexan-2-one (**2c**) (97%) as a white crystalline solid: mp 91–92 °C; IR (neat) 1702, 1603, 1451 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.05 (s, 3H), 1.12 (s, 3H), 1.83–1.92 (m, 2H), 2.10 (dd, 1H, J = 13.5 and 7.7 Hz), 2.78 (ddd, 1H, J = 13.5, 13.0, and 7.1 Hz), 3.74 (dd, 1H, J = 13.0 and 7.7 Hz), 7.20–7.35 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 16.6, 25.6, 26.5, 26.6, 40.4, 55.4, 126.1, 127.2, 127.7, 136.1, 212.0; HRMS calcd for $C_{14}H_{16}O$ 200.1202, found 200.1199.

A solution containing 0.10 g (0.44 mmol) of diazo ketone **1c** in 50 mL of CH_2Cl_2 was treated with 5 mg of rhodium(II) perfluorobutyrate. The mixture was allowed to stir at room temperature for 30 min and was then concentrated under reduced pressure. Chromatography of the resulting oil on silica gel gave 1,3-dihydro-1-(3-methyl-2-butenyl)-2*H*-inden-2-one (**3c**) (82%) as a colorless oil: IR (neat) 1752, 1667, 1142 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.55 (s, 3H), 1.64 (s, 3H), 2.58 (dd, 2H, J = 6.7 and 6.6 Hz), 3.40 (m, 3H), 5.08 (t, 1H, J = 6.7 Hz), 7.25–7.31

(m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 17.8, 25.6, 30.2, 43.2, 53.1, 119.8, 124.6, 127.2, 134.4, 136.8, 141.9, 217.6; HRMS calcd for $C_{14}H_{16}O$ 200.1202, found 200.1205.

A solution containing 10 mg (0.05 mmol) of α-diazo ketone **1c** in 10 mL of CH_2Cl_2 was treated with 2 mg of rhodium(II) acetate, and the mixture was allowed to stir at room temperature for 1 h. The solution was then concentrated under reduced pressure to give two compounds whose spectral and physical properties were identical to those described above for **2c** (40%) and **3c** (48%).

Preparation and Transition Metal Catalyzed Decomposition of 1-Diazo-3-phenyl-5-hexen-2-one (1d). To a solution containing 6.0 g (44 mmol) of diisopropylamine in 100 mL of THF was added 28 mL (45 mmol) of a 1.6 M *n*-butyllithium solution dropwise at −78 °C, and the mixture was allowed to warm to 0 °C for 1 h. The light yellow solution was cooled to −78 °C and treated with 2.7 g (20 mmol) of phenylacetic acid, and the mixture was allowed to warm to 0 °C for 1.5 h. The mixture was then cooled to −78 °C and treated with 5.0 g (30 mmol) of 1-iodo-2-propene. The resulting mixture was warmed to room temperature for 1.5 h, after which 7 mL of water was added at 0 °C. The product was extracted with 0.5 M KOH, washed with ether, acidified to pH 2, and extracted again with ether. The resulting organic layer was washed with water and brine and dried over Na_2SO_4. The solution was concentrated under reduced pressure to give 2.5 g (70%) of 2-phenyl-4-pentenoic acid as a clear oil: IR (neat) 1707, 1644, 920 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.53 (ddd, 1H, J = 14.3, 7.3, and 7.0 Hz), 2.82 (ddd, 1H, J = 14.3, 7.3, and 7.0 Hz), 3.64 (dd, 1H, J = 7.3 and 7.0 Hz), 5.00–5.11 (m, 2H), 5.65–5.79 (m, 1H), 7.25–7.33 (m, 5H), 9.79 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 36.4, 50.8, 116.7, 127.0, 127.4, 128.1, 134.3, 137.2, 179.0.

To a solution containing 1.5 g (8.5 mmol) of 2-phenyl-4-pentenoic acid and 0.8 mL (10 mmol) of methyl chloroformate in 150 mL of ether was added 0.84 mL (8.5 mmol) of triethylamine. The resulting white suspension was treated as previously described for **1a** with eventual immediate addition of 40 mmol of freshly prepared diazomethane at 0 °C. The mixture was allowed to warm to room temperature overnight, and the excess diazomethane was removed under reduced pressure. The resulting yellow oil was chromatographed on a silica gel column to give 1.5 g (88%) of 1-diazo-3-phenyl-5-hexen-2-one (**1d**) as a yellow oil: IR (neat) 2105, 1642, 1495 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.49 (ddd, 1H, J = 15.0, 7.3, and 7.0 Hz), 2.87 (ddd, 1H, J = 15.0, 7.3, and 7.0 Hz), 3.49–3.58 (m, 1H), 4.95–5.06 (m, 2H), 5.12 (s, 1H), 5.62–5.76 (m, 1H), 7.22–7.35 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 22.5, 41.0, 48.5, 55.1, 112.5, 113.8, 129.0, 142.0, 157.5, 181.0.

A solution containing 0.18 g (8.9 mmol) of α-diazo ketone **1d** in 50 mL of CH_2Cl_2 was treated with 5 mg of rhodium(II) caprolactamate. The mixture was allowed to stir at 45 °C for 1 h and was then concentrated under reduced pressure. Chromatography of the resulting oil on silica gel gave 3-phenylbicyclo[3.1.0]hexan-2-one (**2d**) (72%) as a clear oil: IR (neat) 1782, 1690, 1449 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.94–0.98 (m, 1H), 1.11–1.19 (m, 1H), 1.89–1.95 (m, 1H), 2.04–2.12 (m, 1H), 2.30–2.36 (m, 1H), 2.69–2.80 (m, 1H), 3.53–3.58 (m, 1H), 7.15–7.30 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 12.6, 20.5, 28.5, 30.0, 50.0, 127.0, 127.5, 128.5, 139.5, 213.5; HRMS calcd for $C_{12}H_{12}O$ 172.0888, found 172.0891.

A solution containing 0.17 g (0.85 mmol) of α-diazo ketone **1d** in 50 mL of CH_2Cl_2 was treated with 5 mg of rhodium(II) perfluorobutyrate. The mixture was allowed to stir at room temperature for 30 min and was then concentrated under reduced pressure. Chromatography of the resulting oil on silica gel gave 1,3-dihydro-1-(2-propenyl)-2*H*-inden-2-one (**3d**) (95%) as a clear oil: IR (neat) 1752, 1640, 1480 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.45–2.63 (m, 1H), 2.67–2.76 (m, 1H), 3.41–3.60 (m, 3H), 5.00–5.08 (m, 2H), 5.65–5.78 (m, 1H), 7.25–7.35 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 42.8, 44.6, 52.9, 117.2, 123.3, 125.1, 125.9, 127.7, 133.0, 136.2, 140.8, 216.5; HRMS calcd for $C_{12}H_{12}O$ 172.0888, found 172.0888.

A solution containing 0.15 g (0.75 mmol) of α-diazo ketone **1d** in 50 mL of CH_2Cl_2 was treated with 5 mg of rhodium(II) acetate, and the mixture was allowed to stir at room temperature for 1 h. The solution was then concentrated under reduced pressure to give two compounds whose spectral and physical properties were identical to those described above for **2d** (66%) and **3d** (33%).

Preparation and Transition Metal Catalyzed Decomposition of 1-Diazo-6-methyl-3-(2-propenyl)-5-hepten-2-one (4). To a solution containing 2.2 g (22 mmol) of 4-pentenoic acid in 75 mL of THF was added 31 mL (49 mmol) of 1.6 M *n*-butyllithium dropwise at −78 °C, and the mixture was allowed to stir at −78 °C for 2 h. The reaction mixture was then treated with 6.7 mL (67 mmol) of 4-bromo-2-methyl-2-butene, and the resulting mixture was allowed to warm to room temperature for 12 h. The reaction was quenched with 50 mL of a saturated ammonium chloride solution, and the product was extracted with 10% NaOH. The aqueous layer was washed with ether, acidified with 1.5 M HCl, and washed again with ether. The organic layer was then washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure to yield 2.5 g (66%) of 6-methyl-3-(2-propenyl)-4-hexanoic acid as a pale yellow liquid: IR (neat) 3090, 2919, 1712, 1643 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.60 (s, 3H), 1.69 (s, 3H), 2.19–2.56 (m, 5H), 5.05–5.10 (m, 3H), 5.66–5.89 (m, 1H), 11.61 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 17.7, 25.7, 30.0, 35.4, 45.5, 116.9, 120.6, 134.2, 135.2, 182.1.

To a solution containing 1.7 g (10 mmol) of 6-methyl-3-(2-propenyl)-4-hexanoic acid and 0.93 mL (12 mmol) of methyl chloroformate in 75 mL of ether was added 1.4 mL (10 mmol) of triethylamine. The resulting white suspension was stirred at room temperature for 1 h. The precipitated triethylamine hydrochloride was removed by filtration, the resulting clear solution was immediately treated with 40 mmol of freshly prepared diazomethane at 0 °C, and the mixture was then allowed to warm to room temperature overnight. The excess diazomethane was removed under reduced pressure, and the resulting crude oil was chromatographed on a silica gel column to give 0.25 g (13%) of 1-diazo-6-methyl-3-(2-propenyl)-5-hepten-2-one (**4**) as a bright yellow oil: IR (neat) 2103, 1738, 1642 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.45 (s, 3H), 1.54 (s, 3H), 2.02–2.24 (m, 5H), 4.85–4.93 (m, 3H), 5.22 (s, 1H), 5.55–5.64 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 17.6, 25.6, 30.4, 35.9, 50.7, 54.4, 116.6, 120.9, 133.6, 135.4, 197.4.

