mL of THF. To this cooled solution (0 °C) was added an equivalent of LDA in THF, and the reaction mixture was stirred for 40 min at which time was added an equivalent of *trans*-(Cl)$SiPh_2CH$=CHPh dissolved in 10 mL of THF. The solution was permitted to warm to room temperature and stirred for 30 min. After removal of the solvents and extraction with a 40:60 methylene chloride/hexane solvent mixture, the crude material was placed on a silica gel column, 2.5 × 20 cm made up in hexane, and eluted with a 20:80 methylene chloride/hexane solvent mixture. The resulting material was recrystallized from hexane to yield 0.86 g (1.61 mmol, 71%) of the title compound.

Independent Synthesis of $(\eta^5\text{-}C_5H_5)Fe(CO)_2SiPh_2$-*trans*-CH=CHPh (IV). To a solution of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^-Na^+$ prepared from 1.6 g (9.04 mmol) of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ in THF was added an equivalent of (Cl)$SiPh_2$-*trans*-CH=CHPh. The mixture was stirred for 30 min, and workup as above yielded IV (1.5 g, 3.2 mmol, 35%).

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Synthesis and Characterization of Rhodium(I) Amino–Olefin Complexes

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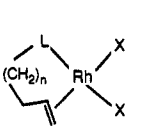
The syntheses of $[(CH_2CR_1CH_2CH_2NR_2R_3)RhClL]$ complexes (R_1 = CH_3, H, R_2 = *n*-Bu, R_3 = H; R_1 = CH_3, H, R_2 = R_3 = CH_3, L = CO or dimer; **19–32** and **38–43**) are reported. The complexes are prepared by the reaction of unsaturated amines with bis(μ-chloro)tetracarbonyldirhodium(I) (**3**) or bis(μ-chloro)-tetrakis(ethylene)dirhodium(I) (**4**) at ambient temperature. Compound **19**, [*N*-(*trans*-3-pentenyl)*n*-butylamine]carbonylrhodium(I) chloride, crystallized in the monoclinic space group $P2_1/c$ with cell dimensions a = 17.699 (5), b = 8.442 (1), and c = 20.119 (5) Å, and β = 120.19 (2)°.

Introduction

As part of our research program directed toward the regioselective functionalization of simple olefins by prior coordination to transition metals,[1] we found the need for Rh(I) complexes containing bidentate olefinic ligands. Numerous Rh(I) complexes with bidentate ligands are known;[2] however, none proved suitable for our purpose.

Diolefin complexes[2] would not be useful because of the question of regiocontrol during alkene functionalization if an unsymmetrical diolefin was utilized. We were interested in complexes, such as **1**, which incorporated bidentate, monoolefin ligands where a heteroatom was tethered to the olefin by a carbon chain to yield a chelated ligand. Olefinic phosphines[3,4] have been shown to give rise to Rh(I) complexes (e.g. **2**) containing bidentate ligands.[5]



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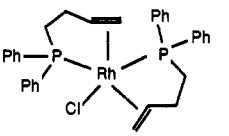

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However, subsequent synthetic utility of the phosphine ligand after olefin functionalization was questionable. While allylic amines have been shown to give rise to polymeric materials[6a,b] upon reaction with bis(μ-chloro)-tetracarbonyldirhodium(I) (**3**), we found that homoallylic and bishomoallylic amines reacted with both **3** and bis-(μ-chloro)tetrakis(ethylene)dirhodium(I) (**4**) to give rise to a series of new complexes containing bidentate olefinic ligands.[6c] We now report our results on the synthesis and characterization of these new Rh(I) complexes.

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(6) (a) Fougeroux, P.; Denise, B.; Bonnaire, R.; Pannetier, G. *J. Organomet. Chem.* **1973**, *60*, 375. (b) Maisonnat, A.; Kalck, P.; Poilblanc, R. *Inorg. Chem.* **1974**, *13*, 2996. (c) Ibers[6d] has shown that *N*-allylaniline reacts with **4** in THF to give a bidentate olefinic amine complex. We found that reaction of allylamine with **4** in CH_2Cl_2 gave rise to an uncharacterizable orange solid. (d) Aresta, M.; Quaranta, E.; Treglia, S.; Ibers, J. A. *Organometallics* **1988**, *7*, 577.

