Amine-Directed Alkene Hydrocarboxylation

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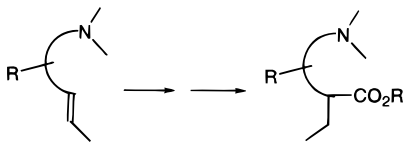
Received March 2, 1998

Homo- and bishomoallylic secondary and tertiary amines react with Rh(I) complexes di-μ-chloro(tetracarbonyl)dirhodium(I) $[(CO)_2RhCl]_2$ (**1**), di-μ-chloro(diethylene)(dicarbonyl)-dirhodium(I) $[(CO)(CH_2CH_2)RhCl]_2$ (**2**), or di-μ-chloro(tetraethylene)dirhodium(I) $[(CH_2CH_2)_2$-$RhCl]_2$ (**11**) to yield bidentate mono- or dimeric complexes. The facial selectivity of binding is influenced by the presence of stereogenic centers on the tether between the alkene and amine. Addition of anhydrous HCl to the complex at −78 °C followed by $P(OMe)_3$ in MeOH yields lactams from secondary amine complexes or amino esters from reaction of the corresponding tertiary amine complexes in a highly stereoselective fashion. Isolation of intermediate Rh(III) alkyls **21**−**23** or Rh(III) acyls **24** or **25** upholds the proposed mechanistic hypothesis. Reaction with a trisubstituted alkenylamine supports the expected syn addition across the alkene and carbonylation with retention of configuration. Reaction of allylic dideutero-substituted bishomoallylamine complex **59** yielded valerolactam **70**. The lack of deuterium scrambling suggested that π-allyl intermediates are not present during hydrometalation and carbonylation.

One of our research goals is the regio- and stereoselective functionalization of unactivated alkenes using transition metals.[1] We have developed a rhodium-promoted alkene hydrometalation/carbonylation sequence[2−5] which occurs with high selectivity (eq 1).[6−9]



(1)

The reaction outcome is aided by an amine which acts as a ligand for rhodium.[10]

The rhodium(I) carbonyl complexes were prepared by the reaction of di-μ-chloro(tetracarbonyl)dirhodium(I) $[(CO)_2RhCl]_2$ (**1**)[11] or di-μ-chloro(diethylene)(dicarbonyl)dirhodium(I) $[(CO)(CH_2CH_2)RhCl]_2$ (**2**)[12] with the corresponding amine in methylene chloride/hexane mixtures at ambient temperature. Representative examples[3] of reactions with secondary olefinic amines and symmetrically substituted tertiary amines are listed in Table 1. Allyl butylamine and 5-pentenyl butylamine

(1) For leading references, see: A. J. Pearson *Metallo-Organic Chemistry*; Wiley: New York, 1985. Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987. Davies, S. G. *Organotransition Metal Chemistry: Applications to Organic Synthesis*; Pergamon: Oxford, 1982. *Advances in Metal-Organic Chemistry*; Liebeskind, L. S., Ed.; JAI Press: Greenwich, CT, 1989. Thompson, D. J. In Comprehensive Organic Synthesis; Pergamon: New York, 1991; Vol. 3, p 1015. Hegedus, L. S. *Transition Metals in the Synthesis of Complex Organic Molecules*; University Science Books: Mill Valley, CA, 1994. *Catalytic Asymmetric Synthesis*; Ojima, I., Ed.; VCH: New York, 1993. Ojima, I.; Clos, N.; Bastos, C. *Tetrahedron* **1989**, *45*, 6901. For leading references to work in the areas of hydrometalations and hydrocarbonylations, see refs 6−9.

(2) Krafft, M. E.; Wilson, L. J.; Onan, K. D. *Tetrahedron Lett.* **1989**, *29*, 6421.

(3) Krafft, M. E.; Wilson, L. J.; Onan, K. D. *Organometallics* **1988**, *7*, 2528.

(4) Krafft, M. E. *Tetrahedron Lett.* **1989**, *30*, 539.

(5) Krafft, M. E.; Yu, X. Y.; Milczanowski, S. E.; Donnelly, K. D. *J. Am. Chem. Soc.* **1992**, *114*, 9215.

(6) For representative examples of rhodium-mediated hydrometalations, see: Anastasiou, D.; Jackson, W. R. *J. Organomet. Chem.* **1991**, *413*, 399. Anastasiou, D.; Campi, E. M.; Chaouk, H.; Jackson, W. R.; McCubbin, Q. J. *Tetrahedron Lett.* **1992**, *33*, 2211. Anastasiou, D.; Chaouk, H.; Jackson, W. R. *Tetrahedron Lett.* **1991**, *32*, 2499. Campi, E. M.; Fallon, G. D.; Jackson, W. R.; Nilson, Y. *Aust. J. Chem.* **1992**, *45*, 1167. Bergman, D. J.; Campi, E. M.; Jackson, W. R.; McCubbin, Q. J.; Patti, A. F. *Tetrahedron Lett.* **1997**, *38*, 4315. Campi, E. M.; Jackson, W. R.; McCubbin, Q. J.; Trnacek, A. E. *J. Organomet. Chem.* **1997**, *539*, 147.

(7) For representative examples of regioselective hydrometalations, see: Alper, H.; Leonard, D. *J. Chem. Soc., Chem. Commun.* **1985**, 511. Knifton, J. F. *J. Organomet. Chem.* **1980**, *188*, 223. Jackson, W. R.; Perlmutter, P.; Sun, G.-H. *J. Chem. Soc., Chem. Commun.* **1987**, 724. Anastasiou, D.; Jackson, W. R. *Tetrahedron Lett.* **1990**, *31*, 4795. Ojima, I.; Korda, A. *Tetrahedron Lett.* **1989**, *30*, 6283. Ojima, I.; Zhang, Z. *Organometallics* **1990**, *9*, 3122. Cuny, G. D.; Buchwald, S. C. *J. Am. Chem. Soc.* **1993**, *115*, 2066. Zhou, J.-Q.; Alper, H. *J. Org. Chem.* **1992**, *57*, 3328. See also: Wang, M. D.; Alper, H. *J. Am. Chem. Soc.* **1992**, *114*, 7018. Alper, H. *Pure Appl. Chem.* **1988**, *60*, 35.

(8) Colquhoun, H. M.; Thompson, D. J.; Twigg, M. V. *Carbonylation*; Plenum: New York, 1991. Wilkinson, G. *Comprehensive Organometallic Chemistry*; Pergamon: Oxford, 1982; Vol. 8.

(9) For representative examples of diastereoselective hydrometalations, see: Burke, S. D.; Cobb, J. E. *Tetrahedron Lett.* **1986**, *27*, 4237. Sakai, K.; Ishiguro, Y.; Funakoshi, K.; Huemane, H. *Tetrahedron Lett.* **1984**, *25*, 961. Zahn, I.; Wagner, B.; Polborn, K.; Beck, W. *J. Organomet. Chem.* **1990**, *394*, 601. Jackson, W. R.; Moffat, M. R.; Perlmutter, P.; Tasdelen, E. E. *Aust. J. Chem.* **1992**, *45*, 823. Zhang, Z.; Ojima, I. *J. Organomet. Chem.* **1993**, *454*, 281.

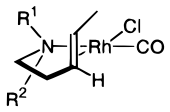
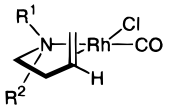
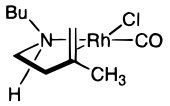
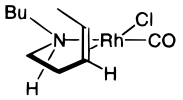
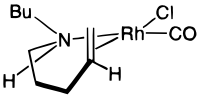
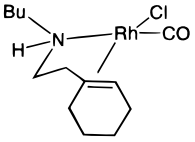
(10) For examples of heteroatom-directed reactions, see: Hoveyda, A. H.; Evans, D. A.; Fu, G. C. *Chem. Rev.* **1993**, *93*, 1307. Eisch, J. J. *J. Organomet. Chem.* **1980**, *200*, 101. Holton, R. A.; Kjonaas, R. A. *J. Am. Chem. Soc.* **1977**, *99*, 4177. Hauser, F. M.; Ellenberger, S. R.; Clardy, J. C.; Bass, L. S. *J. Am. Chem. Soc.* **1984**, *106*, 2458. Johnson, C. R.; Barbachyn, M. R. *J. Am. Chem. Soc.* **1984**, *106*, 2459. Evans, D. A.; Morrissey, M. M.; Dow, R. L. *Tetrahedron Lett.* **1985**, *26*, 6005. Crabtree, R. H.; Davis, M. W. *J. Org. Chem.* **1986**, *51*, 2655 and references therein. Krafft, M. E. *J. Am. Chem. Soc.* **1988**, *110*, 968. Thompson, H. W.; McPherson, E. *J. Org. Chem.* **1977**, *42*, 3350. Tamao, K.; Nakagawa, Y.; Arai, H.; Higuchi, N.; Ito, Y. *J. Am. Chem. Soc.* **1988**, *110*, 3712. Behrens, C. H.; Sharpless, K. B. *Aldrichimica Acta* **1983**, *16*, 67. Park, J.; Pedersen, S. F. *J. Org. Chem.* **1990**, *55*, 5924.

(11) McCleverty, J.; Wilkinson, G. *Inorg. Synth.* **1966**, *8*, 211.

(12) Powell, J.; Shaw, B. *J. Chem. Soc. A.* **1968**, 211.

S0276-7333(98)00145-9 CCC: $15.00
Publication on Web 04/24/1998

Table 1

Rh(I) complex		yield (%)	
	**3**	98	R1=nBu, R2=H
	4	90	R1=Me, R2=Me
	**5**	97	R1=nBu, R2=H
	6	92	R1=Me, R2=Me
	**7**	98	
	**8**	98	
	**9**	98	
	**10**	91	

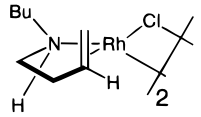
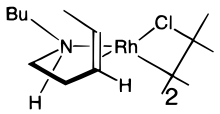
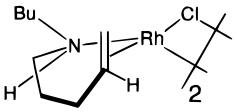
failed to provide the corresponding bidentate complex, yielding only the monodentate amino complex bearing an uncomplexed alkene upon reaction with either Rh(I) complex **1** or **2**.

While the ^{1}H NMR spectrum showed a distinct upfield shift of the alkene protons and a downfield shift of the amino methylene protons, suggesting bidentate coordination, crystallographic analysis of **3** confirmed the bidentate nature of the complex and the orientation of the alkene and the configuration at the nitrogen center.[3] The alkene is approximately perpendicular to the square-planar coordination sphere[13] with equivalent Rh−C distances. The CO ligand is trans to the nitrogen but cis to the alkene. The stereochemistry of the complex presumably accounts for the success of the hydrocarboxylation process. The relative stereochemistry at the metal center for other related Rh(I) carbonyl complexes has been inferred from this crystallographic analysis.

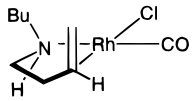
Trisubstituted alkenylamines required the use of Rh(I) complex **2** for efficient complexation, generating, in some cases, only modestly stable complexes.[4] Use of di-μ-chloro(tetraethylene)dirhodium(I) $[(CH_2CH_2)_2RhCl]_2$ (**11**)[14] in place of Rh(I) complexes **1** or **2** yielded Rh(I) dimeric complexes (Table 2), which readily underwent cleavage to monomers using triphenylphosphine or pyridine (vide infra).[3,15]

Two diastereomeric complexes **15** or **16** could arise from the reaction of alkenylamines lacking stereogenic

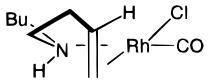
Table 2

Rh(I) complex		yield (%)
	**12**	98
	**13**	97
	**14**	93

centers with Rh(I) complexes **1** or **2**. With secondary amines, **15** is the major or only diastereomer formed. (Throughout this paper, the minor isomers have not been isolated and, thus, their identity has only been inferred from the available data.) Our results (vide infra) suggest that the ligand exchange to generate the bidentate complexes is an equilibrium process and that the resulting complexes are in equilibrium. In complexes made from secondary alkenylamines, the larger amino substituent generally occupies the site cis to the terminus of the alkene, as shown in **15**. The stereo-



15
OBSERVED



16
NOT OBSERVED

chemical assignments were determined from ^{1}H NMR NOE experiments in addition to the crystallographic analysis of **3**. These data suggest that one amine substituent must lie very nearly in the plane of the coordination sphere, thus the preference for the smaller group, hydrogen in this case, to reside in the most sterically encumbered position.

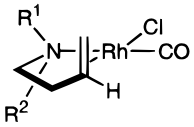
Since steric considerations are thought to be responsible for the observed selectivity in Rh(I) bidentate complex formation, an investigation into the stereochemical outcome of reactions with unsymmetrically substituted tertiary amines was warranted (Table 3). The results from reactions of tertiary amino alkenes seems to support the steric argument with the larger amino substituent preferring to occupy the side of the complex cis to the alkene terminus (i.e., R^1). These complexes appear to be in equilibrium, and the major isomer has been identified and is illustrated in Table 3. However, the stereochemistry of the amine substituents in complex **17** has been assumed based on data from the other complexes, since unambiguous stereochemical assignment was not possible from the available spectral data.

(13) Evans, J. A.; Russell, D. R. *J. Chem. Soc., Chem. Commun.* **1971**, 197. Guggenberger, L. J.; Cramer, R. *J. Am. Chem. Soc.* **1972**, *94*, 3779. Ibers, J. A.; Snyder, R. G. *Acta Crystallogr.* **1962**, *15*, 923. Coetzer, J.; Gafner, G. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1970**, *B26*, 985. Albright, T. A.; Hoffmann, R.; Thibeault, J. C.; Thorn, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 3801.

(14) Cramer, R. *Inorg. Synth.* **1974**, *15*, 14.

(15) For discussions on the mechanism of ligand exchange, see: Atwood, J. D. *Inorganic and Organometallic Reaction Mechanisms* Brooks/Cole: Monterey, CA, 1985. Heck, R. F. *Organotransition Metal Chemistry, A Mechanistic Approach* Academic: New York, 1974 and ref 1.