A solution containing 250 mg (48 mmol) of α-diazo ketone **4** in 30 mL of CH_2Cl_2 was treated with 5 mg of rhodium(II) acetate. The mixture was allowed to stir at room temperature for 30 min and then concentrated under reduced pressure. Chromatography of the resulting oil on silica gel gave *syn*-6,6-dimethyl-3-(2-propenyl)bicyclo[3.1.0]hexan-2-one (***syn*-5**) (35%) as a clear liquid, *anti*-6,6-dimethyl-3-(2-propenyl)bicyclo[3.1.0]-hexan-2-one (***anti*-5**) (15%) as a clear oil, and 3-(3,3-dimethyl-2-propenyl)bicyclo[3.1.0]hexan-2-one (**6**) (42%). Compound ***syn*-5**: IR (neat) 1720, 1641 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.11 (s, 3H), 1.14 (s, 3H), 1.44 (d, 1H, J = 6.3 Hz), 1.68 (t, 1H, J = 5.5 Hz), 1.74–1.79 (m, 1H), 1.87 (ddd, 1H, J = 13.2, 7.0, and 6.3 Hz), 2.34–2.43 (m, 2H), 2.49 (dd, 1H, J = 14.2 and 5.0 Hz), 5.00–5.07 (m, 2H), 5.63–5.76 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 17.1, 25.2, 26.4, 27.1, 31.3, 32.9, 40.5, 51.7, 115.7, 136.5, 215.0; HRMS calcd for $C_{11}H_{16}O$ 164.1202, found 164.1202. Compound ***anti*-5**: IR (neat) 1719, 1642 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.86 (t, 1H, J = 6.3 Hz), 1.10 (s, 3H), 1.13 (s, 3H), 1.66 (d, 1H, J = 4.8 Hz), 1.83 (dd, 1H, J = 11.4 and 6.6 Hz), 1.89–1.94 (m, 1H), 1.97–2.07 (m, 2H), 2.42–2.47 (m, 1H), 4.99–5.06 (m, 2H), 5.62–5.76 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 16.3, 26.6, 27.3, 29.7, 34.0, 37.0, 41.3, 47.1, 116.7, 135.6, 215.6; HRMS calcd for $C_{11}H_{16}O$ 164.1202, found 164.1202. Compound **6**: IR (neat) 1725, 1447 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.77–0.81 (m, 1H), 1.10–1.18 (m, 2H), 1.55 (s, 3H), 1.64 (s, 3H), 1.78–1.83 (m, 1H), 1.89–1.98 (m, 2H), 2.21–2.38 (m, 3H), 4.94–4.99 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.6, 17.8, 19.8, 25.7, 28.3, 28.6, 31.6, 46.7, 121.7, 133.2, 216.8; HRMS calcd for $C_{11}H_{16}O$ 164.1202, found 164.1211.

A solution containing 22 mg (0.11 mmol) of α-diazo ketone **4** in 10 mL of CH_2Cl_2 was treated with 2 mg of rhodium(II) perfluorobutyrate, and the mixture was allowed to stir at room temperature for 1 h. The solution was then concentrated under reduced pressure to give three compounds whose spectral and physical properties were identical to those described above for ***syn*-5** (33%), ***anti*-5** (14%), and **6** (51%).

A solution containing 26 mg (0.14 mmol) of α-diazo ketone **4** in 10 mL in CH_2Cl_2 was treated with 2 mg of rhodium(II) caprolactamate, and the mixture was allowed to stir at room temperature for 1 h. The solution was then concentrated under reduced pressure to give three compounds whose spectral and physical properties were identical to those described above for ***syn*-5** (35%), ***anti*-5** (6%), and **6** (50%).

Preparation and Transition Metal Catalyzed Decomposition of 1-Diazo-5-methyl-3-(2-propenyl)-2-hexanone (7). To a solution containing 14 g (94 mmol) of diisopropylamine in 100 mL of THF was added 80 mL (96 mmol) of 1.2 M *n*-butyllithium dropwise at −78 °C, and the mixture was allowed to warm to 0 °C for 1.5 h. The light yellow mixture was cooled to −78 °C and treated with 5.0 g (43 mmol) of 4-methylpentanoic acid, and the resulting mixture was then warmed to 0 °C for 2 h. The solution was cooled to −78 °C and treated with 6.0 mL (66 mmol) of allyl iodide, and the mixture as stirred for 3 h, after which time 13 mL of water was added at 0 °C. The product was extracted with 0.5 M KOH, washed with ether, acidified to pH 2, and reextracted with ether. The organic

layer was washed with brine and water and concentrated under reduced pressure to give 1.1 g (16%) of 4-methyl-2-(2-propenyl)pentanoic acid. For characterization, a small portion of the acid was treated with freshly prepared diazomethane at 0 °C and the mixture was allowed to warm to room temperature for 1 h. The excess diazomethane was removed under reduced pressure to give methyl 4-methyl-2-(2-propenyl) pentanoate as a clear liquid: bp 38 °C (5 mm); IR (neat) 1740, 1644, 1169, 917 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.80 (d, 3H, J = 5.0 Hz), 0.82 (d, 3H, J = 5.0 Hz), 1.13–1.23 (m, 1H), 1.40–1.56 (m, 2H), 2.13 (dt, 1H, J = 14.0 and 7.0 Hz), 2.24 (dt, 1H, J = 14.0 and 7.0 Hz), 2.41–2.50 (m, 1H), 3.59 (s, 3H), 4.91–4.99 (m, 2H), 5.58–5.72 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.8, 22.7, 25.9, 36.8, 40.9, 43.2, 51.0, 116.4, 135.2, 176.0.

To a solution containing 0.30 g (1.9 mmol) of 4-methyl-2-(2-propenyl)-pentanoic acid in 50 mL of benzene was added 0.26 mL (2.0 mmol) of oxalyl chloride. The resulting solution was stirred at room temperature until gas evolution ceased. The excess oxalyl chloride and benzene were distilled off under reduced pressure, and the resulting pale-yellow oil was added dropwise to a solution of freshly prepared diazomethane at 0 °C. The mixture was allowed to warm to room temperature overnight. The excess diazomethane was removed under reduced pressure, and the resulting yellow oil was chromatographed on a silica gel column to give 0.20 g (56%) of 1-diazo-5-methyl-3-(2-propenyl)-2-hexanone (**7**) as a yellow oil: IR (neat) 2103, 1790, 1640 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.83 (d, 3H, J = 6.1 Hz), 0.84 (d, 3H, J = 6.1 Hz), 1.14–1.24 (m, 1H), 1.48–1.59 (m, 2H), 2.10 (dt, 1H, J = 14.0 and 6.9 Hz), 2.28 (dt, 1H, J = 14.0 and 6.9 Hz), 2.36–2.48 (m, 1H), 4.95–5.03 (m, 2H), 5.22 (s, 1H), 5.62–5.76 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 22.1, 22.9, 25.7, 37.1, 41.1, 48.5, 54.3, 116.6, 135.3, 197.9.

A solution containing 0.10 g (18 mmol) of α-diazo ketone **7** in 50 mL of CH_2Cl_2 was treated with 5 mg of rhodium(II) caprolactamate. The mixture was allowed to stir at 45 °C for 1 h and was then concentrated under reduced pressure. Chromatography of the resulting oil on silica gel gave 3-(2-methylpropyl)bicyclo[3.1.0]hexan-2-one (**8**) (76%) as a clear oil: IR (neat) 1723, 1468, 1187, 932 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.74–0.80 (m, 1H), 0.83 (d, J = 6.2 Hz), 0.87 (d, 3H, J = 6.2 Hz), 1.03–1.12 (m, 1H), 1.14–1.21 (m, 1H), 1.54–1.58 (m, 1H), 1.68 (dd, 1H, J = 13.1 and 3.1 Hz), 1.80–1.86 (m, 1H), 1.93–2.00 (m, 1H), 2.22–2.30 (m, 1H), 2.36–2.46 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.3, 19.5, 20.8, 22.5, 26.3, 27.9, 29.0, 43.0, 43.8, 226.1. Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 78.88; H, 10.65.

A solution containing 0.10 g (18 mmol) of α-diazo ketone **7** in 50 mL of CH_2Cl_2 was treated with 5 mg of rhodium(II) perfluorobutyrate. The mixture was allowed to stir at room temperature for 30 min and was then concentrated under reduced pressure. Chromatography of the resulting oil on silica gel gave 4,4-dimethyl-2-(2-propenyl)cyclopentanone (**9**) (56%) as a clear oil: IR (neat) 1777, 1642, 1463 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.92–0.98 (m, 2H), 1.04 (s, 3H), 1.16 (s, 3H), 1.89–2.09 (m, 1H), 1.99 (d, 1H, J = 18.0 Hz), 2.15 (d, 1H, J = 18.0 Hz), 2.32–2.44 (m, 1H), 2.47–2.55 (m, 1H), 4.98–5.09 (m, 2H), 5.65–5.79 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 27.3, 29.0, 29.1, 34.0, 42.6, 47.1, 52.7, 115.8, 135.2, 219.9. Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 79.00; H, 10.64.