0276-7333/88/2307-2528$01.50/0

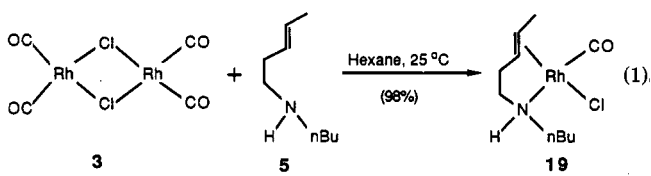
Table I. Rhodium(I) Carbonyl Complexes

ENTRY	AMINE	CONDITIONS	YIELD (%)	Rh(I) COMPLEX	ν_{CO} (cm^{-1})
1	5 R_1 = H; R_2 = nBu	A	98	19 R_1 = H; R_2 = nBu	2030
2	6 R_1 = R_2 = CH_3	A	90	20 R_1 = R_2 = CH_3	2040
3	7 R_1 = H; R_2 = nBu	A	97	21 R_1 = H; R_2 = nBu	2040
4	8 R_1 = R_2 = CH_3	A	92	22 R_1 = R_2 = CH_3	2040
5	9 R_1 = H; R_2 = nBu	A	98	23 R_1 = H; R_2 = nBu	2030
6	10 R_1 = R_2 = CH_3	A	97	24 R_1 = R_2 = CH_3	2040
7	11	A	98	25	2050
8	12 R_1 = R_2 = H	A	98	26 R_1 = R_2 = H	2030
9	13 R_1 = H; R_2 = CH_3	A	95	27 R_1 = H; R_2 = CH_3	2020
10	14 R_1 = CH_3; R_2 = H	A	97	28 R_1 = CH_3; R_2 = H	2030
11	15	A	98	29	2040
12	16	B	99	30	2030
13	17	B	99	31	2040
14	18	B	91	32	2020

Results and Discussion

A variety of different unsaturated amines reacted with either $[Rh(CO)_2Cl]_2$ (**3**) or $[(CH_2CH_2)_2RhCl]_2$ (**4**) to yield new four-coordinate rhodium(I) complexes. In general, the resulting rhodium carbonyl complexes were very stable and not air sensitive, but the analogous dimeric complexes were more susceptible to decomposition at ambient temperature.

Rhodium(I) Carbonyl Complexes. A hexane solution of rhodium carbonyl **3** reacted with (*trans*-3-pentenyl)-butylamine (**5**), at ambient temperature, to give rise to complex **19** in 98% yield as shown in eq 1. A 1.0–1.5 ppm



3 **5** **19**

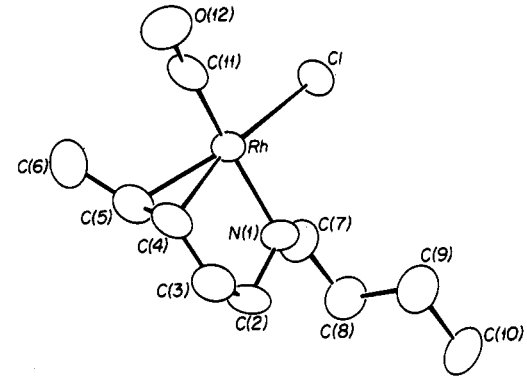
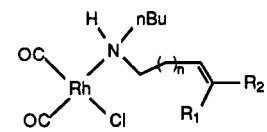


Figure 1. Perspective drawing of one of the two independent molecules of [*N*-(*trans*-pentenyl)*n*-butylamine]carbonylrhodium(I) chloride (**19**) indicating the crystallographic numbering scheme. Thermal ellipsoids have been drawn at the 50% probability level, and hydrogen atoms have been omitted for clarity.

upfield shift of the olefinic protons and a downfield shift of the amino methylene protons were observed in the 270-MHz ^1H NMR spectrum of **19**, clearly indicating that both the olefin and the amine had complexed. The IR spectrum showed a sharp, intense band in the region of 2020–2050 cm^{-1}, characteristic of a metal carbonyl. A number of homoallylic and bishomoallylic amines also reacted with **3** to yield analogous complexes, and these results are summarized in Table I.

In most cases (entries 1–11), the unsaturated amine formed a bidentate ligand complex at ambient temperature (procedure A in Table I). However, with amines **16–18**, only monodentate[6,7] complexes (i.e. **33**) were formed at ambient temperature, and thus it was necessary to warm a chloroform solution of the complex for 6–24 h to complete the ligand substitution process (procedure B in Table I).