Table 3



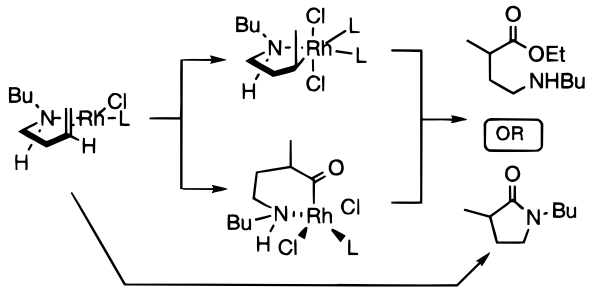
	R^1	R^2	yield (%)[a,b]
17	iPr	nBu	5:1 95
18	nBu	Me	9:1 95
19	CH_2Ph	Me	12:1 88
20	Ph	Me	>95:5 95

[a] The stereochemistry of complexes **18**, **19**, and **20** was determined by ^1H NOE experiments, see Experimental Section. [b] Isolated yield.

The formation of isolable complexes bearing tertiary amino ligands is notable. Secondary nonchelating amines are known to react with **1** to give rise to the corresponding mononuclear dicarbonyl amino Rh(I) complex.[16] However, analogous reactions with nonchelating tertiary amines gave complexes that rapidly decomposed at ambient temperature. Thus, the stabilization promoted by bidentate chelation is clearly illustrated.

With the Rh(I) alkenylamine complexes in hand, the hydrometalation and subsequent carbonylation[1,8] could be investigated in either a stepwise or one-flask operation (Scheme 1). Addition of an ethereal solution of

Scheme 1

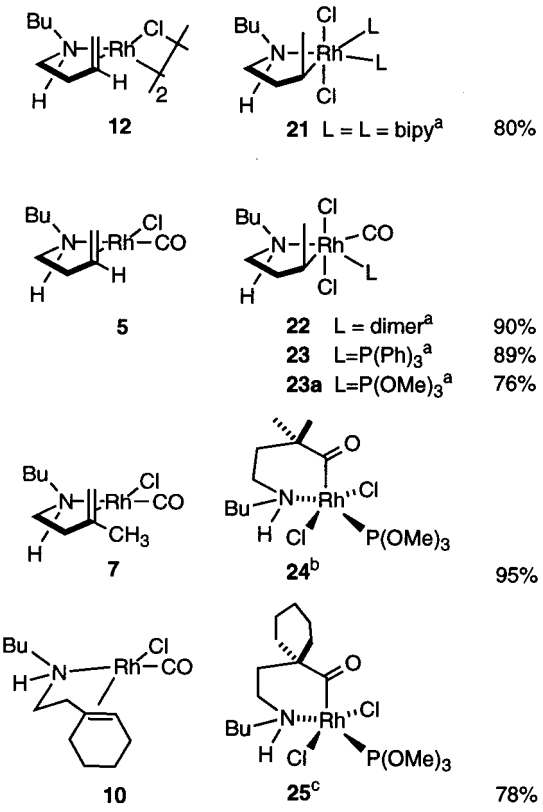


anhydrous HCl to Rh(I) dimeric complex **12** at −78 °C resulted in the formation of Rh(III) complex **21** after addition of bipyridine (Table 4). Substitution of triphenylphosphine for bipyridine led to isolation of the original alkenylamine. These complexes were modestly stable, allowing only spectral characterization, and were successfully isolated only from mono- and some disubstituted alkenes. Reaction of the carbonyl complex **5** with anhydrous HCl in CH_2Cl_2 yielded dimer **22** or, after addition of triphenylphosphine, complex **23**. However, with Rh(I) carbonyl complexes of internally disubstituted or trisubstituted homoallylic amines, i.e., **7** and **10**, stable Rh(III) acyl complexes **24** and **25** were formed,[2] respectively, upon addition of anhydrous HCl at −78 °C. Evidently a tertiary metal−carbon bond is formed but not directly observed as carbonyl insertion immediately occurs.

Attempted carbonylation of **21** or similar compounds under a variety of conditions (high pressure and temperature) failed to yield products of carbonyl insertion but rather led to products resulting from β-elimination.

(16) Maisonnat, A.; Kalck, P.; Poilblanc, R. *Inorg. Chem.* **1974**, *13*, 2996. Vallarino, L. M.; Sheargold, S. W. *Inorg. Chim. Acta* **1979**, *36*, 243.

Table 4



12 — **21** L = L = bipy[a] 80%

5 — **22** L = dimer[a] 90%; **23** L=$P(Ph)_3$[a] 89%; **23a** L=$P(OMe)_3$[a] 76%

7 — **24**[b] 95%

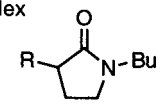
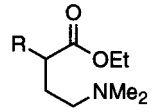
10 — **25**[c] 78%

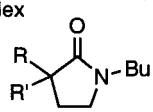
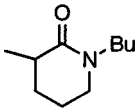
[a] Stereochemistry at the metal center is unknown. [b] Stereochemistry at the metal center determined by X-ray. [c] Stereochemistry at the metal center assigned by analogy to **24**.

From this and other related results, it became apparent that the carbonyl ligand had to be incorporated on the metal center prior to the oxidative-addition step. Reaction of **22**, **23**, or **23a** with excess trimethyl phosphite in methanol at ambient temperature yielded lactam **26**. Acyl complexes **24** and **25** yielded the corresponding lactams **30** and **31**, respectively, under the same conditions. While these carbonylation results were encouraging and demonstrated the intermediacy of the Rh(III) alkyl and acyl complexes, limited success in reactions to generate more substituted Rh(III) alkyls led us to investigate the process without the isolation of intermediates.

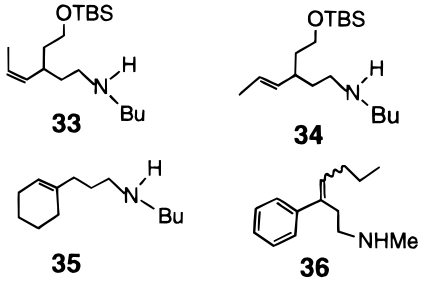
The hydrometalation/carbonylation proceeds very efficiently, in most cases, without the isolation of intermediates (Table 5).[2] The one-flask reaction is carried

Table 5

Rh(I) complex	Lactam		Yield (%)
5, 3, 8		**26** R=Me	86
		27 R=Et	70
		27	62
4, 6		**28** R=Et	40
		29 R=Me	73

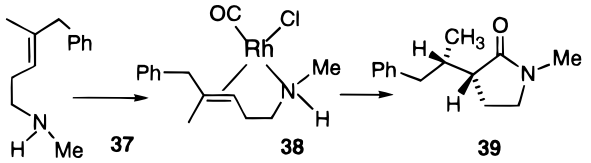
Rh(I) complex	Lactam		Yield (%)
7, 10		**30** R=R'=Me	85
		31 R=R'=$(CH_2)_4$	79
9		**32**	80

out by the addition of an excess of an ethereal solution of anhydrous HCl to a solution of the complex in CH_2Cl_2 at −78 °C. After 1 h at that temperature, 10 equiv of trimethyl phosphite was added and the solution warmed to ambient temperature and stirred for 12 h. Subsequent addition of MeOH and $P(OMe)_3$ followed by stirring for an additional 12 h led to the isolation of the observed lactams. Due to our inability to generate the requisite bidentate Rh(I) alkenylamine complex, seven-membered lactams could not be synthesized via this method. Several alkenylamines **33**−**36** would form Rh(I) bidentate complexes but would not undergo hydrocarbonylation and, instead, yielded the original olefinic amine in addition to other unidentified products.



In general, the overall reaction is highly regioselective, generating the smaller intermediate metallacycle upon alkene insertion into the putative Rh−H bond resulting from oxidative addition of HCl to the Rh(I) complex. The bidentate nature of the intermediate alkyl complex apparently provides stabilization so that β-elimination is not a problem.

The stereochemical outcome of the directed hydrocarboxylation was determined by reaction with trisubstituted alkenylamine **37**. Treatment of **37** with complex **2** yielded Rh(I) complex **38**, which was stable in solution for only a short period of time at ambient temperature, eq 2. Alkene complex **38** was subjected

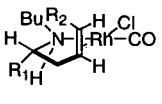
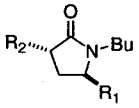
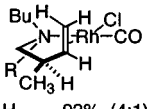
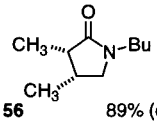
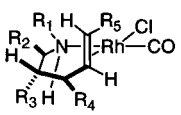
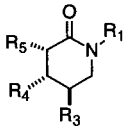
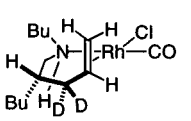
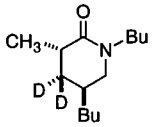
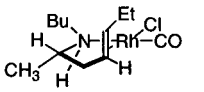
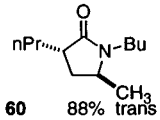
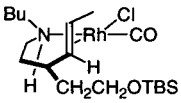
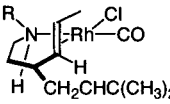
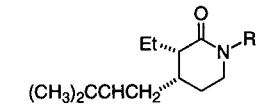


(2)

to the standard hydrocarboxylation conditions and yielded lactam **39** in 49% yield. In the ^{1}H NMR spectrum of the crude reaction mixture, no other lactam isomers were observed. ^{1}H NMR NOE experiments verified the stereochemistry of the lactam which results from the anticipated syn addition[4] across the alkene and retention of configuration during carbonyl insertion.[17]

Having established the stereo- and regioselectivity of the hydrometalation/carbonylation process, we turned our attention to an evaluation of the diastereofacial selectivity of the process as influenced by the existence of stereogenic centers on the tether connecting the alkene and amine. Our investigations show that the amine-directed hydrocarboxylation is a highly stereoselective process as a result of the selectivity in the formation of the Rh(I) bidentate complexes and the syn selectivity of alkene insertion. Both five- and six-membered lactams were formed diastereoselectively by hydrometalation/carbonylation[5] of the corresponding Rh(I) complexes (Table 6). The structure of the major Rh(I) complex, determined by ^{1}H NOE experiments, is depicted in the Table 6. We were never able to obtain the minor isomer in pure form, thus its identity remains unknown. Assignment of the stereochemistry at the Rh center was based on analogy to an X-ray structure of a similar Rh(I) complex.[3] Formation of the cis disubstituted lactam **56** from complex **43a** as the exclusive product suggests that, once formed, the product does not equilibrate under the reaction conditions. The

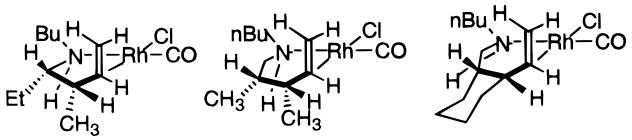
Table 6[b]

Rh(I) complex	lactam (yield)[a]
	
40 R_1=Ph, R_2=H, 86%	**53** R_1=Ph, R_2=CH_3 90% (trans only)
41 R_1=CH_3, R_2=H 85% (14 : 1)	**54** R_1=CH_3, R_2=CH_3 40% (trans only)
42 R_1=CH_3, R_2=Et 95% (8 : 1)	**55** R_1=CH_3, R_2=Pr 86% (+3%cis)
	
43a R=H 92% (4:1)	**56** 89% (cis only)
43b R=Me 87% (8:1)d	
	
44 R_1=Bu, R_2=R_4=R_5=H, R_3=CH_3 90%	**57** R_1=Bu, R_4=H, R_3=R_5=CH_3 (trans only) 90%
45 R_1=Pr, R_2=R_3=H, R_4=Ph, R_5=CH_3 81% (6:1)	**58** R_1=Pr, R_3=H, R_4=Ph, R_5=Et (cis only) 25%
46 R_1=Bu, R_2=CH_3, R_3=R_4=R_5=H 85% (7.5:1)	---[c]
47 R_1=H, R_2=Ph, R_3=R_4=R_5=H 86%	---[c]
	
48 80%	**59** 71% (trans only)
	
49 95%	**60** 88% trans only
	no lactam observed
50 85% (3:1)	
	
51 R=Bu 85% (3:1)	**61** 30% cis only
52 R=Bn 70% (3:1)	**62** 10%

[a] Isolated yields. Reactions run at −78 °C. [b] Ratio determined by ^{1}H NMR. [c] See text for explanation. [d] Hydrocarboxylation not attempted.

(17) Hoffmann, R.; Thorn, D. L. *J. Am. Chem. Soc.* **1978**, *100*, 2079. Hoffmann, R.; Stockis, A. *J. Am. Chem. Soc.* **1980**, *102*, 2952. Rakowsky, M. H.; Woolcock, J. C.; Wright, L. L.; Green, D. B.; Rettig, M. F.; Wing, R. M. *Organometallics* **1987**, *6*, 1211. Doherty, N. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1985**, *107*, 2670. Schunn, R. A. *Inorg. Chem.* **1970**, *9*, 2567. Berke, H.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 7224.

enhanced selectivity in the formation of Rh(I) complex **49** compared to complex **42** might be attributed to the interactions between the cis alkene substituent and the *N*-butyl group. Interestingly, reaction of bishomoallylic amine complexes **44**−**46** yielded only the unexpected butyrolactams if the reaction was performed at 0 °C. Fortunately, bishomoallylic amine complexes **44**, **45**, **48**, **51**, and **52** gave the desired valerolactam upon reaction at −78 °C, albeit in modest yields for three of the examples. Complex **46** failed to give a valerolactam at −78 °C, and reactions with complex **47** were less satisfactory and no lactams were isolated from reactions attempted under a variety of conditions. Surprisingly, Rh(I) complexes **63**, **64**, and **65** failed to yield lactams under these hydrocarboxylation conditions.