A solution containing 10 mg (0.06 mmol) of α-diazo ketone **7** in 10 mL of CH_2Cl_2 was treated with 2 mg of rhodium(II) acetate, and the mixture was allowed to stir at room temperature for 1 h. The solution was then concentrated under reduced pressure to give two compounds whose spectral and physical properties were identical to those described above for **8** (43%) and **9** (54%).

Preparation and Transition Metal Catalyzed Decomposition of 1-Diazo-5-methyl-3-phenyl-2-hexanone (10). To a solution containing 5.0 g (37 mmol) of phenylacetic acid in 150 mL of THF was added 72 mL (81 mmol) of 1.6 M n-butyllithium dropwise at –78 °C, and the mixture was allowed to stir at –78 °C for 2 h. The reaction mixture was then treated with 12 mL (0.11 mol) of 1-bromo-2-methylpropane, and the resulting mixture was allowed to warm to room temperature for 12 h. The reaction was quenched with 100 mL of saturated NH_4Cl solution and the product extracted with 10% NaOH. The aqueous layer was washed with ether, acidified with 1.5 M HCl, and washed again with ether. The organic layer was then washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The crude solid was recrystallized from an ether/hexane mixture to give 6.6 g (93%) of 4-methyl-2-phenylpentanoic acid as a white crystalline solid: mp 73–74 °C; IR (neat) 3050, 2956, 1692, 1601 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.91 (d, 6H, J = 6.0 Hz), 1.45–1.54 (m, 1H), 1.70 (ddd, 1H, J = 13.8, 7.6, and 7.0 Hz), 1.96 (ddd, 1H, J = 13.8, 7.8, and 7.0 Hz), 3.67 (dd, 1H, J = 7.8 and 7.6 Hz), 7.25–7.33 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 22.2, 22.6, 25.7, 42.0, 49.5, 127.4, 128.1, 128.6, 138.6, 180.6.

To a solution containing 1.9 g (10 mmol) of 4-methyl-2-phenylpentanoic acid and 0.93 mL (12 mmol) of methyl chloroformate in 75 mL of ether was added 1.4 mL (10 mmol) of triethylamine. The resulting white suspension was stirred at room temperature for 1 h. The precipitated triethylamine hydrochloride was removed by filtration, the resulting clear solution was immediately treated with 40 mmol of freshly prepared diazomethane at 0 °C, and the mixture was then allowed to warm to room temperature overnight. The excess diazomethane was removed under reduced pressure, and the resulting crude oil was chromatographed on a silica gel column to give 1.4 g (63%) of 1-diazo-5-methyl-3-phenyl-2-hexanone (**10**) as a bright yellow oil: IR (neat) 2103, 1640 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.88 (d, 6H, J = 6.0 Hz), 1.40–1.47 (m, 1H), 1.70 (ddd, 1H, J = 14.0, 7.3, and 7.0 Hz), 1.98 (ddd, 1H, J = 14.0, 7.7, and 7.3 Hz), 3.55–3.76 (m, 1H), 5.14 (s, 1H), 7.23–7.34 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 22.1, 22.9, 25.6, 29.7, 41.3, 54.7, 127.2, 128.1, 128.8, 139.5, 195.2.

A solution containing 0.50 g (23 mmol) of α-diazo ketone **10** in 50 mL of CH_2Cl_2 was treated with 5 mg of rhodium(II) acetate. The mixture was allowed to stir at room temperature for 30 min and was then concentrated under reduced pressure. Chromatography of the resulting oil on silica gel gave 1,3-dihydro-1-(2-methylpropyl)-2*H*-inden-2-one (**11**) (62%) as a clear liquid and 4,4-dimethyl-2-phenylcyclopentanone (**12**) (34%) as a white solid. Compound **11**: IR (neat) 1750, 1465, 1187 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.91 (d, 3H, J = 6.6 Hz), 0.96 (d, 3H, J = 6.6 Hz), 1.62 (ddd, 1H, J = 13.9, 7.0, and 7.0 Hz), 1.77 (ddd, 1H, J = 13.9, 7.0, and 6.8 Hz), 1.91–1.97 (m, 1H), 3.47 (dd, 1H, J = 7.0 and 6.8 Hz), 3.55 (s, 2H), 7.25–7.28 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 22.5, 22.7, 25.4, 41.2, 43.1, 51.3, 124.7, 127.2, 136.6, 142.7, 218.0. Anal. Calcd for $C_{13}H_{16}O$: C, 82.94; H, 8.57. Found: C, 82.88; H, 8.58. Compound **12**: IR (neat) 1746, 1603 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.18 (s, 3H), 1.28 (s, 3H), 2.04 (dd, 1H, J = 12.8 and 12.3 Hz), 2.25–2.36 (m, 3H), 3.62 (dd, 1H, J = 12.3 and 8.6 Hz), 9.19–7.36 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 27.6, 29.8, 33.8, 45.9, 53.6, 54.2, 126.8, 128.1, 128.6, 138.8, 217.9. Anal. Calcd for $C_{13}H_{16}O$: C, 82.94; H, 8.57. Found: C, 82.94; H, 8.51.

A solution containing 18 mg (0.08 mmol) of α-diazo ketone **10** in 10 mL of CH_2Cl_2 was treated with 2 mg of rhodium(II) perfluorobutyrate, and the mixture was allowed to stir at room temperature for 1 h. The solution was then concentrated under reduced pressure to give a compound whose spectral and physical properties were identical to those described above for **11** (96%).

A solution containing 18 mg (0.08 mmol) of α-diazo ketone **10** in 10 mL of CH_2Cl_2 was treated with 2 mg of rhodium(II) caprolactam and allowed to stir at room temperature for 1 h. The solution was then concentrated under reduced pressure to give two compounds whose spectral and physical properties were identical to those described above for **11** (28%) and **12** (36%).

Preparation and Transition Metal Catalyzed Decomposition of 1-Diazo-5-methyl-4-phenyl-5-hexen-2-one (13). To a solution containing 17 mL (8.2 mmol) of 0.5 M potassium bis(trimethylsilyl)amide in 50 mL of THF was added 1.0 mL (7.5 mmol) of phenylacetone in 10 mL of THF dropwise, and the mixture was allowed to stir for 0.75 h at 78 °C. The solution was then treated with 1.9 g (11 mmol) of ethyl 2-bromoacetate, and the mixture was stirred for 3 h, after which 10 mL of water was added at 0 °C. The solution was extracted with 0.5 M KOH, washed with ether, acidified to pH 2, and reextracted with ether. The organic layer was washed with water and brine and dried over Na_2SO_4. The solution was concentrated under reduced pressure to give 1.5 g (91%) of ethyl 4-oxo-3-phenylpentanoate as a clear oil: IR (neat) 1707, 1601, 1290 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.62 (s, 3H), 1.69 (s, 3H), 2.51 (dt, 1H, J = 14.5 and 7.4 Hz), 2.83 (dt, 1H, J = 14.5 and 7.4 Hz), 3.61 (t, 1H, J = 7.4 Hz), 5.11 (t, 1H, J = 7.4 Hz), 7.24–7.44 (m, 5H), 11.83 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 17.7, 25.6, 31.7, 51.8, 120.5, 127.3, 128.0, 128.5, 134.2, 138.2, 180.4.

To a solution containing 4.1 g (11 mmol) of methyltriphenylphosphonium bromide in 75 mL of THF was added 7 mL (11 mmol) of a 1.6 M n-butyllithium solution dropwise at –78 °C. The mixture was allowed to warm to room temperature, and 1.7 g (7.7 mmol) of ethyl 4-oxo-3-phenylpentanoate was added. The solution was then refluxed for 36 h and the reaction quenched with 50 mL of saturated ammonium chloride. The organic layer was washed with water and brine, dried over $MgSO_4$, and concentrated under reduced pressure. Chromatography of the crude oil on silica gel gave 1.0 g (61%) of ethyl 4-methyl-3-phenyl-4-pentenoate as a golden oil: IR (neat) 1737, 1647 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz)

δ 1.17 (t, 3H, J = 7.1 Hz), 1.62 (s, 3H), 2.71 (dd, 1H, J = 15.1 and 7.9 Hz), 2.86 (dd, 1H, J = 15.1 and 8.1 Hz), 3.81 (dd, 1H, J = 8.1 and 7.9 Hz), 4.07 (q, 2H, J = 7.1 Hz), 4.89 (s, 1H), 4.92 (s 1H), 7.18–7.33 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.1, 21.6, 39.3, 48.6, 60.3, 110.4, 126.7, 127.7, 128.4, 142.0, 146.7, 172.1.