In general, mono- and disubstituted homoallylic amines readily formed bidentate ligand complexes. However, trisubstituted olefin **34** would only coordinate through the amino group giving **33** (R_1 = R_2 = Me, n = 1). Attempts



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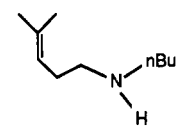


34

to force the coordination of the olefin by refluxing the rhodium(I) complex in chloroform or toluene led only to decomposition. In addition, allylic amines would only form monodentate ligand complexes and attempts to force coordination of the olefin were also unsuccessful.[6c,d,8] We feel this is due to a preference of the C=C to be orthogonal to the coordination square plane in Rh(I) complexes.[9] The ring size is apparently too small in the case of the allylic amines, thus preventing the proper orbital overlap necessary to achieve the desired orthogonal coordination.

Each of the complexes **26–28**, generated from the reaction of cyclic amines **12–14** with complex **3**, was an inseparable mixture of isomers. The ca. 4–5:1 isomer ratio was evident upon inspection of the 270-MHz ^1H NMR spec-

(7) Gallay, J.; DeMontauzon, D.; Poilblanc, R. *J. Organomet. Chem.* **1972**, *38*, 179. Vallarino, L. M.; Sheargold, S. W. *Inorg. Chim. Acta* **1979**, *36*, 243.
(8) Krafft, M. E., unpublished results.
(9) 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.

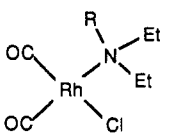
trum and integration of the olefinic resonances. The other complexes appeared to be one isomer.

Crystallographic analysis of **19** confirms the bidentate nature and the orientation of the amino olefin ligand (Figure 1). The amine nitrogen is trans to the carbonyl ligand and the olefin is trans to the chloride. Since CO is a better trans directing ligand than is chloride, the coordination sphere of **19** supports the proposition that the amino olefin reacts in a stepwise fashion, first coordinating the nitrogen and then coordinating the olefin. This is consistent with the observations on the coordination of amines **16–18**.

As is normal in Rh–ethylene complexes, the ethylene C–C vector is approximately perpendicular[9] to the square-planar coordination sphere and the Rh–C distances are equivalent. Specifically, for the two independent molecules the angles between the C(3)–C(6) planes and the coordination planes, defined by Cl, N(1), and C(11) and the centroid of the C(4)–C(5) bond, are 87.0 and 92.6°, respectively. The orientation of the double bond should become a very important factor in subsequent olefin functionalization reactions.[10] The Rh–C lengths are 2.130 (12) and 2.132 (12) Å in one molecule and 2.091 (13) and 2.127 (13) Å in the other. These lengths are similar to those found in, for instance, $[\eta^5\text{-}C_5(C_6H_5)_4Cl]Rh(C_2H_4)_2$ (mean 2.115 (8) Å)[11] or bis(μ-chloro)tetrakis(4-methylpenta-1,3-diene)dirhodium (I) (2.120–2.165 Å).[12] The C=C lengths of the coordinated olefins (1.39 (2) and 1.41 (2) Å) are naturally longer than that in ethylene, 1.337 (2) Å, and are similar to those found in other Rh–olefin complexes.[11-13]

The Rh–Cl bond lengths (2.363 (3) and 2.379 (3) Å) are normal for Rh–Cl bonds trans to a π olefin,[14] and the Rh–N and Rh–C(O) lengths fall within acceptable ranges. Though the estimated standard deviations are rather large, there appears to be a small, but real, difference in the two independent molecules with regards to the trans Rh–C(O) and Rh–N lengths. In the primed complex the Rh–N length of 2.108 (9) Å and the Rh–C(O) length of 1.860 (12) Å are unexceptional. In the unprimed molecule, however, the Rh–N length, 2.141 (9) Å, is at the long end of the normal range and the Rh–C(O) length, 1.804 (13) Å, is at the short end of the normal range.

It is known that secondary, nonchelating amines readily react with **3** and give rise to dicarbonyl complexes.[6,7] For example, diethylamine yields complex **35** upon reaction with complex **3**. However, the analogous complexes prepared from nonchelating, tertiary amines (i.e. **36**) are



35 R = H
36 R = Et, alkyl

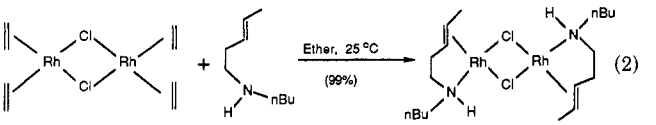
unstable and rapidly decompose at ambient temperature.[8]