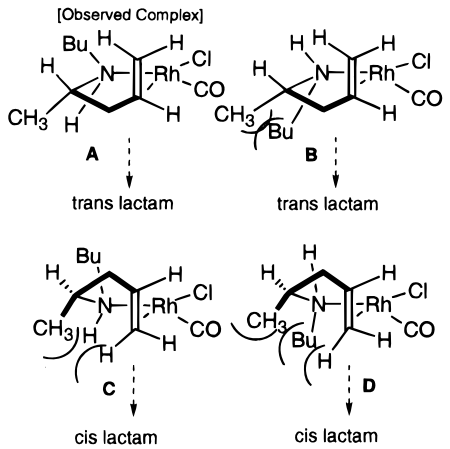
63 90% (only isomer) **64** 86% (12:1) **65** 80%

Rhodium(I) complex **43a** was isolated as a 4:1 mixture of diastereomers from the reaction of the corresponding amino alkene with Rh(I) complex **1**. A 10:1 mixture was obtained after recrystallization from a hexane/CH_2Cl_2 solvent mixture. However, upon standing in $CDCl_3$ overnight, clean conversion to the original 4:1 mixture occurred, strongly supporting the equilibrating nature of the ligand exchange process.

To rule out the possibility that π-allyl intermediates might be present during the hydrometalation, allylic dideuterio-substituted butylamine complex **48** was prepared. Subsequent reaction under the previous conditions gave lactam **59** with no evidence of deuterium scrambling, thus eliminating the intermediacy of π-allyl complexes.

With the possibility of π-allyl intermediates discounted and the evidence for syn insertion, the high diastereoselectivity in the formation of lactams (Table 6) can be attributed to a thermodynamic selectivity in Rh(I) complex formation. For complex **41**, four possible diastereomeric complexes are illustrated in Scheme 2. Steric interactions that may be responsible for the selectivity in complex formation are noted. While the minor isomer has never been identified or isolated in any of the examples in Table 6, its identity may be inferred, at least in the case of the reaction of **43a** which gives an 89% yield of lactam **56** from a 4:1 mixture of Rh(I) complexes. However, even this specific example does not rule out the possibility of equilibration of the Rh(I) complexes prior to hydrometalation, but the rate would be expected to be much slower at −78 °C than at ambient temperature.

Scheme 2



In summary, the amine-directed hydrometalation/carbonylation is a highly regioselective process. It has also been shown to occur in a syn fashion across the alkene. Substituents on the tether influence the π-facial binding in homo- and bishomoallylic amines so that substituted pyrrolidinones and piperidinones are formed with excellent stereoselectivity.

Experimental Section

For a discussion of general experimental details, see ref 3. For full experimental details on the preparation of compounds **3**−**10** and **12**−**14**, Tables 1 and 2, see ref 3. Rh(I) complexes **1**,[11] **2**,[12] and **11**[14] were prepared according to literature procedures. Silica-gel chromatography refers to flash chromatography.[18] Protons were assigned by ^{1}H NOE or decoupling experiments.

Preparation of Rh(I) Complex 1. Prepared as previously described,[11] with the following modifications: the $RhCl_3 \cdot 3H_2O$ was added to the apparatus, and carbon monoxide was passed through the reaction vessel for 30 min at 25 °C, then at 100 °C for 36 h. The water was not wiped out of the vessel as previously reported. The red crystals which collected on the sides of the flask were dissolved in hexane and filtered through Celite with additional hexane. Solvent removal, in vacuo at 25 °C, yielded uniform, brick-red crystals in 70−90% yield.

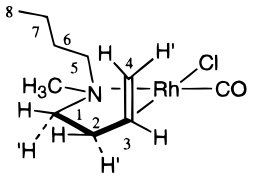
The Rh(I) complexes in Table 3, **17**−**20**, were not stable enough in solution for long periods of time to permit recrystallization and analysis.

[*N*-(3-Butenyl)-*N*-isopropylbutylamine]carbonylrhodium(I) Chloride (17). To a stirred solution of dichlorotetracarbonyldirhodium(I) (39 mg (0.2 mmol) in 5 mL of $CHCl_3$) was added 34 mg (0.20 mmol) of *N*-(3-butenyl)-*N*-isopropylbutylamine. After the mixture was stirred at 25 °C for 20 min, the solvent was removed in vacuo. Filtration through a plug of silica gel (50% EtOAc/hexane), followed by solvent removal in vacuo, gave 64 mg (95%) of complex **17** as a 5:1 mixture of isomers. ^{1}H NMR (500 MHz, C_6D_6): δ 0.58 (d, J = 6.9 Hz, 3H), 0.98 (t, J = 6.9 Hz, 3H), 1.20 (m, 2H), 1.28 (d, J = 6.9 Hz, 3H), 1.40 (m, 2H), 1.48 (m, 1H), 1.86 (ddd, J = 5.5, 12.8, 12.8 Hz, 1H), 2.08 (m, 1H), 2.45 (ddd, J = 5.0, 11.9, 11.9 Hz, 1H), 2.60 (m, 1H), 2.78 (dm, J = 12.8 Hz, 1H), 3.10 (dm, J = 12.8 Hz, 1H), 3.20 (ddm, J = 11.9, 11.9 Hz, 1H), 3.38 (qq, J = 6.9, 6.9 Hz, 1H), 3.90 (m, 1H).

[*N*-(3-Butenyl)-*N*-methylbutylamine]carbonylrhodium(I) Chloride (18). To a stirred solution of dichlorotetracarbonyldirhodium(I) (39 mg (0.2 mmol) in 5 mL of $CHCl_3$) was added 28 mg (0.20 mmol) of *N*-(3-butenyl)-*N*-methylbutylamine. After the mixture was stirred at 25 °C for 20 min, the solvent was removed in vacuo. Filtration through a plug of silica gel (50% EtOAc/hexane), followed by solvent removal in vacuo, gave 58 mg (95%) of complex **18** as a 9:1 mixture of isomers. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.82 (t, J = 7.5 Hz, 3H, CH_2CH_3), 1.30 (qddd, J = 7.5, 7.5, 7.5, 15.0 Hz, 1H, CH_2CHHCH_3), 1.34 (qddd, J = 7.5, 7.5, 7.5, 15.0 Hz, 1H,

(18) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.
(19) Lindlar, H.; Dubois, R. *Org. Synth.* **1966**, *46*, 89.
(20) Okude, Y.; Hirano, S.; Hiyama, T.; Nozaki, H. *J. Am. Chem. Soc.* **1977**, *99*, 3179. Hiyama, T.; Kimura, K.; Nozaki, H. *Tetrahedron Lett.* **1981**, *22*, 1037.

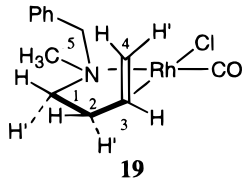
CH_2CHHCH_3), 1.49 (ddddd, J = 7.3, 7.3, 7.3, 7.3, 15 Hz, 1H, $CH_2CHHCH_2CH_3$), 1.86 (dm, J = 15 Hz, 1H, NCH_2CHH-$CH{=}CH_2$), 1.90 (ddddd, J = 7.3, 7.3, 7.3, 7.3, 15 Hz, 1H, CH_2-$CHHCH_2CH_3$), 2.10 (dd, J = 5.0, 12.4 Hz, 1H, $NCHHCHHC$-$H{=}CH_2$), 2.28 (ddd, J = 5.0, 12.4, 12.4 Hz, 1H, CH_3CH_2-CH_2CHHN), 2.51 (dddd, J = 5.5, 5.5, 15, 15 Hz, 1H, CH_2-$CHHCH{=}CH_2$), 2.64 (s, 3H, NCH_3), 2.86 (ddd, J = 4.6, 14.2, 14.2 Hz, 1H, $NCHHCH_2CH{=}CH_2$), 3.02 (ddd, J = 4.1, 12.4, 12.4 Hz, 1H, $NCHHCH_2CH_2CH_3$), 3.42 (dd, J = 1.0, 11.9 Hz, 1H, $CH{=}CHH$), 3.54 (dd, J = 1.0, 7.9 Hz, 1H, $CH{=}CHHH$), 4.53 (m, 1H, $CH_2CH{=}CH_2$).



18

Irradiation	H_1	H_4	H'_6
NOE Observation	H_2, H_4 H_6, H'_1	H_1 H'_4	H_4, H_6, H_7, H_5 H_1, 8-CH_3

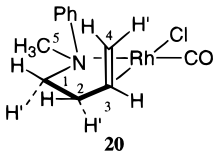
[*N*-(3-Butenyl)-*N*-methylbenzylamine]carbonylrhodium(I) Chloride (19). To a stirred solution of dichlorotetracarbonyldirhodium(I) (39 mg (0.2 mmol) in 5 mL of $CHCl_3$) was added 35 mg (0.20 mmol) of *N*-(3-butenyl)-*N*-methylbenzylamine. After the mixture was stirred at 25 °C for 20 min, the solvent was removed in vacuo. Filtration through a plug of silica gel (50% EtOAc/hexane), followed by solvent removal in vacuo, gave 60 mg (88%) of complex **19** as a 12:1 mixture of isomers. ^{1}H NMR (500 MHz, C_6D_6) δ 0.93 (dd, 2.8, 14.0 Hz, 1H, $CH_2CHHCH{=}CH_2$), 1.00 (dd, J = 5.5, 12.4 Hz, 1H, CH_2-$CHHN$), 1.72 (dddd, J = 5.5, 5.5, 14.0, 14.0 Hz, 1H, CH_2C-$HHCH{=}CH_2$), 1.85 (br d, J = 12.4 Hz, 1H, $CH_2CH{=}CHH$), 2.12 (ddd, J = 5.5, 13.0, 14.0 Hz, 1H, $CHHCH_2CH{=}CH_2$), 2.30 (s, 3H, NCH_3), 2.39 (d, J = 11.0 Hz, 1H, NCH_2Ph), 2.62 (dd, J = 1.4, 8.2 Hz, 1H, $CH{=}CHH$), 3.69 (m, 1H, $CH_2CH{=}CH_2$), 4.80 (d, J = 12.4 Hz, 1H, NCH_2Ph), 7.10 (m, 3H, phenyl protons), 7.68 (m, 2H, phenyl protons).



19

Irradiation	H_1	H_4	Phenyl
NOE Observation	H_4, H_5, H'_1 phenyl protons	H_1, H_5, H'_4 phenyl protons	H_5, H'_5, H_1, H_4

[*N*-(3-Butenyl)-*N*-methylphenylamine]carbonylrhodium(I) Chloride (20). To a stirred solution of dichlorotetracarbonyldirhodium(I) (39 mg (0.2 mmol) in 5 mL of $CHCl_3$) was added 32 mg (0.20 mmol) of *N*-(3-butenyl)-*N*-methylbutylamine. After the mixture was stirred at 25 °C for 20 min, the solvent was removed in vacuo. Filtration through a plug of silica gel (50% EtOAc/hexane), followed by solvent removal in vacuo, gave 60 mg (95%) of complex **20** as one isomer. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.08 (br d, J = 16.5 Hz, 1H, NCH_2-$CHHCH$), 2.74 (m, 2H, $CHHCHHCH{=}CH_2$), 3.02 (m, 1H, $NCHHCH_2CH$), 3.11 (s, 3H, NCH_3), 3.49 (d, J = 17.4 Hz, 1H, $CH{=}CHH$), 3.53 (d, J = 13.0 Hz, 1H, $CH{=}CHH$), 4.64 (m, 1H, $CH_2CH{=}CH_2$), 7.22 (m, 1H, phenyl proton), 7.38 (m, 2H, phenyl protons), 7.62 (m, 2H, phenyl protons).



20

Irradiation	phenyl	5-CH_3
NOE Observation	H_1, H_2, H_4 5-CH_3	H'_1 phenyl protons

Bipyridine Complex 21. To a stirred solution of 53 mg (0.1 mmol) of complex **12** in 4 mL of CH_2Cl_2 at −78 °C was added 0.2 mL of HCl/Et_2O over 5 min. After 1 h, 187 mg (1.2 mmol) of 2,2′-bipyridine dissolved in 1.5 mL of CH_2Cl_2 was added over 10 min while maintaining the temperature at −78 °C. Stirring continued for 12 h, over which time the temperature had warmed from −78 to 20 °C. The mixture was then diluted with CH_2Cl_2, washed twice with 5% aqueous HCl, and dried over Na_2SO_4, and the solvent was removed to give 73 mg (80%) of a yellow solid: mp 171 °C. IR ($CHCl_3$): 3260, 3000, 2900, 1610, 1480, 1450, 1170, 1140, 1060, 970 cm^{-1}. ^{1}H NMR (270 MHz): δ 1.0 (t, 3H, J = 7 Hz), 1.13 (d, 1H, J = 13 Hz), 1.43 (d, 3H, J = 7 Hz), 1.47 (m, 1H), 1.6 (m, 2H), 1.87 (m, 1H), 2.22 (m, 1H), 2.63 (dq, 1H, J = 3.5 Hz, J = 10 Hz), 3.0 (m, 1H), 3.13 (m, 1H), 3.36 (m, 1H), 3.9 (s, 1H), 4.5 (m, 1H), 7.4 (dt, 1H, J = 1.5, 6.5 Hz), 7.62 (m, 1H), 7.83 (dt, 1H, J = 1.5, J = 8 Hz), 7.97 (dt, 1H, J = 1.5, 9 Hz), 8.07 (d, 1H, J = 8 Hz), 8.17 (d, 1H, J = 8 Hz), 9.13 (t, 2H, J = 6 Hz).

Complex 22. To a stirred solution of 92 mg (0.3 mmol) of complex **5** in 5 mL of CH_2Cl_2 at 0 °C was added 0.3 mL of HCl/Et_2O, and stirring was continued for 1 h. Then the solution was diluted with CH_2Cl_2 and dried over Na_2SO_4, and the solvent was removed to give 98 mg (90%) of an orange solid: mp 133 °C. IR ($CHCl_3$): 3020, 2980, 2950, 2900, 2080, 1470, 1380, 1140, 1080 cm^{-1}. ^{1}H NMR (270 MHz): δ 1.0 (t, 3H, J = 7 Hz), 1.28 (d, 3H, J = 6 Hz), 1.5 (m, 4H), 1.75 (m, 2H), 2.83 (m, 1H), 3.15 (m, 2H), 3.45 (m, 1H), 3.78 (s, 1H), 4.5 (s, 1H). MS (NCI): 331 (29, M + 2), 329 (37, M$^+$), 235 (12), 204 (21), 202 (16), 201 (17), 176 (13), 174 (21), 168 (34), 166 (100). Anal. Calcd for $C_9H_{18}Cl_2ONRh$: C, 32.75; H, 5.49. Found: C, 32.55; H, 5.47.