To a solution of 0.85 g (3.9 mmol) of ethyl 4-methyl-3-phenyl-4-pentenoate in 20 mL of methanol was added 20 mL of 3.0 M KOH. The reaction mixture was stirred at 60 °C for 8 h, cooled to room temperature, and washed with ether. The aqueous layer was acidified with 5.0 M HCl and washed with ether. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure to yield 0.46 g (62%) of 4-methyl-3-phenyl-4-pentenoic acid as a thick viscous oil: IR (neat) 3082, 2979, 1702, 1492 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.61 (s, 3H), 2.75 (dd, 1H, J = 15.7 and 7.7 Hz), 2.90 (dd, 1H, J = 15.7 and 8.0 Hz), 3.77 (dd, 1H, J = 8.0 and 7.7 Hz), 4.90 (s, 1H), 4.92 (s, 1H), 7.15–7.32 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.7, 39.2, 48.2, 110.7, 126.9, 127.8, 141.8, 146.4, 178.8.

To a solution containing 0.33 g (1.7 mmol) of 4-methyl-3-phenyl-4-pentenoic acid and 0.16 mL (2.1 mmol) of methyl chloroformate in 35 mL of ether was added 0.24 mL (1.7 mmol) of triethylamine. The resulting white suspension was treated as previously described for **1a** with subsequent immediate addition of 20 mmol of freshly prepared diazomethane at 0 °C, and the mixture was then allowed to warm to room temperature overnight. The excess diazomethane was removed under reduced pressure, and the resulting crude oil was chromatography on a silica gel column to give 0.30 g (81%) of 1-diazo-5-methyl-4-phenyl-5-hexen-2-one (**13**) as a bright yellow oil: IR (neat) 2105, 1746, 1640 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.61 (s, 3H), 2.70 (dd, 1H, J = 14.5 and 8.0 Hz), 2.85 (dd, 1H, J = 14.5 and 7.5 Hz), 3.83 (dd, 1H, J = 8.0 and 7.5 Hz), 4.88 (s, 1H), 4.89 (s, 1H), 5.11 (s, 1H), 7.21–7.31 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.8, 45.3, 48.4, 55.2, 110.4, 126.7, 127.7, 128.5, 142.1, 146.7, 193.2.

A solution containing 0.25 g (1.2 mmol) of α-diazo ketone **13** in 30 mL of CH_2Cl_2 was treated with 5 mg of rhodium(II) caprolactamate. The mixture was allowed to stir at room temperature for 30 min and was then concentrated under reduced pressure. Chromatography of the resulting oil on silica gel gave *anti*-1-methyl-2-phenylbicyclo[3.1.0]hexan-4-one (***anti*-14**) (75%) as a clear oil and *syn*-1-methyl-2-phenylbicyclo-[3.1.0]hexan-4-one (***syn*-14**) (25%) as a clear oil. Compound ***anti*-14**: IR (neat) 1726, 1496 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.25 (dd, 1H, J = 9.0 and 5.1 Hz), 1.35 (s, 3H), 1.57 (dd, 1H, J = 5.1 and 3.0 Hz), 1.73 (dd, 1H, J = 9.0 and 3.0 Hz), 2.32 (dd, 1H, J = 17.8 and 10.6 Hz), 2.46 (dd, 1H, J = 17.8 and 8.9 Hz), 3.52 (dd, 1H, J = 10.6 and 8.9 Hz), 7.24–7.38 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 19.3, 20.0, 33.4, 34.9, 40.9, 45.9, 126.9, 127.4, 128.6, 140.3, 212.0; HRMS calcd for $C_{13}H_{14}O$ 186.1045, found 186.1040. Compound ***syn*-14**: IR (neat) 3029, 2970, 1724, 1678 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.95 (s, 3H), 1.19 (ddd, 1H, J = 8.8, 4.5, and 1.2 Hz), 1.29 (dd, 1H, J = 4.5 and 2.5 Hz), 1.84 (dd, 1H, J = 8.8 and 2.5 Hz), 2.14 (d, 1H, J = 18.4 Hz), 2.71 (ddd, 1H, J = 18.4, 8.5, and 1.2 Hz), 3.43 (d, 1H, J = 8.5 Hz), 7.20–7.34 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.9, 21.1, 34.6, 35.2, 42.3, 45.4, 126.7, 127.5, 128.7, 144.1, 214.2; HRMS calcd for $C_{13}H_{14}O$ 186.1045, found 186.1028.

A solution containing 0.25 g (1.2 mmol) of α-diazo ketone **13** in 30 mL of CH_2Cl_2 was treated with 5 mg of rhodium(II) acetate. The mixture was allowed to stir at room temperature for 30 min and was then concentrated under reduced pressure. Chromatography of the resulting oil on silica gel gave three compounds, two whose spectral and physical properties were identical to those described above for ***syn*-14** (25%) and ***anti*-14** (10%) and, additionally, 1,2,4-hexahydro-1-(2-propen-2-yl)-3*H*-azulen-3-one (**15**) (65%), which rearranges on treatment with silica gel to give 1,2,5-hexahydro-1-(2-propenyl)-3*H*-azulen-3-one (**15a**) as a clear liquid: IR (neat) 1701, 1647, 1438 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.55 (s, 3H), 2.33 (dd, 1H, J = 18.0 and 2.0 Hz), 2.71 (dd, 1H, J = 18.0 and 6.9 Hz), 2.74 (d, 2H, J = 6.2 Hz), 3.58 (dd, 1H, J = 6.9 and 2.0 Hz), 4.91 (d, 1H, J = 1.2 Hz), 4.94 (d, 1H, J = 1.2 Hz), 5.35 (dt, 1H, J = 9.8 and 6.2 Hz), 6.15 (dd, 1H, J = 9.8 and 5.7 Hz), 6.56 (dd, 1H, J = 11.1 and 5.7 Hz), 6.76 (d, 1H, J = 11.1 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.2, 29.0, 41.6, 49.6, 114.2, 121.9, 122.2, 128.7, 131.4, 137.5, 143.9, 166.7, 204.6; HRMS calcd for $C_{13}H_{14}O$ 186.1045, found 186.1059.

A solution containing 16 mg (0.07 mmol) of α-diazo ketone **13** in 10 mL of CH_2Cl_2 was treated with 2 mg of rhodium(II) acetate, and the mixture was allowed to stir at room temperature for 1 h. The solution was then concentrated under reduced pressure to give three compounds whose spectral and physical properties were identical to those described above for ***syn*-14** (40%), ***anti*-14** (12%), and **15** (47%).

Preparation and Transition Metal Catalyzed Decomposition of 1-Diazo-5-phenyl-3-(2-methyl-2-propenyl)pentan-2-one (16). Under nitrogen, 49 g (0.30 mol) of 4-phenylbutanoic acid was placed in a 500-mL flask with 12 mL of sulfuric acid and 250 mL of anhydrous methanol, and the mixture was allowed to reflux for 18 h. After cooling, the solution was extracted with 200 mL of CH_2Cl_2 and washed with two portions each of water, saturated sodium bicarbonate, and saturated sodium chloride. The crude solution was concentrated and purified by silica gel chromatography to give 47 g (88%) of methyl 4-phenylbutanoate as a colorless liquid: IR (neat) 2952, 1740, 1455, 1437 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.92 (q, 2H, J = 7.5 Hz), 2.32 (t, 2H, J = 6.0 Hz), 2.64 (t, 2H, J = 7.5 Hz), 7.15–7.30 (m, 5H).

A solution of 1.8 mL (13 mmol) of diisopropylamine in 20 mL of THF was cooled to 0 °C, and 8 mL (13 mmol) of a 1.6 M *n*-butyllithium solution was added. The mixture was cooled to −78 °C, 1.8 g (15 mmol) of methyl 4-phenylbutanoate was added dropwise, and the resulting mixture was allowed to warm to room temperature over a period of 3 h. The reaction mixture was then cooled to −78 °C, and 1.5 mL (15 mmol) of methylallyl iodide was added slowly. The solution was allowed to warm to room temperature and stir for 12 h, and then the reaction was quenched with saturated NH_4Cl. The organic layer was extracted with ether, washed with brine, dried over Na_2SO_4, concentrated under reduced pressure, and purified by flash silica gel chromatography to give 1.0 g (45%) of methyl 2-(2-methyl-2-propenyl)-4-phenylbutanoate as a yellow oil: IR (neat) 1732, 1455, 1164 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.67 (s, 3H), 1.70–1.80 (m, 1H), 1.85–1.99 (m, 1H), 2.17 (dd, 1H, J = 6.6 Hz), 2.37 (dd, 1H, J = 8.2 Hz), 2.60–2.70 (m, 3H), 3.66 (s, 3H), 4.71 (d, 2H, J = 18.0 Hz), 7.15–7.35 (m, 5H).