Table II. Dimeric Rhodium(I) Olefinic Amine Complexes

ENTRY	AMINE	YIELD (%)	Rh(I) COMPLEX
1	**5**	99	**38**
2	**7**	98	**39**
3	**16**	99	**40**
4	**17**	93	**41**
5	**14** R_1 = H; R_2 = nBu; R_3 = CH_3	97	**42** R_1 = H; R_2 = nBu; R_3 = CH_3
6	**37** R_1 = R_2 = CH_3; R_3 = H	99	**43** R_1 = R_2 = CH_3; R_3 = H

We observed a similar difference in reactivity between the reactions of secondary and tertiary amino olefins with complex **3**. If the secondary amine complexed to form a bidentate ligand complex at ambient temperature, then the analogous tertiary amino olefin also formed a stable complex (entries 2, 4, and 6 in Table I). However, for unsaturated secondary amines which required heating to complete the ligand displacement (**16** and **17**), the analogous monodentate, tertiary amine complexes decomposed very readily at room temperature. The successful formation of tertiary amine complexes **20**, **22**, and **24** clearly shows the stabilizing power of the bidentate ligand.

Other Rhodium(I) Complexes. Homoallylic and bishomoallylic amines also cleanly reacted with $[(CH_2C\text{-}H_2)_2RhCl]_2$ (**4**), generating dimeric Rh(I) complexes.[15] Reaction of amine **5** with **4** gave rise to the chloro-bridged Rh(I) complex **38**[16] in 99% yield (eq 2). Similar results were obtained with other unsaturated amines, and these are summarized in Table II.



4 **5** **38** (2)

(10) Hoffman, R.; Thorn, D. L. *J. Am. Chem. Soc.* **1978**, *100*, 2079. Hoffman, 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. *Organometalllics* **1987**, *6*, 1211. Albright, T. A.; Hoffman, R.; Thibeault, J. C.; Thorn, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 3801. Doherty, N. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1985**, *107*, 2670.

(11) Day, V. W.; Stults, B. R.; Reimer, K. J.; Shaver, A. *J. Am. Chem. Soc.* **1974**, *96*, 1227.

(12) Drew, M. G. B.; Nelson, S. M.; Sloan, M. *J. Chem. Soc., Dalton Trans.* **1973**, 1484.

(13) Visscher, M. O.; Huffman, J. C.; Streib, W. E. *Inorg. Chem.* **1974**, *13*, 792.

(14) Malone, J. F. *J. Chem. Soc., Dalton Trans.* **1974**, 1699.

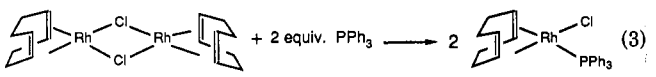
(15) Kinoshita, I.; Terai, Y.; Kashiwara, K.; Kido, H.; Saito, K. *J. Organomet. Chem.* **1977**, *127*, 237. Nelson, S. M.; Sloan, M.; Drew, M. G. B. *J. Chem. Soc., Dalton Trans.* **1973**, 2195. Cramer, R. *Inorg. Chem.* **1962**, *1*, 723.

(16) We cannot rule out the cis orientation of the amino olefin ligands.

The dimeric complexes were not stable in solution for more than a couple of hours at ambient temperature. The structures were confirmed by 270-MHz ^{1}H NMR analysis, which showed the absence of ethylene ligands, and mass spectral analysis, which showed molecular ions for the dimers (negative chemical ionization). In addition, a comparison of the ^{1}H NMR spectrum of the complexed and uncomplexed amine shows a downfield shift of the amino methylene protons and an upfield shift of the olefin protons. Both of the shifts support the proposed bidentate nature of the organic ligand.

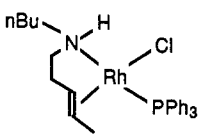
It is interesting to note that complexes **40** and **41** (entries 3 and 4, Table II) were readily formed at ambient temperature. However, formation of the analogous carbonyl complexes **30** and **31** (entries 12 and 13, Table I) required heating in $CHCl_3$ for 6–12 h. We feel that the lability of the ethylene vs carbon monoxide ligands is responsible for the dramatic effect.

Triphenylphosphine is known to cleave analogous diolefin chloro-bridged dimers to give monomeric complexes (eq 3).[6,17] Complex **38** reacted with triphenylphosphine



(3)

in anhydrous ether at ambient temperature and yielded a new monomeric Rh(I) complex **44** in 97% yield. The monomeric nature of the complex and the number and types of ligands have been confirmed by ^{1}H NMR and mass spectral analysis. However, the stereochemistry of the complex has not been determined. Reaction of complexes **40** or **42** with triphenylphosphine caused decomplexation of the olefin.