Acyl complexes **24** and **25** were also prepared using the procedure for the preparation of **22**.

Rh(I) Acyl Complex 24.[2,3] Reaction of 154 mg (0.5 mmol) of complex **7** gave 229 mg (98%) of bright yellow crystals: mp 141 °C. IR ($CHCl_3$): 3020, 2980, 2950, 2900, 1730, 1700, 1470, 1180, 1080, 1040, 950, 770 cm^{-1}. ^{1}H NMR (270 MHz): δ 0.93 (t, 3H, J = 7 Hz), 1.3 (s, 6H), 1.43 (m, 1H), 1.67 (m, 3H), 2.0 (t, 1H, J = 10.5 Hz), 2.87 (m, 2H), 3.15 (q, 1H, J = 12 Hz), 3.57 (m, 2H), 3.87 (d, 9H, J = 9 Hz). MS (NCI): 469 (M + 2, 12), 467 (M$^+$, 16), 345 (43), 343 (61), 329 (12), 327 (66), 325 (100). Anal. Calcd for $C_{13}H_{29}Cl_2O_4NPRh$: C, 33.35; H, 6.24. Found: C, 33.25; H, 6.23.

Rh(I) Acyl Complex 25. Reaction of 104 mg (0.3 mmol) of complex **10** gave 120 mg (78%) of a bright yellow solid: mp 140 °C. IR ($CHCl_3$): 3020, 2980, 2950, 2900, 1720, 1470, 1180, 1080, 1040, 950, 770 cm^{-1}. ^{1}H NMR (270 MHz): δ 0.9 (t, 3H, J = 7 Hz), 1.5 (m, 10H), 1.8 (m, 3H), 2.03 (m, 2H), 2.83 (m, 2H), 3.07 (q, 1H, J = 9 Hz), 2.53 (m, 2H), 3.83 (d, 9H, J = 10 Hz). MS (NCI): 509 (M + 2, 6), 507 (M$^+$, 7), 385 (50), 383 (68), 329 (24), 327 (89), 325 (100), 204 (9), 202 (7). Anal. Calcd for $C_{16}H_{33}Cl_2O_4NPRh$: C, 37.81; H, 6.24. Found: C, 37.71; H, 6.50.

Lactam 26. To a stirred solution of complex **5** (294 mg, 1 mmol), in 20 mL of CH_2Cl_2 at −78 °C, was added 1 mL of 4 M

HCl/Et_2O (as described previously for the preparation of **22**) over the course of 5 min. After 1 h at −78 °C, 1.25 g of $P(OMe)_3$ (10.7 mmol) dissolved in 1.5 mL of CH_2Cl_2 was added over a 10 min period. Stirring was continued for 12 h, over which time period the temperature had risen from −78 to 20 °C, and the reaction mixture had changed in color, from a bright intense yellow to a pale yellow color. Then 5 mL of MeOH and 500 mg of $P(OMe)_3$ (4.03 mmol) were added, and stirring at 25 °C was continued for 24 h. At this point the reaction was stopped, and the resulting mixture was taken up in CH_2Cl_2 and washed once with aqueous $NaHCO_3$. The aqueous layer was back-extracted once with CH_2Cl_2, and the combined CH_2Cl_2 portions were washed once with aqueous NaCl and dried over Na_2SO_4. Solvent removal, in vacuo, gave a light yellow oil, which was filtered through a 2 in. plug of silica gel with EtOAc. Solvent removal, followed by flash column chromatography (100% EtOAc), yielded 107 mg (86%) of a clear oil. IR ($CHCl_3$): 3010, 2980, 2950, 2900, 1661, 1500, 1476, 1440, 1300 cm^{-1}. ^1H NMR (270 MHz): δ 0.92 (t, 3H, J = 7 Hz), 1.15 (d, 3H, J = 7 Hz), 1.28 (m, 2H), 1.47 (q, 2H, J = 7.5 Hz), 1.6 (m, 1H), 2.2 (m, 1H), 2.43 (m, 1H), 3.25 (m, 4H). MS (EI): 155 (52, M^+), 140 (9), 126 (12), 113 (56), 112 (100), 98 (9), 84 (71), 56 (12), 55 (17).

Lactam 27. Using 62 mg (0.2 mmol) of complex **3**, 23 mg (67%) of lactam **27** was obtained as a clear oil. IR ($CHCl_3$): 3020, 2980, 2950, 2900, 1661, 1500, 1470, 1440, 1280 cm^{-1}. ^1H NMR (270 MHz): δ 0.90 (t, 3H, J = 7.5 Hz), 0.96 (t, 3H, J = 7.5 Hz), 1.30 (m, 2H), 1.47 (m, 2H), 1.63 (dq, 1H, J = 8 Hz, J = 13 Hz), 1.83 (m, 1H), 2.15 (m, 1H), 2.33 (m, 1H), 3.26 (m, 4H). MS (EI): 169 (32, M^+), 154 (10), 141 (32), 127 (39), 126 (60), 98 (100), 69 (30), 56 (15), 55 (20). Anal. Calcd for $C_{10}H_{19}NO$: C, 70.96; H, 11.31. Found: C, 70.61; H, 11.27.

Lactam 27 from Complex 8. Reaction of 61 mg (0.2 mmol) of complex **8** gave 21 mg (62%) of a clear oil with spectral properties identical to **27** from the previous reaction.

Amino Esters 28 and 29. To a solution of 238 mg (0.9 mmol) of complex **6** in 18 mL of CH_2Cl_2 at −78 °C was added 1.2 mL of HCl/Et_2O over a 5 min period. After 1 h, 470 mg (1.8 mmol) of triphenylphosphine was added in 2 mL of CH_2Cl_2 over 10 min. Stirring was continued over 12 h, during which time the temperature had risen from −78 to 15 °C. Solvent removal gave 948 mg (168%) of a yellow foam, which was a mixture of isomers by ^1H NMR. To a stirred solution of 480 mg (3.6 mmol) of $AlCl_3$ in 5 mL of $CHCl_3$ at 25 °C, under a carbon monoxide atmosphere, the crude product from the previous reaction (948 mg), dissolved in 5 mL of $CHCl_3$, was added. After 3 h of stirring under a carbon monoxide atmosphere, 3 mL of EtOH (100%) was added and stirring continued for an additional 30 min. The mixture was then diluted with CH_2Cl_2 and washed twice with aqueous $NaHCO_3$, and the aqueous layers were back-extracted twice with CH_2Cl_2. The organic layers were combined and dried over Na_2SO_4, and the solvent was removed. The crude product was then taken up in Et_2O and extracted twice with 5% aqueous HCl. The aqueous layers were combined, neutralized with K_2CO_3(s), and extracted with Et_2O 3 times. The organic layers were combined and dried over Na_2SO_4, the solvent was removed, and the resulting oil was Kugelrohr-distilled to give 113 mg (73%) of ester **29** as a clear oil. IR ($CHCl_3$): 3000, 2960, 2880, 2840, 2800, 1720, 1470, 1380, 1270, 1170, 1080 cm^{-1}. ^1H NMR (270 MHz): δ 1.17 (d, 3H, J = 7.5 Hz), 1.26 (t, 3H, J = 7 Hz), 1.57 (m, 1H), 1.85 (m, 1H), 2.23 (s, 6H), 2.28 (m, 2H), 2.5 (m, 1H), 4.13 (q, 2H, J = 7 Hz). MS (EI): 173 (37, M^+), 129 (6), 128 (51), 98 (4), 59 (8), 58 (100), 55 (4), 45 (4).

Following the above procedure, ester **28** was prepared in 40% yield from complex **4**. Flash chromatography with CH_2Cl_2/MeOH/NH_4OH (95:4.5:0.5) gave ethyl ester **28** as a clear oil. IR ($CHCl_3$): 3020, 2980, 2960, 2900, 2840, 2800, 1720, 1470, 1380, 1270, 1150, 1040 cm^{-1}. ^1H NMR (270 MHz): δ 0.9 (t, 3H, J = 7.5 Hz), 1.25 (t, 3H, J = 7 Hz), 1.59 (m, 3H), 1.76 (m, 1H), 2.2 (s, 6H), 2.23 (m, 2H), 2.3 (m, 1H), 4.13 (q, 2H, J = 7.5 Hz). MS (EI): 187 (M^+, 19), 186 (63), 143 (48), 142 (27), 128 (11), 115 (43), 112 (14), 97 (10), 73 (12), 71 (10), 69 (16), 58 (100), 57 (17), 55 (11).

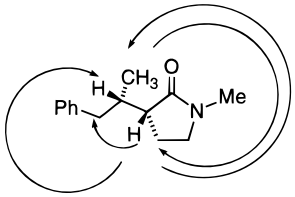
Lactam 30. Complex **7** (61 mg, 0.2 mmol) reacted to give 23 mg (85%) of **30** as a clear oil. IR ($CHCl_3$): 3010, 2980, 2950, 2890, 1661, 1500, 1470, 1450, 1290 cm^{-1}. ^1H NMR (270 MHz): δ 0.93 (t, 3H, J = 7 Hz), 1.15 (s, 6H), 1.3 (m, 2H), 1.5 (dt, 2H, J = 7.5, 7.5 Hz), 1.85 (t, 3H, J = 7 Hz), 3.25 (dt, 4H, J = 2, 7 Hz). MS (EI): 169 (M^+, 40), 154 (11), 140 (13), 127 (55), 126 (100), 112 (12), 98 (26), 70 (10), 56 (15).

Lactam 31. Using 130 mg (0.38 mmol) of complex **10**, 62 mg (79%) of **31** was obtained as a clear oil. IR ($CHCl_3$): 3010, 2980, 2950, 2880, 1661, 1500, 1460, 1440, 1310 cm^{-1}. ^1H NMR (270 MHz): δ 0.93 (t, 3H, J = 7 Hz), 1.31 (m, 6H), 1.5 (m, 2H), 1.68 (m, 6H), 1.90 (t, 2H, J = 7 Hz), 3.25 (m, 4H). MS (EI): 209 (34, M^+), 208 (11), 168 (12), 167 (23), 166 (26), 154 (100), 141 (14), 128 (23), 67 (13), 55 (10). Anal. Calcd for $C_{13}H_{23}NO$: C, 74.59; H, 11.07. Found: C, 74.27; H, 11.04.

Lactam 32. In the reaction with 92 mg of complex **9** (0.3 mmol), 34 mg (66%) of **32** was obtained as a clear oil. IR ($CHCl_3$): 3010, 2980, 2950, 2890, 1615, 1500, 1470, 1300, 1180 cm^{-1}. ^1H NMR (270 MHz): δ 0.93 (t, 3H, J = 7 Hz), 1.25 (d, 3H, J = 7 Hz), 1.33 (m, 2H), 1.53 (m, 2H), 1.83 (m, 4H), 2.36 (m, 1H), 3.26 (m, 2H), 3.33 (dt, 2H, J = 2, 7 Hz). MS (EI): 169 (43, M^+), 154 (8), 140 (27), 127 (40), 126 (42), 114 (14), 113 (18), 112 (33), 98 (100), 85 (10), 72 (11), 69 (21), 56 (17), 55 (13). MS (EI) *m/e* calcd for $C_{10}H_{19}NO$; 169.1469, obsd 169.1472.

Amine 37. ^1H NMR (270 MHz): δ 1.4 (bs, 3H, CCH_3), 2.23 (dt, 2H, J = 7 Hz, 7, $CHCH_2$), 2.4 (s, 3H, NCH_3), 2.6 (t, 2H, J = 7 Hz, CH_2N), 3.3 (bs, 2H, $PhCH_2$), 5.25 (tq, 1H, J = 7, 1 Hz, CH), 7.15−7.3 (m, 5H, aromatic). Irradiation of the signal at δ 2.23 generated an enhancement in the signals at δ 5.25 and 1.4. Irradiation of the signal at δ 5.25 generated an enhancement in the signals at δ 3.3, 2.6, and 2.2. Anal. Calcd for $C_{13}H_{19}N\cdot 0.2H_2O$: C, 80.94; H, 9.93; N, 7.26. Found: C, 80.62; H, 9.79, N, 7.22.

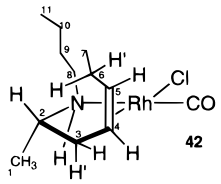
Lactam 39. ^1H NMR (270 MHz, C_6D_6): δ 0.85 (d, 3H, J = 7 Hz, CH_3CH), 1.3 (m, 2H, $CHCH_2CH_2N$), 2.2 (ddd, 1H, J = 4.5, 9, 9 Hz, HCC=O), 2.5, (obscured s, 3H, NCH_3), 2.35−2.65 (m, 5H, $CHCH_2Ph$, CH_2N), 7.1−7.3 (m, 5H, aromatic). Anal. Calcd for $C_{14}H_{19}NO\cdot 0.1H_2O$: C, 76.70; H, 8.74; N, 6.39. Found: C, 76.70; H, 8.81; N, 6.49.