A solution of 2.3 g (9.9 mmol) of methyl 2-(2-methyl-2-propenyl)-4-phenylbutanoate and 3.1 g (24 mmol) of potassium trimethylsilanolate was allowed to reflux in ether for 12 h. The solution was cooled to room temperature, 1.8 g (24 mmol) of methyl chloroformate was added, and the mixture was again heated to reflux for 4.5 h. The reaction mixture was cooled, filtered, and added to 80 mmol of diazomethane, and the resulting mixture was allowed to stir for an additional 12 h. The crude mixture was concentrated under reduced pressure and purified by flash silica gel chromatography to give 0.78 g (34%) of 1-diazo-5-phenyl-3-(2-methyl-2-propenyl)-pentan-2-one (**16**) as a bright yellow oil: IR (neat) 2103, 1640, 1380 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.65 (s, 3H), 1.65–1.80 (m, 1H), 1.80–2.00 (m, 1H), 2.14 (dd, 1H, J = 14.1 and 6.8 Hz), 2.34 (dd, 1H, J = 14.1 and 7.7 Hz), 2.40–2.80 (m, 3H), 4.68 (s, 1H), 4.76 (s, 1H), 5.20 (br s, 1H), 7.15–7.30 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 22.3, 33.4, 33.6, 40.6, 48.1, 54.9, 112.6, 125.9, 128.3, 128.3, 141.5, 142.4, 197.6.

A solution containing 60 mg (0.25 mmol) of α-diazo ketone **16** in 75 mL of CH_2Cl_2 was treated with 5 mg of rhodium(II) caprolactamate. The mixture was allowed to stir at room temperature for 30 min and was then concentrated under reduced pressure. Chromatography of the resulting oil on silica gel gave 1-methyl-3-(2-phenylethyl)bicyclo[3.1.0]-hexan-4-one (**17**) (61%) as a clear oil: IR (neat) 1725, 1455 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.05–1.11 (m, 2H), 1.32 (s, 3H), 1.40–1.70 (m, 3H), 2.00–2.20 (m, 2H), 2.33 (dd, 1H, J = 12.3 and 7.8 Hz), 2.5–2.8 (m, 2H), 7.1–7.3 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.5, 21.9, 28.2, 31.2, 33.4, 35.2, 36.7, 42.0, 125.8, 128.3, 128.3, 141.5, 215.2. Anal. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found: C, 83.95; H, 8.51.

A solution containing 0.10 g (0.41 mmol) of α-diazo ketone **16** in 50 mL of CH_2Cl_2 was treated with 5 mg of rhodium(II) perfluorobutyrate. The mixture was allowed to stir at room temperature for 30 min and then concentrated under reduced pressure. Chromatography of the resulting crude oil gave a compound whose spectral and physical properties were identical to those described above for compound **17** (28%) and 4-methyl-6-(2-phenylethyl)-2-cyclohexenone (**18**) (11%) as a clear oil: IR (neat) 1676, 1454 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.14 (d, 3H, J = 7.2 Hz), 1.60–2.10 (m, 4H), 2.42 (ddd, 1H, J = 18.8, 6.9, and 5.0 Hz), 2.6–2.8 (m, 3H), 5.88 (dd, 1H, J = 10.1 and 1.9 Hz), 6.73 (dd, 1H, J = 10.1 and 3.3 Hz), 7.1–7.4 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 19.4, 28.1, 31.4, 33.2, 35.0, 43.4, 125.8, 127.5, 128.2, 128.3, 141.6, 154.4, 201.8; HRMS calcd for $C_{15}H_{18}O$ 214.1358, found 214.1358.

A solution containing 0.10 g (0.41 mmol) of α-diazo ketone **16** in 50 mL of CH_2Cl_2 was treated with 5 mg of rhodium(II) acetate, and the mixture was allowed to stir at room temperature for 1 h. The solution was then concentrated under reduced pressure to give two compounds whose spectral and physical properties were identical to those described above for **17** (23%) and **18** (7%).

Preparation and Transition Metal Catalyzed Decomposition of *N*-(*tert*-Butyl-*N*-(2-phenylethyl)diazoacetamide (19). To a solution of *tert*-butylamine (5.5 g, 75 mmol), sodium carbonate (5.25 g, 49.5 mmol), and sodium iodide (0.3 g) in 100 mL of dimethylformamide (DMF) at room temperature was added 1-bromo-2-phenylethane (9.25 g, 50.0 mmol) in 20 mL of DMF during a 20-min period. The reaction mixture was heated to 65 °C, maintained at that temperature, with constant stirring, for 4 h, and then cooled to room temperature and left overnight. After the addition of 100 mL of H_2O, the reaction solution was extracted three times with 100-mL portions of CH_2Cl_2. The combined CH_2Cl_2 extract was washed with 100-mL portions of H_2O and saturated NaCl solution and then dried over anhydrous $MgSO_4$, and the solvent was removed under reduced pressure. The resulting brown oil was distilled (bp 54 °C, 0.25 Torr) to yield 6.20 g of a colorless liquid (35.0 mmol, 70% yield) identified as *tert*-butyl(2-phenylethyl)amine: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.06 (s, 9H), 1.32 (br s, 1H), 2.72–2.85 (m, 4H), 7.15–7.32 (m, 5H) for the amine and δ 1.55 (s, 9H), 3.10–3.17 (m, 2H), 3.44–3.55 (m, 2H), 7.15–7.32 (m, 5H), 9.1 (br s, 2H) for the ammonium salt. Styrene was the major byproduct.

To diketene (5.1 g, 60 mmol) in 5 mL of CH_2Cl_2 was added the freshly prepared amine (6.2 g, 35 mmol) in 50 mL of anhydrous THF over a period of 20 min. The reaction mixture was heated to reflux for 1 h and stirred at room temperature for 12 h, 150 mL of saturated aqueous ammonium chloride was added, and the combined mixture was extracted twice with 70-mL portions of CH_2Cl_2. The CH_2Cl_2 extract was washed with H_2O and saturated NaCl solution and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure to yield 8.84 g of a yellow oil identified as *N*-*tert*-butyl-*N*-(2-phenylethyl)acetoacetamide (33.9 mmol, 97% yield): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.52 (s, 3.0H, enol), 1.53 (s, 6.0H, keto), 1.96 (s, 1.0H, enol), 2.23 (s, 2.0H, keto), 2.79–2.90 (m, 2H), 3.43 (s, 1.4H, keto), 3.42–3.52 (m, 2H), 5.16 (s, 0.3H, enol), 7.15–7.37 (m, 5H).

A solution of methanesulfonyl azide (5.0 g, 41 mmol) in 20 mL of anhydrous CH_3CN was added dropwise through an addition funnel over a 30-min period to the acetoacetamide (8.8 g, 34 mmol) in 20 mL of CH_3CN containing triethylamine (4.15 g, 41 mmol), and the resulting reaction solution was stirred continuously overnight. As the reaction progressed, the solution color turned from light yellow to deep orange. After the addition of 250 mL of H_2O, the mixture was extracted three times with 70-mL portions of 1/1 ether/ethyl acetate, and the organic solution was then washed three times with brine. The solvent was evaporated under reduced pressure after drying the organic solution over anhydrous $MgSO_4$, and the resulting orange oil was purified by column chromatography on silica/alumina using 4/1 hexane/ethyl acetate as the eluent to yield 7.8 g of a deep yellow oil identified as *N*-*tert*-butyl-*N*-(2-phenylethyl)diazoacetoacetamide (**19**) (27 mmol, 78% yield): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.55 (s, 9H), 2.15 (s, 3H), 2.86 (t, J = 7.2 Hz, 2H), 3.61 (t, J = 7.2 Hz, 2H), 7.13–7.34 (m, 5H); IR (neat) 2103 (C=N_2), 1650 (C=O) cm^{-1}. Anal. Calcd for $C_{16}H_{21}N_3O_2$: C, 66.87; H, 7.37; N, 14.62. Found: C, 66.78; H, 7.36; N, 14.58.

To a solution composed of 100 mL of H_2O and 20 mL of CH_3CN and containing $LiOH{\cdot}H_2O$ (1.26 g, 30 mmol) was added the diazoacetoacetamide (2.55 g, 8.9 mmol), and the reaction solution was stirred for 20 h at room temperature. The yellow reaction solution was washed twice with 50-mL portions of CH_2Cl_2, and the combined dichloromethane solution was washed with water and then dried over anhydrous $MgSO_4$. The resulting yellow oil was purified by column chromatography on silica gel using 4/1 hexane/ethyl acetate as the eluent to yield 1.80 g of *N*-*tert*-butyl-*N*-(2-phenylethyl)diazoacetamide (7.4 mmol, 83% yield): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.52 (s, 9H), 2.81–2.87 (m, 2H), 3.28–3.34 (m, 2H), 4.96 (s, 1H), 7.14–7.36 (m, 5H); IR (thin film) 2116 (C=N_2), 1608 (C=O) cm^{-1}. Anal. Calcd for $C_{14}H_{19}N_3O$: C, 68.54; H, 7.81; N, 17.13. Found: C, 68.50; H, 7.86; N, 17.11.