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Summary

Several different rhodium(I) complexes containing olefinic amine ligands have been prepared. We feel these new complexes will allow subsequent olefin functionalization in a regiospecific manner. Further results will be reported in due course.

Experimental Section

General Data. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled from potassium prior to each use. Methylene chloride (CH_2Cl_2) and pyridine were distilled from calcium hydride. Hexane, chloroform ($CHCl_3$), methanol (MeOH), and ethyl acetate (EtOAc) were distilled. Infrared spectra (IR) were obtained on a Perkin-Elmer 1320 infrared spectrophotometer. ^{1}H NMR spectra were obtained at 270 MHz on a Bruker WP270SY instrument. Chemical shifts are reported in parts per million downfield relative to tetramethylsilane (δ 0.00); coupling constants are reported in hertz. The following abbreviations are used for the multiplicities: s, singlet; b s, broad singlet; d, doublet; t, triplet; q, quartet; p, pentuplet; sex., sextet; m, multiplet. Low-resolution mass spectra were obtained on a Finnigan 4510 GC/MS instrument. High-resolution mass spectra were obtained on a AEI MS 902 instrument. Mass spectral data is reported as *m/e* (relative intensity). Chromatography refers to flash chromatography as reported by Still.[18] Melting points were taken on a Bristoline hostage microscope melting point apparatus. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.[19] Bis(μ-chloro)tetrakis(ethylene)dirhodium(I) (**4**) was prepared according to an established procedure.[20] All yields refer to isolated material. Rhodium trichloride was obtained from the Johnson Matthey Co. metal loan program.

Preparation of Bis(μ-chloro)tetracarbonyldirhodium(I) (3). Prepared as previously described,[21] 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 and then at 100 °C for 36 h. The water was not wiped out of the vessel as previously reported by Wilkinson.[21] 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.

Preparation of Rhodium(I) Carbonyl Complexes Listed in Table I. General Procedure A: Preparation of [*N*-(3-Butenyl)*n*-butylamine]carbonylrhodium(I) Chloride (21). To a stirred solution of **3** (194.4 mg, 0.5 mmol) in 15 mL of hexane was added 133.5 mg (1.05 mmol) of amine **7** in 1.5 mL of hexane. After stirring at 25 °C for 1 h, the solvent was removed in vacuo at 25 °C. Filtration through a 1-in. plug of silica gel using hexane/ethyl acetate (1:1) followed by solvent removal in vacuo at 25 °C gave 284.7 mg (97%) of complex **21** as a yellow precipitate: mp 119 °C; IR ($CHCl_3$) 3280, 3010, 2980, 2950, 2890, 2040, 1470, 1220, 1090 cm^{-1}; ^{1}H NMR δ 0.94 (t, 3 H, J = 7 Hz), 1.33 (sex., 2 H, J = 7.5 Hz), 1.57 (m, 2 H), 2.05 (d, 1 H, J = 16.5 Hz), 2.32 (dq, 1 H, J = 4 Hz, J = 12 Hz), 2.63 (m, 2 H), 2.86 (m, 2 H), 3.26 (dd, 2 H, J = 8 Hz, J = 14 Hz), 3.38 (b s, 1 H), 4.67 (m, 1 H); MS (EI), *m/e* (relative intensity) 293 (14, M$^+$), 265 (31), 227 (100), 185 (26), 158 (17), 126 (43), 103 (21), 86 (76), 55 (67). Anal. Calcd for $C_9H_{17}NORhCl$: C, 36.82; H, 5.84. Found: C, 36.88; H, 5.73.

[*N*-(*trans*-3-Pentenyl)*n*-butylamine]carbonylrhodium(I) Chloride (19). Reaction of 148.2 mg (1.05 mmol) of amine **5** and 194.4 mg of **3** gave 301.4 mg (98%) of complex **19** as orange-yellow crystals: mp 135 °C; IR ($CHCl_3$) 3290, 3020, 2980, 2950, 2030, 1460, 1390, 1230, 1140, 1115 cm^{-1}; ^{1}H NMR δ 0.97 (t, 3 H, J = 7 Hz), 1.36 (m, 2 H), 1.47 (m, 2 H), 1.7 (dd, 3 H, J = 6 Hz, J = 2.5 Hz), 2.1 (d, 1 H, J = 17.5 Hz), 2.25 (d, t, 1 H, J = 4 Hz, J = 11 Hz), 2.5 (m, 1 H), 2.67 (m, 1 H), 2.83 (m, 1 H), 3.05 (m, 1 H), 4.0 (dq, 1 H, J = 2.5 Hz, J = 6 Hz), 4.38 (d, 1 H, J = 12.5 Hz); MS (EI), *m/e* (relative intensity) 307 (3, M$^+$), 279 (3), 243 (5), 241 (16), 199 (4), 183 (2), 140 (5), 103 (3), 98 (8), 86 (100), 69 (14), 57 (14).