Relevant NOE observations for Lactam **39**

[*N*-(*cis*-2-Hept-4-enyl)-*n*-butylamine]carbonylrhodium-(I) Chloride (42). To a stirred solution of dichlorotetracarbonyldirhodium(I) (39 mg (0.2 mmol) in 5 mL of hexane and CH_2Cl_2 (1:1)) was added 36 mg (0.21 mmol) of *N*-(*cis*-2-hept-4-enyl)butylamine. After the mixture was stirred at 25 °C for 20 min, the solvent was removed in vacuo. Filtration through a plug of silica gel (50% EtOAc/hexane), followed by solvent removal in vacuo, gave 61 mg (95%) of complex **42** as a yellow solid: mp = 118 °C. ^1H NMR (500 MHz): δ 0.92 (t, J = 7.3 Hz, 3H, $NCH_2CH_2CH_2CH_3$), 1.30 ((t, J = 7.3 Hz, 3H, $CHCH_2CH_3$), (ddq obscured, J = 7.3, 7.3, 7.3 Hz, 2H, $NCH_2CH_2CH_2CH_3$)), 1.54 (m, 2H, $NCH_2CH_2CH_2CH_3$), 1.64 (d, J = 6.4 Hz, 3H, CH_3CH), 1.90 (qdd-br peaks, J = 7.3, 7.3, 14.2 Hz, 1H, $CHCHHCH_3$), 2.05 (ddd-br peaks, J = 4.1, 6.9, 14.7

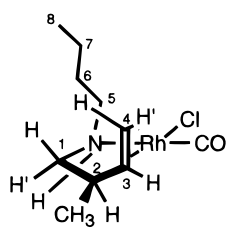
Hz, 1H, CHCH*H*CHN), 2.18 (qdd-br peaks, J = 7.3, 7.3, 14.2 Hz, 1H, CHCH*H*CH$_3$), 2.28 (ddd-br peaks, J = 5.5, 7.3, 14.7 Hz, 1H, CHC*H*HCHN), 2.58 ((dddd, J = 9.6, 6.9, 6.9, <1 Hz, 1H, NCH*H*CH$_2$CH$_2$CH$_3$), (br m obscured, 1H, NH)), 2.70 (dddd, J = 9.6, 6.9, 6.9, <1 Hz, 1H, NC*H*HCH$_2$CH$_2$CH$_3$), 3.33 (br m, 1H, NC*H*CH$_3$), 4.01 (dddd, J = 2.0, 7.3, 7.3, 7.3 Hz, 1H, CH$_3$-CH$_2$C*H*CH), 4.66 (dddd J = 2.5, 6.9, 6.9, 7.3 Hz, 1H, CH$_3$CH$_2$-CHC*H*). IR (cm^{-1}): 1067, 1282, 1450, 1998, 2011, 2863, 2922, 2954, 3239. Anal. Calcd for $C_{12}H_{23}ClNORh$: C, 42.94; H, 6.86. Found C, 42.99; H, 6.70.



42

Irradiation	$_1$CH$_3$	H$_2$	H$_3$
NOE Observation	H$_2$ H$_3$' H$_4$, NH	$_1$CH$_3$, H$_3$, H$_6$ H$_6$', 2H$_9$	H$_2$ H$_3$', H$_4$ H$_6$, H$_6$'
Irradiation	H$_4$	H$_6$	H$_8$
NOE Observation	$_1$CH$_3$ H$_3$', H$_3$ H$_5$	H$_2$ H$_5$, H$_6$' H$_8$	H$_2$, H$_3$ H$_6$, H$_6$' H$_8$'

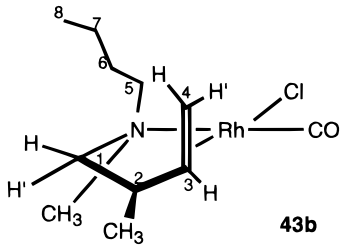
[*N*-(2-Methyl-3-butenyl)-*n*-butylamine]carbonylrhodium(I) Chloride (43a). To a stirred solution of dichlorotetracarbonyldirhodium (39 mg (0.2 mmol) in 5 mL of hexane and CH_2Cl_2 (1:1)) was added 33 mg (0.21 mmol) of *N*-(2-methyl)-3-butenylbutylamine. After the mixture was stirred at 25 °C for 20 min, the solvent was removed in vacuo. Filtration through a plug of silica gel (50% EtOAc/hexane), followed by solvent removal in vacuo, yielded 64 mg (92%) of complex **43a** as a yellow solid (4:1 mixture of isomers): mp 105 °C. The complex was recrystallized to a 10:1 mixture, see text for details. ^{1}H NMR (500 MHz, C_6D_6): δ 0.64 (d, J = 6.9 Hz, 3H, CHC*H*$_3$), 0.78 (t, J = 7.3 Hz, 3H, CH$_2$C*H*$_3$), 1.06 (tq, J = 7.3, 7.3 Hz, 2H, CH$_3$C*H*$_2$CH$_2$), 1.14 (m, 1H, CH$_3$-CH$_2$C*H*HCH$_2$N), 1.27 (m, 1H, CH$_3$CH$_2$C*H*HCH$_2$N), 1.30 (m (obscured), 1H, CHCH*H*N), 2.07 (ddd, J = 5.5, 5.5, 11.5 Hz, 1H, CHCH*H*N), 2.32 (dddd, J = 4.6, 8.7, 10.0, 13.0 Hz, 1H, NC*H*HCH$_2$), 2.51 (ddqd, J = 5.0, 5.0, 6.9, 12.3 Hz, 1H, allylic-H), 2.62 (dd, J = 1.4, 12.8 Hz, 1H, C*H*H=CHCHCH$_3$), 2.69 (dddd, J = 1.8, 6.0, 11.0, 13.0 Hz, 1H, NC*H*HCH$_2$), 2.72 (d, J = 7.8 Hz, 1H, CH*H*=CHCHCH$_3$), 3.43 (m, 1H, NH), 4.25 (dddd, J = 1.0, 4.1, 7.8, 12.8 Hz, 1H, vinyl C*H*CHCH$_3$). IR (cm^{-1}): 1068, 1089, 1457, 2007, 2866, 2922, 2954, 3182, 3431. MS (EI) *m*/*e* 307 (M$^+$), 279, 241, 140, 86. Anal. Calcd for $C_{10}H_{19}ClNORh$: C, 39.04; H, 6.22. Found: C, 39.15; H, 6.12.



43a

Irradiation	H$_1$'	CH$_3$(C-2)	H$_3$ (C$_6$D$_6$)	H$_5$	NH (C$_6$D$_6$)
NOE Observation	CH$_3$(C-2) H$_1$, H$_2$, , NH	H$_1$, H$_1$' H$_2$, H$_3$	H$_2$ CH$_3$(C-2)	H$_1$ H$_4$, H$_5$'	H$_1$', H$_2$ H$_5$, H$_5$'

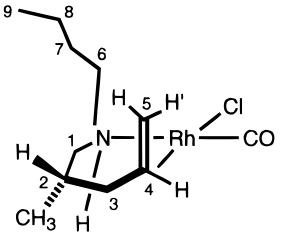
[*N*-(2-Methyl-3-butenyl)-*N*-methyl-*n*-butylamine]carbonylrhodium(I) Chloride (43b). To a stirred solution of dichlorotetracarbonyldirhodium(I) (39 mg (0.2 mmol) in 5 mL of hexane and CH_2Cl_2 (1:1)) was added 33 mg (0.21 mmol) of *N*-(*cis*-2-hept-4-enyl)-*N*-butylamine. After the mixture was stirred at 25 °C for 20 min, the solvent was removed in vacuo. Filtration through a plug of silica gel (50% EtOAc/hexane), followed by solvent removal in vacuo, gave 58 mg (87%) of complex **43b** (8:1 mixture of isomers) as a yellow solid: mp 114 °C. ^{1}H NMR (500 MHz): δ 0.96 (t, J = 7.3 Hz, 3H, CH$_2$C*H*$_3$), 1.24 (d, J = 6.4 Hz, 3H, CHC*H*$_3$), 1.26 (ddt, J = 7.3, 7.3, 7.3 Hz, 1H, CH$_2$C*H*HCH$_3$), 1.36 (ddt, J = 7.3, 7.3, 7.3 Hz, 1H, CH$_2$CH*H*CH$_3$), 1.52 (m, 1H, NCH$_2$C*H*HCH$_2$), 1.95 (m, 1H, NCH$_2$CH*H*CH$_2$), 2.03 (dd, J = 5.0, 11.0 Hz, 1 H, NC*H*HCH), 2.64 (dd, J = 10.0, 12.4 Hz, 1H, NC*H*HCH), 2.64 (s, 3H, NC*H*$_3$), 2.90 (ddd, J = 4.6, 12.4, 16.9 Hz, 1H, NC*H*HCH$_2$), 3.32 (dd, J = 1.8, 7.8 Hz, 1H, CH=C*H*H), 3.37 (dd, J = 1.8, 12.4 Hz, 1H, CH=CH*H*), 4.46 (ddd, J = 6.4, 7.8, 12.4 Hz, 1H, C*H*=CH$_2$). IR (cm $^{-1}$): 645, 1226, 1462, 1999, 2019, 2817, 2866, 2924, 2957, 3051, 3461. MS (EI): *m*/*e* 320 (M$^+$), 293, 255, 254, 100. ^{13}C NMR (75 MHz): δ 13.6, 17.9, 20.1, 27.2, 35.0, 47.1, 49.8 (d, J = 15.0 Hz, alkene), 59.0, 60.6, 80.3 (d, J = 7.5 Hz, alkene), 183.2 (d, J = 67.5 Hz, carbonyl).



43b

Irradiation	N-CH$_3$ (C$_6$D$_6$)	H$_2$ (C$_6$D$_6$)
NOE Observation	H$_2$ H$_5$, H$_5$'	H$_1$', H$_3$, N-CH$_3$ CH$_3$(C-2)
Irradiation	H$_3$	CH$_3$(C-2) (C$_6$D$_6$)
NOE Observation	H$_2$, H$_4$' CH$_3$(C-2)	H$_1$, H$_2$ H$_3$, H$_4$

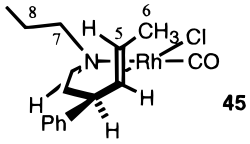
[*N*-(2-Methyl-4-pentenyl)-*n*-butylamine]carbonylrhodium(I) Chloride (44). To a stirred solution of dichlorotetracarbonyldirhodium(I) (39 mg, 0.2 mmol) in 5 mL of hexane and CH_2Cl_2 (4:1) was added 33 mg (0.21 mmol) of *N*-(2-methyl)-4-pentenylbutylamine. After the mixture was stirred at 25 °C for 25 min, the solvent was removed in vacuo. Filtration through a plug of silica gel (50% EtOAc/hexane), followed by solvent removal in vacuo, yielded 59 mg (85%) of complex **44** as a dark yellow oil. ^{1}H NMR (500 MHz): δ 0.90 (d, J = 6.4 Hz, 3H, CHC*H*$_3$), 0.97 (t, J = 7.3 Hz, 3H, CH$_2$C*H*$_3$), 1.39 (tq, J = 7.3, 7.3 Hz, 1H, CH$_2$C*H*HCH$_3$), 1.40 (tq, J = 7.3, 7.3 Hz, 1H, CH$_2$C*H*HCH$_3$), 1.7 (m, 1H, NCH$_2$C*H*HCH$_2$), 1.83 (dqdd, J = 4.6, 6.4, 11.5, 12.6 Hz, 1H, C*H*CH$_3$), 1.95 (m, 1H, NCH$_2$-CH*H*CH$_2$), 2.05 (ddd, J = 3.7, 11.5, 17.4 Hz. 1H, CHC*H*HCH), 2.18 (d, J = 17.4 Hz, 1H, CHC*H*HCH), 2.35 (dddd, J = 1.4, 5.5, 10.5, 11.4 Hz, 1H, NC*H*HCH$_2$), 2.42 (ddd, J = 1.0, 12.8, 12.8 Hz, 1H, CHCH*H*NCH$_2$), 2.46 (ddd, J = 4.6, 12.8, 12.8 Hz, 1H, CHCH*H*NCH), 2.91 (dddd, J = 5.5, 10.1, 11.0, 11.4 Hz, 1H, NC*H*HCH$_2$), 3.03 (dd, J = 1.8, 13.3 Hz, 1H, CH$_2$-CH=C*H*H), 3.23 (m, 1H, NH), 3.40 (dd, J = 1.8, 8.2 Hz, 1H, CH$_2$CH=C*H*H), 4.64 (m, 1H, CH$_2$=C*H*CH$_2$CH). IR (cm^{-1}): 1058, 1277, 1452, 1998, 2022, 2867, 2924, 2954, 3055, 3222. ^{13}C NMR (75 MHz): δ 13.5, 20.0, 20.2, 23.7, 31.4, 39.7, 48.4 (d, J = 12.6, alkene), 50.4, 58.3, 72.8 (d, J = 13.7 Hz, alkene), 184.4 (d, J = 69.9 Hz, carbonyl). Modest instability precluded rigorous purification for elemental analysis.