Diazoacetamide **19** (0.245 g, 1.00 mmol) in 5.0 mL of CH_2Cl_2 was added via a syringe pump at a rate of 1.0 mL/h to a stirred solution of $Rh_2(pfb)_4$ (11 mg, 0.010 mmol) in 15 mL of anhydrous CH_2Cl_2 at room temperature under nitrogen. The solvent was removed under reduced pressure (80% yield), and an NMR spectrum was taken to determine the relative product ratio. Chromatographic purification of the mixture which contained the catalyst was accomplished on silica gel, pretreated with 1% triethylamine in hexane to reduce acid-catalyzed reactions of **20**, using 6/1 hexane/ethyl acetate as the eluent. A light brown solid was isolated (0.145 g, 67% yield) and identified as 3-*tert*-butyl-3-azabicyclo[5.4.0]-undeca-6,8,10-trien-2-one (**20**): mp 56–58 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.42 (s, 9H), 2.43–2.59 (m, 3H), 3.33–3.42 (m, 2H), 5.36 (dd, J = 9.2 and 5.2 Hz, 1H), 5.92 (d, J = 5.2 Hz, 1H), 6.13 (dd, J = 9.2 and 4.3 Hz, 1H), 6.42–6.53 (m, 2H); IR (thin film) 1650, 1634, 1612 cm^{-1}. Anal. Calcd for $C_{14}H_{19}NO$: C, 77.38; H, 8.81; N, 6.45. Found: C, 77.21; H, 8.89; N, 6.50.

Diazoacetamide **19** (64 mg, 0.26 mmol) in 10 mL of anhydrous CH_2Cl_2 was added via a syringe pump over a 1.25-h period to a stirred solution of $Rh_2(cap)_4$ (1.9 mg, 0.0026 mmol) in 15 mL of CH_2Cl_2 at room temperature under nitrogen. The solvent was removed under reduced pressure (82% yield), and an NMR spectrum was taken to determine the relative product ratio. Chromatographic purification on silica gel with 6/1 hexane/ethyl acetate as the eluent produced a colorless oil (46 mg, 63% yield) identified as *N*-*tert*-butyl-4-phenyl-2-pyrrolidone (**21**): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.43 (s, 9H), 2.55 (dd, J = 16.7 and 9.0 Hz, 1H), 2.77 (d, J = 16.7 and 9.1 Hz, 1H), 3.39–3.51 (m, 2H), 3.81–3.90 (m, 1H), 7.22–7.37 (m, 5H); IR (thin film) 1680 cm^{-1}; mass spectrum m/e (relative abundance) 218 (M + 1, 1.5), 217 (m, 7.7), 203 (13), 202 (100), 174 (21), 145 (18), 117 (16), 105 (16), 104 (29), 103 (16), 91 (22), 77 (17), 58 (15), 57 (21). Anal. Calcd for $C_{14}H_{19}NO$: C, 77.38; H, 8.81; N, 6.45. Found: C, 77.16; H, 8.85; N, 6.55.

Treatment of diazoacetamide **19** (0.18 g, 0.73 mmol) with 0.5 mg of $Rh_2(OAc)_4$ or $Rh_2(acam)_4$ according to the same procedure produced, after solvent evaporation, two products whose spectral and physical properties were identical to those described above for compounds **20** (58% with $Rh_2(OAc)_4$, 18% with $Rh_2(acam)_4$) and **21** (27% with $Rh_2(OAc)_4$, 62% with $Rh_2(acam)_4$).

Preparation and Transition Metal Catalyzed Decomposition of *N*-*tert*-Butyl-*N*-(2-*p*-anisylethyl)diazoacetamide (22). 2-*p*-Anisylethyl *p*-toluenesulfonate was prepared in 86% yield according to the procedure of Streitwieser. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.43 (s, 3H), 2.88 (t, J = 7.1 Hz, 2H), 3.77 (s, 3H), 4.16 (t, J = 7.1 Hz, 2H), 6.78 (d, J = 8.8 Hz, 2H), 7.02 (d, J = 8.8 Hz, 2H), 7.28 (d, J = 8.3 Hz, 2H), 7.69 (d, J = 8.3 Hz, 2H). To a solution of *tert*-butylamine (4.38 g, 60 mmol), sodium carbonate (3.2 g, 30 mmol), and sodium iodide (0.3 g) in 70 mL of DMF at room temperature was added the *p*-toluenesulfonate ester (9.25 g, 30.2 mmol) in 20 mL of DMF during a 15-min period. The reaction mixture was heated to 65 °C, maintained at that temperature, with constant stirring, for 2 h, and then cooled to room temperature and left for 4 h. After the addition of 200 mL of H_2O, the reaction solution was extracted three times with 60-mL portions of ethyl acetate. The combined ethyl acetate extract was washed with 100 mL of H_2O and twice with 100-mL portions of brine and then dried over anhydrous $MgSO_4$, and the solvent was removed under reduced pressure to afford an oil identified as *tert*-butyl(2-*p*-anisylethyl)amine (6.3 g, 99% yield): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.07 (s, 9H), 2.69–2.84 (m, 4H), 3.79 (s, 3H), 6.84 (d, J = 8.6 Hz, 2H), 7.14 (d, J = 8.6 Hz, 2H).

To a solution of diketene (3.2 g, 38 mmol) in 10 mL of anhydrous THF cooled to 10 °C was added the freshly prepared amine (6.2 g, 30 mmol) in 50 mL of THF over a 30-min period, and the resulting solution was stirred at room temperature for 12 h. Workup according to the procedure for the preparation of **19** afforded 9.1 g of an oil identified as *N*-*tert*-butyl-*N*-(2-*p*-anisylethyl)acetoacetamide (25 mmol, 83% yield): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.51 (s, 3.0H, enol), 1.52 (s, 6.0H, keto), 1.96 (s, 1.0H, enol), 2.23 (s, 2.0H, keto), 2.75–2.82 (m, 2H), 3.43 (s, 1.4H, keto), 3.39–3.46 (m, 2H), 3.79 (s, 2.0H, keto), 3.80 (s, 1.0H, enol), 5.14 (s, 3.0H, enol), 6.83–6.88 (m, 2H), 7.06–7.15 (m, 2H).

N-*tert*-Butyl-*N*-(2-*p*-anisylethyl)diazoacetoacetamide was prepared by the same diazo-transfer procedure described for the synthesis of **19** using 9.1 g of the crude acetoacetamide and then used without prior purification in acetyl cleavage with $LiOH{\cdot}H_2O$ (1.9 g, 45 mmol). Extraction with ether, followed by chromatography on silica gel using 4/1 hexane/ethyl acetate, and recrystallization from ether/hexane afforded 2.5 g of a yellow solid identified as **22** (26% overall yield from reactant alcohol): mp 61 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.51 (s, 9H), 2.75–2.80 (m, 2H), 3.24–3.29 (m, 2H), 2.80 (s, 3H), 4.95 (s, 1H), 6.86 (d, J = 8.6 Hz, 2H), 7.09 (d, J = 8.6 Hz, 2H); IR (thin film) 2112 (C=N_2), 1613 (C=O) cm^{-1}. Anal. Calcd for $C_{15}H_{21}N_3O_2$: C, 65.43; H, 7.69; N, 15.26. Found: C, 65.35; H, 7.75; N, 15.29.

Diazoacetamide **22** (0.250 g, 0.90 mmol) in 5.0 mL of CH_2Cl_2 was added via a syringe pump at a rate of 1.25 mL/h to a stirred solution of $Rh_2(pfb)_4$ (11 mg, 0.010 mmol) in 20 mL of anhydrous CH_2Cl_2 at room temperature under nitrogen. Workup and NMR analysis were performed as described for reactions of **19**. Chromatographic separation employed hexane/ethyl acetate in a gradient from 10/1 to 4/1. A yellow oil (0.180 g, 81% yield) was isolated and identified as 3-*tert*-butyl-9-methoxy-3-azabicyclo[5.4.0]undeca-6,8,10-trien-2-one (**23**): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.48 (s, 9H), 2.45–2.59 (m, 2H), 2.72 (d, J = 4.8 Hz, 1H), 3.37–3.51 (m, 2H), 3.64 (s, 3H), 5.63 (dd, J = 8.9 and 5.7 Hz, 1H), 5.74

(dd, J = 6.6 and 1.7 Hz, 1H), 5.90 (dq, J = 6.6 and 1.2 Hz, 1H), 6.05 (dt, J = 9.9 and 1.7 Hz, 1H); IR (thin film) 1651, 1626, 1602 cm^{-1}. Anal. Calcd for $C_{15}H_{21}NO_2$: C, 72.84; H, 8.56; N, 5.66. Found: C, 72.78; H, 8.47; N, 5.60.

Diazoacetamide **22** (70 mg, 0.25 mmol) in 5.0 mL of anhydrous CH_2Cl_2 was added via a syringe pump at a rate of 0.9 mL/h to a stirred solution of $Rh_2(cap)_4$ (1.9 mg, 0.0026 mmol) in 20 mL of CH_2Cl_2 at room temperature under nitrogen. Workup of the reaction mixture and NMR analysis were performed as previously described. Chromatographic separation was performed with hexane/ethyl acetate as the eluent with a gradient from 4/1 to 3/2. *N-tert*-Butyl-4-*p*-anisyl-2-pyrrolidone (**24**) was isolated as a white solid in 42% yield (93 mg, 0.38 mmol): mp 48–49 °C; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.43 (s, 9H), 2.50 (dd, J = 16.6 and 9.0 Hz, 1H), 2.73 (dd, J = 16.6 and 8.8 Hz, 1H), 3.33–3.46 (m, 2H), 3.77–3.85 (m, 1H), 3.80 (s, 3H), 6.87 (d, J = 8.8 Hz, 2H), 7.16 (d, J = 8.8 Hz, 2H); IR (thin film) 1690 cm^{-1}. Anal. Calcd for $C_{15}H_{21}NO_2$: C, 72.84; H, 8.56; N, 5.66. Found: C, 72.71; H, 8.55; N, 5.61.