44

Irradiation	H_5	H_2
NOE Observation	H_6, H_2, H_5'	CH_3(C-2), H_5 H_6, $H_{3\beta}$, $H_{1\beta}$

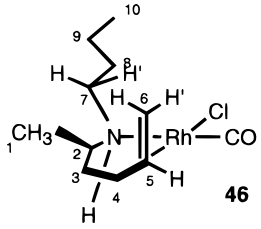
[*N*-(3-Phenyl-4-*trans*-hexenyl)-*n*-propylamine]carbonylrhodium(I) Chloride (45). To a stirred solution of dichlorotetracarbonyldirhodium(I) (39 mg, 0.2 mmol) in 5 mL of $CHCl_3$ was added 43 mg (0.2 mmol) of *N*-(3-phenyl-4-*trans*-hexenyl)propylamine. After the mixture was refluxed at 65 °C for 3 h, the solvent was removed in vacuo. Filtration through a plug of silica gel (50% EtOAc/hexane), followed by solvent removal in vacuo, gave 62 mg (81%) of complex **45** (6:1 mixture of isomers) as a dark yellow oil. Major isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.05 (t, 3H, J = 7.3 Hz, $CH_2CH_2CH_3$), 1.6 (m, 1H, NCH_2CHHCHPh), 1.73 (dd, 3H, J = 2.1, 5.9 Hz, CH_3CHCH), 1.83 (m, 2H, NCH_2CHHCH$_3$, NCH_2CHHCHPh), 2.04 (m, 1H, NCH_2CHHCH$_3$), 2.37 (dddd, 1H, J = 1.0, 5.5, 12.0, 15.1 Hz, NCHHCH$_2$CH$_3$), 2.68 (d-very br peaks, 1H, J = 13.3 Hz, NCHHCH$_2$CH), 2.96 (m, 2H, NCHHCH$_2$CH$_3$, NCHHCH$_2$CH), 3.32 (m, 1H, NH), 3.65 (ddd, 1H, J = 2.1, 2.7, 12.3 Hz, CHPh), 4.02 (dqd, 1H, J = 2.7, 5.9, 12.3 Hz, CH_3CHCH), 4.2 (d-very br peaks, J = 12.3 Hz, 1H, CH_3-CHCHCH), 7.1−7.3 (m, 5H, aromatic); IR (cm^{-1}) 699, 1044, 1255, 1443, 1485, 1591, 1999, 2017, 2867, 2922, 2954, 3017, 3222; ^{13}C NMR (75 MHz) δ 11.5, 22.4, 24.3, 27.8, 48.9, 51.0, 51.9, 66.4 (J = 13.7, alkene), 74.2 (J = 13.7 Hz, alkene), 127.0, 127.2, 128.8, 128.9, 129.1, 144.8, 184.5 (J = 70.6 Hz, carbonyl). Modest instability precluded rigorous purification for elemental analysis.



45

Irradiation	H_5
NOE Observation	H_7, H_8, 6-CH_3, phenyl protons

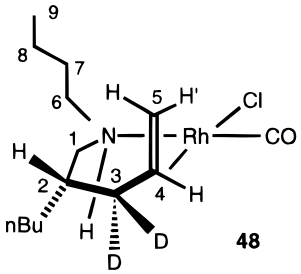
[*N*-(2-Hex-5-enyl)-*n*-butylamine]carbonylrhodium(I) Chloride (46). To a stirred solution of dichlorotetracarbonyldirhodium(I) (39 mg (0.2 mmol) in 5 mL of hexane and CH_2Cl_2 (1:1)) was added 36 mg (0.21 mmol) of *N*-(2-hex-5-enyl)butylamine. After the mixture was stirred at 25 °C for 20 min, the solvent was removed in vacuo. Filtration through a plug of silica gel (50% EtOAc/hexane), followed by solvent removal in vacuo, yielded 59 mg (85%) of complex **46** (7.5:1 mixture of isomers) as a dark yellow oil. Major isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.95 (t, J = 7.3 Hz, 3H, CH_2CH_3), 1.34 (d, J = 6.9 Hz, 3H, $CHCH_3$), 1.36 (ddq, J = 7.3, 7.3, 7.3 Hz, 2H, $CH_2CH_2CH_3$), 1.65 (ddddd, J = 5.0, 7.3, 7.3, 10.0, 12.8 Hz, 1H, NCH_2CHHCH$_2$), 1.85 (dddd, J = 3.0, 3.0, 13, 13 Hz, 1H, CH_3CHNCHHCH$_2$CHCH$_2$), 1.9 (dddd, J = 1.0, 1.9, 13, 13 Hz, 1H, CH_3CHNCHHCH$_2$CHCH$_2$), 1.96 (ddddd, J = 5.0, 7.3, 7.3, 10.0, 12.8 Hz, 1H, NCH_2CHHCH$_2$), 2.38−2.48 (m, 3H, allylic CH_2, NCHHCH$_2$), 2.75 (dddq, J = 1.0, 3.0, 3.6, 6.9 Hz, 1H, NCHCH$_3$), 2.85 (m, 1H, NH), 2.91 (dddd, J = 1.0, 5.0, 10.0, 10.0 Hz, 1H, NCHHCH$_2$), 3.10 (dd, J = 1.4, 13.3 Hz, 1H, CH=CHH), 3.40 (dd, J = 1.4, 8.2 Hz, 1H, CH=CHH), 4.6 (dddd, J = 2.3, 4.5, 8.2, 13.3 Hz, 1H, CH_2=CHCH$_2$); IR (cm^{-1}) 1061, 1254, 1452, 1999, 2019, 2866, 2926, 2955, 3215. Modest instability precluded rigorous purification for elemental analysis.



46

Irradiation	H_6	H_7 (C_6D_6)	H_2
NOE Observation	H_6', H_7', $H_{3\beta}$	H_6, H_7, $_1CH_3$	$_1CH_3$, H_3, $H_{4\alpha}$,

[*N*-(2-Butyl-3,3-dideuterio-4-pentenyl)-*n*-butylamine]carbonylrhodium(I) Chloride (48). To a stirred solution of dichlorotetracarbonyldirhodium(I) (39 mg (0.2 mmol) in 5 mL of hexane and CH_2Cl_2 (4:1)) was added 42 mg (0.21 mmol) of *N*-(2-butyl-3,3-dideuterio)-4-pentenylbutylamine. After the mixture was stirred at 25 °C for 25 min, the solvent was removed in vacuo. Filtration through a plug of silica gel (50% EtOAc/hexane), followed by solvent removal in vacuo, yielded 59 mg (80%) of complex **48** as a dark yellow oil. ^{1}H NMR (500 MHz): δ 0.90 (t, J = 6.9 Hz, 3H, CH_2CH_3), 0.96 (t, J = 7.3 Hz, 3H, CH_2CH_3), 1.2, 1.3 (m, 6H, $CHCH_2CH_2CH_2CH_3$), 1.40 (ddq, J = 7.3, 7.3, 7.3 Hz, 2H, $NCH_2CH_2CH_2CH_3$), 1.60 (m, 1H, 2-H), 1.70 (ddddd, J = 5.5, 7.3, 7.3, 12.5, 12.5 Hz, 1H, NCH_2-CHHCH$_2$), 1.96 (ddddd, J = 5.5, 7.3, 7.3, 10.5, 12.5 Hz, 1H, NCH_2CHHCH$_2$), 2.32 (dddd, J = 5.5, 5.5, 10.5, 10.5 Hz, 1H, HNCHHCH$_2$), 2.48 (m, 2H, $CHCH_2$NH), 2.90 (dddd, J = 5.5, 5.5, 10.5, 12.5 Hz, 1H, NCHHCH$_2$), 3.02 (dd, J = 2.3, 13.7 Hz, 1H, CD_2CH=CHH), 3.28 (m, 1H, NH), 3.38 (dd, J = 2.3, 8.2 Hz, 1H, CD_2CH=CHH), 4.65 (ddd, J = 2.8, 8.2, 13.7 Hz, 1H, CH_2=CHCD$_2$). IR (cm^{-1}): 764, 1042, 1220, 1242, 1458, 1652, 1718, 2025, 2950, 3009, 3219.

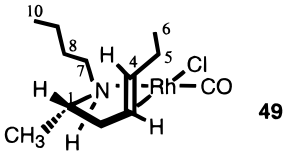


48

Irradiation	H_5	H_6
NOE Observation	H_2, H_5', H_6	H_2, H_6' H_5, H_7

[*N*-(*trans*-2-Hept-4-enyl)-*n*-butylamine]carbonylrhodium(I) Chloride (49). To a stirred solution of dichlorotetracarbonyldirhodium(I) (39 mg (0.2 mmol) in 5 mL of hexane and CH_2Cl_2 (1:1)) was added 36 mg (0.21 mmol) of *N*-(*trans*-

2-hept-4-enyl)-*n*-butylamine. After the mixture was stirred at 25 °C for 20 min, the solvent was removed in vacuo. Filtration through a plug of silica gel (50% EtOAc/hexane), followed by solvent removal in vacuo, gave 64 mg (95%) of complex **49** as a yellow solid: mp 108 °C. ^{1}H NMR (500 MHz): δ 0.68 (d, J = 7.3 Hz, 3H, CHCH_3), 0.89 (t, J = 7.3 Hz, 3H, $CH_2CH_2CH_3$), 1.12 (t, J = 7.3 Hz, 3H, $CHCH_2CH_3$), 1.15 (m, 1H, CH_2-CH_2CHHCH_3), 1.29 (m, 2H, $CH_2CHHCHHCH_3$), 1.45 (d, J = 15.1 Hz, 1H, CHC*H*HCH), 1.55 (dqdd, J = 1.8, 7.3, 7.3 13.7 Hz, 1H, CH=CHCH*H*CH_3), 1.65 (qdd, J = 7.3, 6.3, 13.7 Hz, CHC*H*HCH_3), 1.83 (m, 1H, C*H*HCH_2CH_3), 2.00 (m, 1H, NHC*H*CH_2CH_3), 2.08 (ddd, J = 3.7, 12.4, 12.4 Hz, 1H, C*H*CHHCH=CH), 2.25 (dddd, J = 0.9, 1.4, 11.4, 11.4 Hz, 1H, NHC*H*$HCH_2CH_2CH_3$), 2.99 (m, 1H, N*H*), 3.15 (dddd, J = 5.5, 5.5, 10.5, 11.4 Hz, 1H, NHCH*H*$CH_2CH_2CH_3$), 3.57 (dddd, J = 2.3, 7.3, 7.3, 12.8 Hz, 1H, CH_2CH=C*H*CH_2CH_3), 3.87 (ddd, J = 3.7, 7.3, 12.8 Hz, 1H, C*H*=$CHCH_2CH_3$). IR (cm^{-1}): 707, 1008, 1377, 1455, 1554, 1634, 2009, 2866, 2923, 2956, 3146. ^{13}C NMR (75 MHz): δ 13.4, 15.4, 17.1, 20.3, 30.6, 31.0, 40.3, 47.2, 48.5, 74.5 (J = 13.7 Hz), 77.0 (J = 11.4 Hz), 185.0 (J = 71.7 Hz). Anal. Calcd for $C_{12}H_{23}ClNORh$: C, 42.94; H, 6.90. Found: C, 43.04; H, 6.96.



49

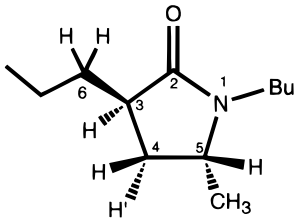
Irradiation	H_4	H_8
NOE Observation	H_1, H_8 H_5, H_5', 6-CH_3	H_4 H_8, H_5, 10-CH_3

[*N*-*trans*-3-(2-*tert*-Butyldimethylsilyloxylethyl)-4-hexenyl-*n*-butylamine]carbonylrhodium(I) Chloride (50). To a stirred solution of dichlorotetracarbonyldirhodium(I) (39 mg (0.2 mmol) in 5 mL of $CHCl_3$) was added 65 mg (0.20 mmol) of *N*-*trans*-3-(2-*tert*-butyldimethylsilyloxyethyl)-4-hexenyl-*n*-butylamine. After the mixture was stirred at 65 °C for 24 h, the solvent was removed in vacuo. Filtration through a plug of silica gel (50% EtOAc/hexane), followed by solvent removal in vacuo, gave 82 mg (85%) of complex **50** (2.8:1 mixture of isomers). IR (cm^{-1}): 650, 760, 891, 1212, 1464, 1515, 1999, 2018, 2851, 2922, 2950, 3011, 3225.

[*N*-(3-*trans*-1-Propenyl)-6-methyl-5-heptenyl-*n*-butylamine]carbonylrhodium(I) Chloride (51). To a stirred solution of dichlorotetracarbonyldirhodium(I) 39 mg (0.2 mmol) in 5 mL of $CHCl_3$ was added 45 mg (0.21 mmol) of *N*-(3-*trans*-1-propenyl)-6-methyl-5-heptenyl-*n*-butylamine. After the mixture was stirred at 65 °C for 24 h, the solvent was removed in vacuo. Filtration through a plug of silica gel (50% EtOAc/hexane), followed by solvent removal in vacuo, gave 66 mg (85%) of complex **51** as a 3:1 mixture of isomers. Major isomer from the ^{1}H NMR spectrum of the mixture of isomers: ^{1}H NMR (500 MHz) δ 0.96 (t, J = 7.3 Hz, 3H, CH_2CH_3), 1.42 (m, 4H, C*H*HCH_2CH_3, CHC*H*HCH_2N), 1.58 (s, 3H, CH=CCH_3-CH_3), 1.66 (dd, J = 1.4, 5.5 Hz, 3H, CH=$CHCH_3$), 1.70 (s, 3H, CH=CCH_3CH_3), 1.70 (m, 1H, CHC*H*HCH_2N), 1.95 (m, 1H, C*H*HCH_2CH_3), 2.07 (ddd, J = 6.9, 6.9, 12.8 Hz, 1H, CHC*H*-HC=CCH_3CH_3), 2.18 (ddd, J = 5.5, 6.9, 12.8 Hz, 1H, CHCH*H*CH=CCH_3CH_3), 2.30 (m, 1H, NC*H*$HCH_2CH_2CH_3$), 2.40 (m, 1H, C*H*CH=CH_3), 2.57 (dd, J = 1.4, 12.8 Hz, 1H, $CHCH_2CH$HNH), 2.75 (dddd, J = 2.3, 4.6, 11.4, 12.8 Hz, 1H, $CHCH_2CH$*H*NH), 2.88 (m, 1H, NC*H*$HCH_2CH_2CH_3$), 3.18 (m, 1H, N*H*), 3.74 (dqd, J = 1.8, 5.5, 12.7 Hz, 1H, CHCH=C*H*-CH_3), 4.16 (d, J = 12.7 Hz, 1H, C*H*=$CHCH_3$), 5.10 (qdd, J = 1.4, 7.7, 7.7 Hz, 1H, CH_3CH_3C=C*H*CH_2); IR (cm^{-1}) 667, 1043, 1212, 1441, 1517, 1721, 1998, 2010, 2924, 2956, 3011, 3225.

[*N*-((3-*trans*-1-Propenyl)-6-methyl-5-heptenyl)benzylamine]carbonylrhodium(I) Chloride (52). To a stirred solution of dichlorotetracarbonyldirhodium(I) (39 mg (0.2 mmol) in 5 mL of $CHCl_3$) was added 51 mg (0.20 mmol) of *N*-(3-*trans*-1-propenyl)-6-methyl-5-heptenyl-*n*-benzylamine. After the mixture was stirred at 65 °C for 24 h, the solvent was removed in vacuo. Filtration through a plug of silica gel (50% EtOAc/hexane), followed by solvent removal in vacuo, gave 60 mg (70%) of complex **52** (3.2:1 mixture of isomers).

1-Butyl-3-propyl-5-methyl-2-pyrrolidinone (55). To a stirred solution of 133 mg (0.37 mmol) of Rh(I) complex **42** in 10 mL of CH_2Cl_2 at −78 °C was added 0.35 mL (2.6 mmol) of a 7.5 M solution of HCl in Et_2O over 5 min. After 1 h at − 78 °C, 0.31 mL (2.6 mmol) of $P(OMe)_3$ dissolved in 1 mL of CH_2Cl_2 was added over a 10 min period. Stirring was continued for 4 h, over which time the temperature had risen from −78 °C to room temperature. Then 2 mL of MeOH and 0.13 mL (1.1 mmol) of $P(OMe)_3$ were added, and stirring at 25 °C was continued for 24 h. Solvent removal in vacuo and filtration through a plug of silica gel with EtOAc, followed by flash chromatography (25% EtOAc/hexane), yielded 63 mg (89%) of lactam **55** as a clear oil. ^{1}H NMR (500 MHz, C_6D_6): δ 0.77 (d, J = 6.6 Hz, 3H, 5-CH_3), 0.90 (t, J = 7.2 Hz, 3H, 3-$CH_2CH_2CH_3$), 0.92 (t, J = 7.2 Hz, 3H, $CH_2CH_2CH_2CH_3$), 1.2 (tq, J = 7.2, 7.2 Hz, 2H, $CH_2CH_2CH_2CH_3$), 1.3−1.4 (m, 6H, 3-$CH_2CH_2CH_3$, $NCH_2CH_2CH_2$), 1.46 (ddd, J = 7.7, 7.7, 12.3 Hz, 1H, 4-H), 1.95 (ddd, J = 3.9, 4.5, 12.3 Hz, 1H, 4-H), 2.3 (m, 1H, 3-H), 2.75 (ddd, J = 6.6, 7.1, 13.2 Hz, 1H, NCH*H*), 3.15 (dqd, J = 3.9, 6.6, 7.7 Hz, 1H, 5-H), 3.73 (ddd, J = 7.7, 7.7, 13.2 Hz, 1H, NCH*H*). IR (cm^{-1}): 1112, 1419, 1682, 2868, 2926, 2955. ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.5, 13.8, 19.2, 19.9, 20.2, 29.3, 30.0, 33.4, 39.6, 40.4, 51.2, 176.8. MS (EI): m/z 197 (M^+), 182, 168, 155, 140, 126.

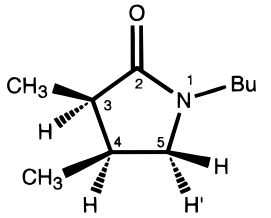


55

Irradiation	H_3	CH_3(C-5)
NOE Observation	H_4', H_6 CH_3(C-5)	H_3, H_4' H_5

1-Butyl-3,4-dimethyl-2-pyrrolidinone (56). To a stirred solution of 179 mg (0.50 mmol) of Rh(I) complex **43a** in 12 mL of CH_2Cl_2 at −78 °C was added 0.54 mL (3.5 mmol) of a 6.5 M solution of HCl in Et_2O over 5 min. After 1 h at −78 °C, 0.42 mL (3.5 mmol) of $P(OMe)_3$ dissolved in 1 mL of CH_2Cl_2 was added over a 10 min period. Stirring was continued for 4 h, over which time the temperature had risen from −78 °C to ambient temperature; 2 mL of MeOH and 0.18 mL (1.5 mmol) of $P(OMe)_3$ were added, and stirring at 25 °C was continued for 24 h. Solvent removal in vacuo and filtration through a plug of silica gel with EtOAc, followed by flash chromatography (25% EtOAc/hexane), yielded 77 mg of lactam **56** as a clear oil (89%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.93 (t, J = 7.3 Hz, 3H, CH_2CH_3), 0.98 (d, J = 6.9 Hz, 3H, 4-CH_3), 1.09 (d, J = 7.3 Hz, 3H, 3-CH_3), 1.32 (tq, J = 7.3, 7.3 Hz, 2H, $CH_2CH_2CH_3$, 1.48 (tt, J = 7.3, 7.3 Hz, 2H, $NCH_2CH_2CH_2CH_3$), 2.45 (dddq, J = 5.0, 6.4, 7.3, 6.9 Hz, 1H, 4-H), 2.50 (dq, J = 7.3, 7.3 Hz, 1H, 3-H), 2.90 (dd, J = 5.0, 9.6 Hz, 1H, 5-H), 3.20 (td, J = 7.3, 13.7 Hz, 1H, NC*H*H), 3.30 (td, J = 7.3, 13.7 Hz, 1H, NC*H*H), 3.4 (dd, J = 6.4, 9.6 Hz, 1H, 5H). IR (cm^{-1}): 1020, 1148, 1190, 1428, 1674, 2866, 2924, 2954. ^{13}C NMR (75 MHz): δ 10.2,

13.5, 14.0, 19.8, 29.2, 30.3, 40.5, 42.0, 52.6, 177.4. MS (EI): *m*/*z* 169 (M^+), 154, 140, 126, 112, 98. Anal. Calcd for $C_{10}H_{19}NO{\cdot}0.2H_2O$: C, 69.48; H, 11.31. Found C, 69.92; H, 11.31.

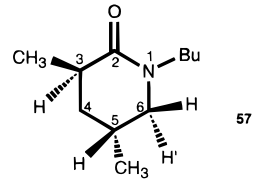


56

Irradiation	H_3	CH_3(C-3)	H_4
NOE Observation	H_4, H_5' CH_3(C-3)	H_3 CH_3(C-4)	H_3, H_5', H_5 CH_3(C-4)

Irradiation	CH_3(C-4)	H_5'	H_5
NOE Observation	H_4, H_5 CH_3(C-3)	H_4 H_5	H_5', CH_3(C-4)

1-Butyl-3,5-dimethyl-2-piperidinone (57). To a stirred solution of 59 mg (0.17 mmol) of Rh(I) complex **44** in 5 mL of CH_2Cl_2 at −78 °C was added 0.16 mL (1.2 mmol) of a 7.5 M solution of HCl in Et_2O over 5 min. After 1 h at −78 °C, 0.2 mL (1.7 mmol) of $P(OMe)_3$ dissolved in 1 mL of CH_2Cl_2 was added over a 10 min period. Stirring was continued for 4 h, over which time the temperature had risen from −78 °C to room temperature. Then 2 mL of MeOH and 0.06 mL (0.51 mmol) of $P(OMe)_3$ were added, and stirring at 25 °C was continued for 24 h. Solvent removal in vacuo and filtration through a plug of silica gel with EtOAc, followed by flash chromatography (25% EtOAc/hexane), yielded 29 mg (90%) of lactam **57** as a clear oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.92 (t, J = 7.3 Hz, 3H, CH_2CH_3), 1.01 (d, J = 6.9 Hz, 3H, 5-CH_3), 1.24 (d, J = 7.3 Hz, 3H, 3-CH_3), 1.30 (tq, J = 7.3, 7.3 Hz, 2H, $CH_2CH_2CH_3$), 1.50 (tt, J = 9.6, 7.3 Hz, 2H, $CH_2CH_2CH_2CH_3$), 1.60 (dddd, J = 1.4, 4.5, 4.5, 13.7 Hz, 1 H, 4-*H*), 1.64 (ddd, J = 5.0, 9.4, 13.5 Hz, 1 H, 4-*H*), 2.09 (dqddd, J = 4.5, 6.9, 6.9, 9.2, 9.5 Hz, 1H, 5-H), 2.5 (ddq, J = 5.0, 7.3, 7.3 Hz, 1H, 3-H), 2.91 (dd, J = 9.2, 12.0 Hz, 1H, 6-*H*), 3.23 (ddd, J = 1.4, 6.9, 12.0 Hz, 1H, 6-*H*), 3.28 (td, J = 7.3, 13.3 Hz, 2H, NC*H*H), 3.35 (td, J = 7.3, 13.3 Hz, 1H, NC*H*H). IR (cm^{-1}) 1092, 1268, 1485, 1637, 2868, 2924, 2954. ^{13}C NMR (75 MHz): δ 13.6, 18.3, 18.8, 19.9, 24.9, 29.0, 34.4, 36.5, 46.9, 54.6, 173.5. MS (EI): *m*/*z* 183 (M^+), 168, 154, 140, 126, 112.

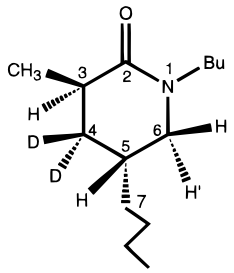


57

Irradiation	CH_3(C-3)	H_5
NOE Observation	H_3, H_4, H_5	H_4, CH_3(C-3) H_6, CH_3(C-5)

Irradiation	CH_3(C-5)	H_6'
NOE Observation	H_4, H_4 H_5, H_6'	CH_3(C-5) H_6

1-Butyl-3-methyl-4,4-dideuterio-5-butyl-2-piperidinone (59). To a stirred solution of 57 mg (0.16 mmol) of Rh(I) complex **48** in 5 mL of CH_2Cl_2 at −78 °C was added 0.17 mL (1.1 mmol) of a 6.5 M solution of HCl in Et_2O over 5 min. After 1 h at −78 °C, 0.17 mL (1.1 mmol) of $P(OMe)_3$ dissolved in 1 mL of CH_2Cl_2 was added over a 10 min period. Stirring was continued for 4 h, over which time the temperature had risen from −78 °C to room temperature. Then 2 mL of MeOH and 0.06 mL (0.51 mmol) of $P(OMe)_3$ were added, and stirring at 25 °C was continued for 24 h. Solvent removal in vacuo and filtration through a plug of silica gel with EtOAc, followed by flash chromatography (25% EtOAc/hexane), yielded 25 mg (71%) of lactam **59** as a clear oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.94 (t, J = 7.1 Hz, 6H, CH_2CH_3, CH_2CH_3), 1.24 (d, J = 7.3 Hz, 3H, $CHCH_3$), 1.33 (m, 8H, $CHCH_2CH_2CH_2CH_3$, $NCH_2CH_2CH_2CH_3$), 1.52 (ddt, J = 7.3, 7.3, 7.3 Hz, 2H, $NCH_2CH_2CH_2$), 1.88 (m, 1H, 5-H), 2.50 (q, J = 7.3 Hz, 1H, CH_3CHCD_2), 2.95 (dd, J = 9.2, 11.9 Hz, 1H, NC*H*HCH), 3.25 (dd, J = 5.0, 11.9 Hz, 1H, NCH*H*CH), 3.28 (ddd, J = 7.3, 7.3, 13.3 Hz, 1H, NCH*H*CH_2), 3.36 (ddd, J = 7.3, 7.3, 13.3 Hz, 1H, NC*H*HCH_2). IR (cm^{-1}): 684, 1258, 1453, 1610, 2866, 2922, 2953. MS (EI): *m*/*z* 227 (M^+), 212, 198, 184, 170, 156.



59

Irradiation	H_5
NOE Observation	CH_3(C-3), H_6, H_7 , H_7'

1-Butyl-3-propyl-5-methyl-2-pyrrolidinone (60). To a stirred solution of 67 mg (0.2 mmol) of Rh(I) complex **49** in 10 mL of CH_2Cl_2 at 0 °C was added 0.19 mL (1.4 mmol) of a 7.5 M solution of HCl in Et_2O over 5 min. After 0.5 h at 0 °C, 0.17 mL (1.4 mmol) of $P(OMe)_3$ dissolved in 1 mL of CH_2Cl_2 was added over a 10 min period. Stirring was continued for 4 h, during which time the temperature had risen from 0 °C to room temperature. Then 2 mL of MeOH and 0.07 mL (0.6 mmol) of $P(OMe)_3$ were added, and stirring at 25 °C was continued for 24 h. Solvent removal in vacuo and filtration through a plug of silica gel with EtOAc, followed by flash chromatography (25% EtOAc/hexane), yielded 35 mg (88%) of lactam **60** as a clear oil. ^{1}H NMR (500 MHz, C_6D_6): δ 0.77 (d, J = 6.6 Hz, 3H, 5-CH_3), 0.90 (t, J = 7.2 Hz, 3H, 3-$CH_2CH_2CH_3$), 0.92 (t, J = 7.2 Hz, 3H, $CH_2CH_2CH_2CH_3$), 1.2 (tq, J = 7.2, 7.2 Hz, 2H, $CH_2CH_2CH_2CH_3$), 1.3−1.4 (m, 6H, 3-$CH_2CH_2CH_3$, $NCH_2CH_2CH_2$), 1.46 (ddd, J = 7.7, 7.7, 12.3 Hz, 1H, 4-H), 1.95 (ddd, J = 3.9, 4.5, 12.3 Hz, 1H, 4-H), 2.3 (m, 1H, 3-H), 2.75 (ddd, J = 6.6, 7.1, 13.2 Hz, 1H, NC*H*H), 3.15 (ddq, J = 3.9, 6.6, 7.7 Hz, 1H, 5-H), 3.73 (ddd, J = 7.7, 7.7, 13.2 Hz, 1H, NCH*H*). IR (cm^{-1}): 1112, 1456, 1659, 2866, 2926. ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.5, 13.7, 19.3, 19.9, 20.2, 29.3, 33.1, 33.4, 39.6, 40.4, 51.3, 176.8. MS (EI) *m*/*e*: 197 (M^+), 182, 168, 155, 140, 126. Anal. Calcd for $C_{12}H_{23}NO{\cdot}0.1H_2O$: C, 72.38; H, 11.64. Found: C, 72.65; H, 11.75.