Treatment of diazoacetamide **22** (0.260 g, 0.95 mmol) with 5 mg of $Rh_2(OAc)_4$ or $Rh_2(acam)_4$ according to the same procedure produced, after solvent evaporation, two products whose spectral and physical properties were identical to those described above for compounds **23** (68% with $Rh_2(OAc)_4$, 29% with $Rh_2(acam)_4$) and **24** (22% with $Rh_2(OAc)_4$, 51% with $Rh_2(acam)_4$).

Preparation and Transition Metal Catalyzed Decomposition of *N-tert*-Butyl-*N*-(2-(*p*-nitrophenyl)ethyl)diazoacetamide (25). *tert*-Butyl(2-(*p*-nitrophenyl)ethyl)amine was prepared from 4-nitrophenethyl bromide according to the procedure described for the synthesis of **19**, and its reaction with diketene followed the standard procedure to produce *N-tert*-butyl-*N*-(2-(*p*-nitrophenyl)ethyl)acetoacetamide (85% yield): ^1H NMR ($CDCl_3$, 300 MHz) δ 1.51 (s, 3.0H, enol), 1.52 (s, 6.0H, keto), 1.95 (s, 1.0H, enol), 2.27 (s, 2.0H, keto), 2.86–2.99 (m, 2H), 3.40–3.60 (m, 2H), 3.50 (s, 1.4H, keto), 5.10 (s, 0.3H, enol), 7.35 (d, J = 8.6 Hz, 2H), 8.17 (d, J = 8.6 Hz, 2H).

N-tert-Butyl-*N*-(2-(*p*-nitrophenyl)ethyl)diazoacetoacetamide was prepared by diazo transfer from methanesulfonyl azide as previously described for the synthesis of **19** and then used without prior purification in acetyl cleavage with $LiOH{\cdot}H_2O$. Chromatographic purification produced *N-tert*-butyl-*N*-(2-(*p*-nitrophenyl)ethyl)diazoacetamide **25** in 22% overall yield from the reactant bromide: ^1H NMR ($CDCl_3$, 300 MHz) δ 1.52 (d, 9H), 2.94–2.99 (m, 2H), 3.35–3.40 (m, 2H), 2.97 (s, 1H), 7.36 (d, J = 8.6 Hz, 2H), 8.20 (d, J = 8.6 Hz, 2H); IR (thin film) 2117 (C=N_2), 1610 (C=O) cm^{-1}. Anal. Calcd for $C_{14}H_{18}N_4O_3$: C, 57.92; H, 6.25; N, 19.30. Found: C, 58.01; H, 6.30; N, 19.34.

Diazoacetamide **25** (0.260 g, 0.90 mmol) in 5.0 mL of CH_2Cl_2 was added via a syringe pump at a rate of 1.0 mL/h to a stirred solution of $Rh_2(acam)_4$ (4.3 mg, 0.01 mmol) in 20 mL of anhydrous CH_2Cl_2 at room temperature under nitrogen. After addition was complete, the reaction solution was stirred for an additional 12 h and then worked up and analyzed as previously described. NMR analysis showed the absence of the product from aromatic cycloaddition, **26**. GC analysis provided the relative yields of **27** and **28**. Chromatographic separation on silica gel with 1/1 hexane/ethyl acetate allowed the isolation of *N-tert*-butyl-4-(*p*-nitrophenyl)-2-pyrrolidone (**27**): mp 58–59 °C; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.44 (s, 9H), 2.53 (dd, J = 16.7 and 7.8 Hz, 1H), 2.84 (dd, J = 16.7 and 8.9 Hz, 1H), 3.44 (dd, J = 9.6 and 6.6 Hz, 1H), 3.58 (quin, J = 8 Hz, 1H0, 3.92 (dd, J = 9.6 and 7.9 Hz, 1H), 7.41 (d, J = 8.9 Hz, 2H), 8.21 (d, J = 8.9 Hz, 2H); IR (thin film) 1692 (C=O) cm^{-1}; mass spectrum m/e (relative abundance) 263 (M + 1, 1.2), 262 (M, 7.3), 248 (16), 247 (100), 219 (24), 207 (18), 143 (12), 115 (11), 58 (16), 57 (18). Anal. Calcd for $C_{14}H_{18}N_2O_3$: C, 64.10; H, 6.92; N, 10.68. Found: C, 64.14; H, 7.01; N, 10.70.

Diazoacetamide **25** (0.270 g, 0.93 mmol) in 5.0 mL of CH_2Cl_2 was added via a syringe pump at a rate of 1.0 mL/h to a stirred solution of $Rh_2(pfb)_4$ (18 mg, 0.016 mmol) in 25 mL of anhydrous CH_2Cl_2 at room temperture under nitrogen. After addition was complete, the reaction solution was stored in a freezer (–20 °C) for 20 h. Analyses were performed as previously described. Chromatographic separation on silica gel using 6/1 hexane/ethyl acetate as the eluent resulted in the isolation of 16 mg of pure 3-*tert*-butyl-9-nitro-3-azabicyclo[5.4.0]undeca-6,8,-10-trien-2-one (**26**): mp 123–125 °C dec; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.50 (s, 9H), 2.60–2.67 (m, 2H), 2.88 (t, J = 4.3 Hz, 1H), 3.44–3.58 (m, 2H), 5.68 (dd, J = 9.7 and 5.5 Hz, 1H), 6.25 (d, J = 6.7 Hz, 1H), 7.01 (d, J = 9.7 Hz, 1H), 7.93 (d, J = 5.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 168.1, 148,9, 142.6, 129.4, 123.4, 118.7, 116.5, 57.2, 47.5, 41.9, 32.1, 27.4; IR (thin film) 1649 (C=O) cm^{-1}. Anal. Calcd for $C_{14}H_{18}N_2O_3$: C, 64.10; H, 6.92; N, 10.68. Found: C, 64.22; H, 6.87; N, 10.60.

Diazoacetamide **25** (0.260 g, 0.90 mmol) was added to a CH_2Cl_2 solution containing $Rh_2(OAc)_4$ (5 mg, 0.01 mmol) as previously described. After NMR analysis, chromatographic separation of the reaction products on silica gel allowed the separation of **26**, **28**, and **27**, in that order, using 1/1 hexane/ethyl acetate as the eluent. *N-tert*-Butyl-4-(*p*-nitrobenzyl)-2-azetidinone (**28**) (15 mg) was isolated as an orange oil with an azine byproduct, and its structure was inferred by spectroscopic analyses: ^1H NMR ($CDCl_3$, 300 MHz) δ 1.44 (s, 9H), 2.42 (dd, J = 4.6 and 2.3 Hz, 1H), 2.73–2.81 (m, 2H), 3.48 (dd, J = 13.7 and 3.6 Hz, 1H), 3.82–3.90 (m, 1H), 7.34 (d, J = 8.8 Hz, 2H), 8.19 (d, J = 8.8 Hz, 2H); mass spectrum m/e (relative abundance) 247 (M – 15, 10), 205 (41), 163 (13), 126 (77), 115 (16), 84 (45), 70 (31), 57 (100).

Preparation and Transition Metal Catalyzed Decomposition of *N-tert*-Butyl-*N*-benzyldiazoacetamide (29). *tert*-Butylbenzylamine (8.19 g, 50.1 mmol) in 60 mL of anhydrous THF was added dropwise over a 30-min period to an ice bath cooled solution of freshly distilled diketene (4.89 g, 58.2 mmol) in 60 mL of THF. After addition was complete, the reaction solution was warmed to room temperature, and stirring was continued for 12 h. Ether (50 mL) was then added to the orange reaction solution, and this solution was extracted with 50 mL of a saturated NH_4Cl solution that was diluted with 50 mL of water. The yellow aqueous layer was extracted twice with 60-mL portions of ether, and the combined ether extract was washed with 50 mL of a saturated sodium chloride solution and then dried over anhydrous $MgSO_4$. The solvent was evaporated under reduced pressure to yield 12.05 g of a dense orange liquid that was identified as *N-tert*-butyl-*N*-benzylacetoacetamide (>90% pure, 97% yield): ^1H NMR ($CDCl_3$, 300 MHz) δ 1.45 (s, 6.8H, keto), 1.46 (s, 2.2H, enol), 1.84 (s, 0.75H, enol), 2.23 (s, 2.25H, enol), 3.45 (s, 1.5H, keto), 4.58 (s, 2H), 4.96 (s, 0.25H, enol), 7.18–7.42 (m, 5H).