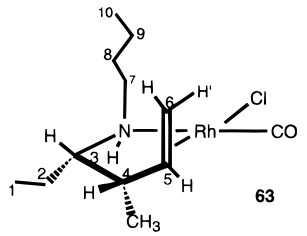
1-Butyl-3-ethyl-4-(3-methyl-2-butenyl)-2-piperidinone (61). To a stirred solution of 70 mg (0.18 mmol) of Rh(I) complex **51** in 5 mL of CH_2Cl_2 at −78 °C was added 0.17 mL (1.3 mmol) of a 7.5 M solution of HCl in Et_2O over 5 min. After 1 h at −78 °C, 0.15 mL (1.3 mmol) of $P(OMe)_3$ dissolved in 1 mL of CH_2Cl_2 was added over a 10 min period. Stirring was continued for 4 h, during which time the temperature had risen

from −78 °C to room temperature. Then 2 mL of MeOH and 0.06 mL (0.5 mmol) of $P(OMe)_3$ were added, and stirring at 25 °C was continued for 24 h. Solvent removal in vacuo and filtration through a plug of silica gel with EtOAc, followed by flash chromatography (50% EtOAc/hexane), yielded 14 mg (30%) of lactam **61** as a clear oil. ^{1}H NMR (500 MHz): δ 0.80 (t, J = 4.1 Hz, 3H, $CH_2CH_2CH_3$), 0.98 (t, J = 4.1 Hz, 3H, $CHCH_2CH_3$), 1.30 (tdd, J = 4.1, 4.1, 4.1 Hz, 2H, $CH_2CH_2CH_3$), 1.30 (m, 1H, $NCH_2CHHCH_2CH_3$), 1.42 (m, 1H, $NCH_2CHHCH_2CH_3$), 1.48 (td, J = 4.1, 4.1 Hz, 2H, CH_3CH_2CH), 1.60 (s, 3H, $CH_2CH{=}CCH_3CH_3$), 1.70 (s, 3H, $CH_2CH{=}CCH_3CH_3$), 1.75 (m, 1H, $CHCHCHHCH_2N$), 1.85 (m, 1H, $CHCHCHHCH_2N$), 1.85 (m, 1H, $CHCHHCH{=}CCH_3CH_3$), 1.95 (m, 1H, $CH_2CHCHCO$), 2.05 (ddd, J = 5.9, 8.8, 11.7 Hz, 1H, $CHCHHCH{=}CCH_3CH_3$), 2.25 (ddd, J = 2.5, 4.1, 6.6 Hz, 1H, $CHCHCO$), 3.25 (ddd, J = 3.3, 3.3, 7.8 Hz, 1H, $NCHHCH_2$), 3.42 (ddd, J = 4.4, 4.4, 7.8 Hz, 1H, $NCHHCH_2$), 5.18 (dd, J = 5.9, 8.8 Hz, 1H, $CH_2CH{=}CCH_3CH_3$). IR (cm^{-1}): 644, 805, 1013, 1255, 1370, 1446, 1606, 1709, 2847, 2918, 2948. MS (EI) *m/e*: 267.4 (M^+), 251.1, 236.2, 208.1, 195.8, 180.2, 149.1, 86.2. The stereochemistry of lactam **61** was determined by ^{1}H NOE difference spectroscopy. Upon irradiation of the lactam α proton, a large enhancement in the signal for the β proton was observed.

1-Benzyl-3-ethyl-4-(3-methyl-2-butenyl)-2-piperidine (62). To a stirred solution of 72 mg (0.17 mmol) of Rh(I) complex **52** in 10 mL of CH_2Cl_2 at 0 °C was added 0.16 mL (1.2 mmol) of a 7.5 M solution of HCl in Et_2O over 5 min. After 0.5 h at 0 °C, 0.16 mL (1.2 mmol) of $P(OMe)_3$ dissolved in 1 mL of CH_2Cl_2 was added over 10 min period. Stirring was continued for 4 h, during which time the temperature had risen from 0 °C to room temperature. Then 2 mL of MeOH and 0.06 mL (0.5 mmol) of $P(OMe)_3$ were added, and stirring at 25 °C was continued for 24 h. Solvent removal in vacuo and filtration through a plug of silica gel with EtOAc, followed by flash chromatography (30% EtOAc/hexane), yielded 5.8 mg (10%) of lactam **62**. ^{1}H NMR (500 MHz): δ 1.00 (t, J = 7.3 Hz, 3H, CH_2CH_3), 1.50 (s, 3H, $CH{=}CCH_3CH_3$), 1.53 (qdd, J = 7.3, 7.3, 14.6 Hz, 1H, $CHCHHCH_3$), 1.67 (s, 3H, $CH{=}CCH_3CH_3$), 1.66 (m, 2H, $CHCH_2CH_2N$), 1.92 (qdd, J = 7.3, 7.3, 14.6 Hz, 1H, $CHCHHCH_3$), 2.00 (m, 2H, $CHCHHCH{=}CCH_3CH_3$), 2.38 (ddd, J = 4.4, 6.4, 7.3 Hz, 1H, CH_3CH_2CHCH), 3.08 (ddd, J = 6.3, 6.3, 11.7 Hz, 1H, CH_2CHHN), 3.14 (ddd, J = 4.9, 6.8, 11.7 Hz, 1H, CH_2CHHN), 4.42 (d, J = 14.7 Hz, 1H, $CHHPh$), 4.72 (d, J = 14.7 Hz, $CHHPh$), 5.04 (dddd, J = 1.0, 1.5, 7.3, 7.3 Hz, 1H, $CH_2CH{=}CCH_3CH_3$), 7.30 (m, 5H, $C_6H_5CH_2$).

Complexes **63**, **64**, and **65** were not stable enough to permit purification for analysis.

[*N*-[3(-*anti*-4-Methyl-5-hexenyl)]-*n*-butylamine]carbonylrhodium(I) Chloride (63). To a stirred solution of dichlorotetracarbonyldirhodium(I) (39 mg (0.2 mmol) in 5 mL of hexane and CH_2Cl_2 (1:1)) was added 36 mg (0.21 mmol) of *N*-[3(-*anti*-4-methyl-5-hexenyl)]-*n*-butylamine. After the mixture was stirred at 25 °C for 20 min, the solvent was removed in vacuo. Filtration through a plug of silica gel (50% EtOAc/hexane), followed by solvent removal in vacuo, gave 60 mg (90%) of complex **63** as an orange oil. ^{1}H NMR (500 MHz): δ 0.92 (t, J = 7.3 Hz, 3H, CH_3CH_2CH), 0.93 (t, J = 7.3 Hz, 3H, $CH_3CH_2CH_2$), 1.35 (d, J = 7.3 Hz, 3H, $CHCH_3$), 1.28 (m, 2H, $CH_3CH_2CH_2$), 1.60 (m, 2H, $CH_3CH_2CHHCH_2$, CH_3CHHCH), 1.78 (m, 2H, $CH_3CHCHHCH_2$, CH_3CHHCH), 2.26 (ddq, J = 6.9, 6.9, 7.3 Hz, 1H, $CHCH{=}CH_2$), 2.34 (m, 1H, NH), 2.62 (m, 1H, CHN), 2.62 (dddd, J = 3.2, 5.0, 12.8, 17.8 Hz, 1H, CH_2CHHN)), 2.92 (dddd, 3.2, 5.5, 12.4, 17.8 Hz, 1H, CH_2CHHN), 3.18 (dd, J = 1.38, 8.2 Hz, 1H, $CH{=}CHH$), 3.18 (dd, J = 1.38, 13.0 Hz, 1H, $CH{=}CHH$), 4.35 (ddd, J = 6.9, 8.2, 13.0 Hz, 1H, $CH{=}CH_2$). IR (cm^{-1}): 761, 1369, 1444, 1584, 1636, 1993, 2015, 2854, 2912, 2942, 3230, 3428. ^{13}C (75 MHz): δ 11.4, 13.4, 13.5, 20.3, 30.5, 37.8, 47.7 (d, J = 12.5 Hz, alkene), 57.3, 83.0 (d, J = 13.7 Hz, alkene), 183.8 (d, J = 69.4 Hz, carbonyl).



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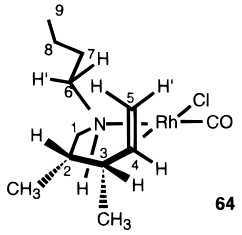
Irradiation	H_5	NH	H_8'
NOE Observation	CH_3(C-4) H_4, H_6'	H_7 CH_3(C-4)	H_6 H_7', H_8

[*N*-(*anti*-2,3-Dimethyl-4-pentenyl)-*n*-butylamine]carbonylrhodium(I) Chloride (64). To a stirred solution of dichlorotetracarbonyldirhodium(I) (39 mg (0.2 mmol) in 5 mL of hexane and CH_2Cl_2 (1:1)) was added 36 mg (0.21 mmol) of *N*-(*anti*-2,3-dimethyl-4-pentenyl)-*n*-butylamine. After the mixture was stirred at 25 °C for 20 min, the solvent was removed in vacuo. Filtration through a plug of silica gel (50% EtOAc/hexane), followed by solvent removal in vacuo, gave 57 mg (85%) of complex **64** as an orange oil. ^{1}H NMR (500 MHz): δ 0.85 (d, J = 6.6 Hz, 3H, CH_3CHCH_2N), 0.92 (t, J = 7.1 Hz, 3H, CH_2CH_3), 1.34 (d, J = 7.1 Hz, 3H, $CH_3CHCH{=}CH$), 1.34 (tq, J = 7.1, 7.1 Hz, 2H, CH_2CH_3), 1.64 (m, 1H, $NHCH_2CHH$), 1.85 (m, 1H, $NHCH_2CHH$), 1.95 (m, 1H, $CHCH_2NH$), 2.00 (m, 1H, $NHCHHCH_2$), 2.08 (m, 1H, $CHCH{=}CH_2$), 2.31 (dddd, J = 5.0, 5.0, 10.0, 15.0 Hz, 1H, $NHCHHCH_2$), 2.63 (ddd, J = 5.5, 12.6, 12.6 Hz, 1H, $CHCHHNH$), 2.90 (dddd, J = 2.2, 6.1, 11.0, 15.0 Hz, 1H, $NHCHHCH_2$), 3.06 (m, 1H, NH), 3.06 (dd, J = 1.1, 13.2 Hz, 1H, $CH{=}CHH$), 3.36 (dd, J = 1.1, 8.2 Hz, 1H, $CH{=}CHH$), 4.40 (ddd, J = 1.65, 8.2, 13.2 Hz, 1H, $CH{=}CH_2$). IR (cm^{-1}): 674, 791, 1370, 1440, 1619, 1993, 2013, 2853, 2910, 2940, 3209, 3409. ^{13}C NMR (75 MHz): δ 12.9, 13.3, 17.6, 20.0, 26.3, 31.3, 37.3, 47.6 (d, J = 12.5 Hz, alkene), 50.6, 51.1, 80.0 (d, J = 17.7 Hz, alkene), 183.8.



64

Irradiation	$H_{1\alpha}$	NH	H_6	H_5
NOE Observation	NH, $H_{1\beta}$, CH_3(C-3)	$H_{1\alpha}$, H_7	H_5 H_6', H_7	H_5' H_6

[*cis*-2-Vinyl-1-(butylaminomethylene)cyclohexane]carbonylrhodium(I) Chloride (65). To a stirred solution of dichlorotetracarbonyldirhodium(I) (39 mg (0.2 mmol) in 5 mL of hexane and CH_2Cl_2 (1:1)) was added 41 mg (0.21 mmol) of *cis*-2-vinyl-1-(butylaminomethylene)cyclohexane. After the mixture was stirred at 25 °C for 20 min, the solvent was removed in vacuo. Filtration through a plug of silica gel (50% EtOAc/hexane), followed by solvent removal in vacuo, gave 58 mg (80%) of complex **65** as an orange oil. ^{1}H NMR (500 MHz): δ 0.95 (t, J = 7.3 Hz, 3H, CH_2CH_3), 1.40 (m, 2H, CH_2CH_3), 1.35−1.6 (m, 5H, protons on the ring), 1.68 (m, 1H, NCH_2CHHCH_2), 1.77 (m, 1H, proton on the ring), 1.87 (m, 2H, NCH_2CHHCH_2, proton on the ring), 2.00 (m, 1H, $CHCH_2NH$), 2.04 (m, 1H, $CHCH{=}CH_2$), 2.17 (m, 1H, proton on the ring),

2.32 (ddd, J = 5.1, 10.0, 16.0 Hz, 1H, NC*H*HCH$_2$), 2.89 (ddd, J = 5.5, 11.9, 16.0 Hz, 1H, NCH*H*CH$_2$), 2.95 (dd, J = 2.3, 13.2 Hz, 1H, CH=C*H*H), 3.15 (dd, J = 4.6, 12.4 Hz, 1H, CHC*H*HN), 3.38 (dd, J = 2.3, 8.2 Hz, 1H, CHCH=CH*H*), 4.33 (ddd, J = 2.3, 8.2, 13.2 Hz, 1H, CHC*H*=CH$_2$). IR (cm^{-1}): 616, 642, 1446, 1999, 2019, 2854, 2924, 2954. ^{13}C NMR (75 MHz): δ 13.4, 20.1, 20.5, 25.9, 27.2, 31.0, 32.3, 40.5, 50.0 (d, J = 22.5 Hz, alkene), 78.8 (d, J = 15.0 Hz, alkene), 184 (d, J = 67.5 Hz carbonyl).

Acknowledgment. This work has been partially supported by grants from the National Institutes of Health, the National Science Foundation, and the Dreyfus Foundation. We acknowledge the early contributions of Dr. Karen Donnelly and Mr. Stephen Milczanowski.

Supporting Information Available: Experimental procedures for the synthesis of the aminoalkenes and NMR spectra for the amines, Rh(I) complexes, and lactams (143 pages). Ordering information is given on any current masthead page.

OM9801453