The crude acetoacetamide (11.62 g, 47 mmol) was combined with methanesulfonyl azide (7.01 g, 58 mmol) in 90 mL of anhydrous acetonitrile. Triethylamine (9.7 g, 96 mmol) in 30 mL of acetonitrile was added dropwise to the orange solution over a 30-min period, and the resulting red-brown solution was stirred at room temperature for 40 h. The reaction solution was then poured into 70 mL of water and extracted four times with 50-mL portions of 1/1 ether/ethyl acetate. The combined extracts were washed three times with 50-mL portions of saturated NaCl solution and then dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure to provide 10.5 g of a dense red-brown liquid that was purified by flash chromatography on silica gel with 1/1 hexane/ethyl acetate as the eluent. The first yellow fraction was collected, and the solvent was evaporated to produce 12.7 g of a dark yellow liquid identified as *N-tert*-butyl-*N*-benzyldiazoacetoacetamide (46.5 mmol, 92% yield): ^1H NMR ($CDCl_3$, 300 MHz) δ 1.45 (s, 9H), 2.24 (s, 3H), 4.59 (s, 2H), 7.18–7.35 (m, 5H); IR (neat) 2105 (C=N_2), 1610 (C=O) cm^{-1}.

The diazoacetoacetamide (5.00 g, 18.3 mmol) was dissolved in 35 mL of acetonitrile and 75 mL of water, and $LiOH{\cdot}H_2O$ (2.33 g, 55.5 mmol) was then added to the mixture, causing the solution to turn dark orange. After 5 h of stirring at room temperature, the orange solution was extracted three times with 50-mL portions of 1/1 ethyl acetate/ether. The combined extracts were then washed with 100 mL of saturated NaCl solution and dried over anhydrous $MgSO_4$. Evaporation of the solvent under reduced pressure afforded a bright orange solid that was recrystallized from ether/pentane to give 3.67 g (16.0 mmol, 87% yield) of a yellow solid identified as *N-tert*-butyl-*N*-benzyldiazoacetamide (**29**): mp 96.5–97.5 °C; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.48 (s, 9H), 4.44 (s, 2H), 4.75 (s, 1H), 7.22–7.39 (m, 5H); IR (polyethylene disk) 2100 (C=N_2), 1609 (C=O) cm^{-1}. Anal. Calcd for $C_{13}H_{17}N_3O$: C, 67.51; H, 7.41; N, 18.16. Found: C, 67.57; H, 7.43; N, 18.11.

Diazoacetamide **29** (0.185 g, 0.800 mmol) in 5.0 mL of CH_2Cl_2 was added via a syringe pump at a rate of 0.8 mL/h to a stirred solution of $Rh_2(OAc)_4$ (3.8 mg, 0.008 mmol) in 10 mL of anhydrous CH_2Cl_2 at 25 °C under nitrogen. The solvent was removed under reduced pressure (98% yield), and an NMR spectrum was taken to determine the relative product ratio. The sole product of this reaction was **30**, which was purified by chromatography on silica gel using 4/1 hexane/ethyl acetate as the eluent to yield 0.140 g (0.69 mmol, 86% yield) of a colorless oil that turns green over time, 3-*tert*-butyl-3-azabicyclo[5.3.0]deca-5,7,9-trien-2-one: ^1H NMR ($CDCl_3$, 300 MHz) δ 1.46 (s, 9H), 3.06 (br s, 1H), 4.29 (s, 2H), 5.27 (dd, J = 9.5 and 3.8 Hz, 1H), 6.11–6.19 (m, 2H), 6.40–6.54 (m, 2H). Anal. Calcd for $C_{13}H_{17}NO$: C, 76.81; H, 8.43; N, 6.89. Found: C, 76.75; H, 8.48; N, 6.91.

Diazoacetamide **29** (0.471 g, 2.04 mmol) in 5.0 mL of CH_2Cl_2 was added via a syringe pump at a rate of 0.8 mL/h to a stirred solution of $Rh_2(5S\text{-MEPY})_4$ (18 mg, 0.019 mmol) in 40 mL of anhydrous CH_2Cl_2 at reflux under nitrogen. After addition was complete, the solvent was removed under reduced pressure (96% yield), and an NMR spectrum was taken to determine the relative product ratio (**30**/**31** = 30/70). This mixture was separated by chromatography on silica gel (20 g) in a gradient elution beginning with hexane and increasing fractionally with each 100 mL of solvent to 70/30 hexane/ethyl acetate. Cycloheptatriene **30** (90 mg) eluted with the third 75-mL fraction. The fourth fraction was *N-tert*-butyl-4-phenyl-2-azetidinone (**31**) (250 mg): mp 64.5–65.5 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.24 (s, 9H), 2.67 (dd, J = 14.6 and 2.3 Hz, 1H), 3.23 (dd, J = 14.6 and 5.4 Hz, 1H), 4.57 (dd, J = 5.4 and 2.3 Hz, 1H), 7.42–7.25 (m, 5H); IR (polyethylene disk) 1746 cm^{-1}. Anal. Calcd for $C_{13}H_{17}NO$: C, 76.81; H, 8.43; N, 6.89. Found: C, 76.73; H, 8.39; N, 6.95. Reactions with $Rh_2(cap)_4$ were performed in the same manner. Enantiomeric excesses from reactions with $Rh_2(5S\text{-MEPY})_4$ were obtained by GC with baseline separation on a γ-cyclodextrin trifluoroacetate column.

Transition Metal Catalyzed Decomposition of *N-tert*-Butyl-*N*-(2-phenylethyl)diazoacetoacetamide (37). The diazoacetoacetamide (0.286 g, 1.00 mmol) in 10.0 mL of benzene was added via a syringe pump at a rate of 2.0 mL/h to a stirred solution of $Rh_2(pfb)_4$ (0.013 g, 0.012 mmol) in 20 mL of refluxing benzene. After addition was complete, the solvent was removed under reduced pressure (85% yield), and an NMR spectrum was taken to determine the relative product ratio. The reaction products were separated by column chromatography on silica gel using 5/1 hexane/ethyl acetate as the eluent. The first fraction yielded 0.15 g of a colorless liquid identified as *trans-N-tert*-butyl-3-acetyl-4-phenyl-2-pyrrolidone (**39**): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.42 (s, 9H), 2.40 (s, 3H), 3.41 (dd, J = 9.5 and 6.4 Hz, 1H), 3.69 (d, J = 7.6 Hz, 1H), 3.85 (dd, J = 9.5 and 7.5 Hz, 1H), 3.94 (dt, J = 7.6 and 6.4 Hz, 1H), 7.19–7.36 (m, 5H); IR (thin film) 1720, 1688 cm^{-1}; mass spectrum m/e (relative abundance) 260 (M + 1, 6), 259 (M, 30), 245 (17), 244 (100), 216 (41), 203 (10), 202 (22), 176 (11), 175 (81), 160 (62), 147 (17), 145 (17), 131 (44), 119 (23), 103 (24), 91 (13), 77 (16), 58 (41). Anal. Calcd for $C_{16}H_{21}NO_2$: C, 74.10; H, 8.16; N, 5.40. Found: C, 74.18; H, 8.10; N, 5.32. The second fraction yielded 11 mg of a colorless liquid identified as *trans-N-tert*-butyl-3-acetyl-4-benzyl-2-azetidinone (**38**): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.42 (s, 9H), 2.07 (s, 3H), 2.66 (dd, J = 14.0 and 10.4 Hz, 1H), 3.39 (dd, J = 14.0 and 4.2 Hz, 1H), 3.66 (d, J = 2.2 Hz, 1H), 4.29 (ddd, J = 10.4, 4.2, and 2.2 Hz, 1H), 7.13–7.33 (m, 5H); IR (thin film) 1750, 1712 cm^{-1}; mass spectrum m/e (relative abundance) 259 (M, 0.2), 202 (13), 168 (55), 160 (26), 145 (18), 127 (14), 126 (27), 117 (35), 115 (20), 112 (100), 91 (35), 84 (20), 70 (49), 57 (98). Anal. Calcd for $C_{26}H_{21}NO_2$: C, 74.10; H, 8.16; N, 5.40. Found: C, 74.02; H, 8.23; N, 5.36. Reactions with $Rh_2(OAc)_4$ and $Rh_2(acam)_4$ were performed in the same fashion.

Table III. Parameters Used in Extended Hückel Calculations

orbital	H_{ii}, eV	ζ
Rh 4d	−12.50	4.290, 1.970
Rh 5p	−4.570	2.100
Rh 5s	−8.09	2.350
N 2s	−26.0	1.95
N 2p	−18.6	1.95
O 2s	−32.3	2.275
O 2p	−14.8	2.275
C 2s	−21.40	1.625
C 2p	−11.40	1.625
H 1s	−13.60	1.30

[a] Contraction coefficients used in the double-ζ expansion are c_1 = 0.5807 and c_2 = 0.5685.

Calculations were performed using the Tektronix CAChe System, Version 3.0. Organometallic structures used in all calculations were those obtained by minimization using the Molecular Mechanics packages provided. CAChe uses an augmented version of Allinger's MM2 force field[40] whereby force field parameters are estimated for cases not explicitly addressed by MM2 (*i.e.*, octahedrally disposed nuclei). In these calculations rhodium was given a 2+ charge, *i.e.*, Rh(II), each acetate ligand carried a negative charge, and the carbene carbon had a double bond to rhodium. Molecular orbital calculations was performed using either the extended Hückel[41] or the Zindo methods provided. H_{ii}'s and orbital exponents used in the extended Hückel calculations are listed in Table III.

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