[*N*,*N*-Dimethyl(*trans*-3-pentenyl)amine]carbonylrhodium(I) Chloride (20). Reaction of 124.5 mg (1.1 mmol) of amine **6** and 194.4 mg of **3** gave 251.6 mg (90%) of complex **20** as a yellow solid: mp 126 °C; IR ($CHCl_3$) 3010, 2910, 2040, 1470, 1230, 1040, 1000, 940 cm^{-1}; ^{1}H NMR δ 1.7 (dd, 3 H, J = 2.5 Hz, J = 5.5 Hz), 2.0 (d, 1 H, J = 13.5 Hz), 2.2 (d, 1 H, J = 7 Hz), 2.5 (s, 3 H), 2.6 (s, 3 H), 2.6 (m, 2 H), 4.2 (m, 2 H); MS (EI), *m/e* (relative intensity) 279 (18, M$^+$), 251 (12), 215 (43), 211 (30), 103 (10), 58 (100). Anal. Calcd for $C_8H_{15}NORhCl$: C, 34.37; H, 5.41; N, 5.01. Found: C, 34.58; H, 5.36; N, 4.87.

[*N*,*N*-Dimethyl(3-butenyl)amine]carbonylrhodium(I) Chloride (22). Addition of 109 mg (1.1 mmol) of amine **8** to 194.4 mg of **3** gave 244.2 mg (92%) of complex **22** as pale yellow crystals: mp 114 °C; IR ($CHCl_3$) 3010, 2920, 2040, 1470, 1010, 980, 950 cm^{-1}; ^{1}H NMR δ 1.97 (d, 1 H, J = 15 Hz), 2.25 (d, 1 H, J = 8.5 Hz), 2.47 (s, 3 H), 2.57 (s, 3 H), 2.57 (m, 2 H), 3.43 (d, 3 H, J = 6 Hz), 3.46 (d, 1 H, J = 8 Hz), 4.48 (m, 1 H); MS (EI), *m/e* (relative intensity) 265 (54, M$^+$), 237 (55); 201 (100), 199 (75), 197 (95), 178 (37), 144 (22), 103 (27), 58 (59). Anal. Calcd for $C_7H_{13}NORhCl$: C, 31.66; H, 4.93. Found: C, 31.52; H, 5.14.

[*N*-(3-Methyl-3-butenyl)*n*-butylamine]carbonylrhodium(I) Chloride (23). Addition of 148.2 mg (1.05 mmol) of amine

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(18) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

(19) We were unable to recrystallize complexes **25**, **26**, **30**, **31**, and **44** without significant decomposition, and complexes **38–43** were stable in solution for only short periods of time; thus we were unable to obtain pure samples for analysis.

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

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

9 to 194.4 mg (0.5 mmol) of 3 gave 301.2 mg (98%) of complex 23 as a bright yellow solid: mp 137 °C; IR ($CHCl_3$) 3280, 3010, 2980, 2950, 2030, 1460, 1380, 1230, 1080, 1050, 1000 cm^{-1}; ^1H NMR δ 0.95 (t, 3 H, J = 8 Hz), 1.33 (sex., 2 H, J = 8 Hz), 1.5 (m, 1 H), 1.64 (m, 1 H), 1.86 (s, 3 H), 2.33 (t, 1 H, J = 13 Hz), 2.5 (m, 1 H), 2.67 (m, 1 H), 2.9 (m, 2 H), 3.15 (s, 1 H), 3.25 (s, 1 H) 3.36 (b s, 1 H); MS (EI), m/e (relative intensity) 307 (3, M^+), 279 (3), 241 (17), 197 (3), 171 (3), 140 (4), 103 (4), 98 (6), 86 (100), 69 (8), 57 (17). Anal. Calcd for $C_{10}H_{19}NORhCl$: C, 39.04; H, 6.23. Found: C, 39.08; H, 6.29.

[*N*,*N*-Dimethyl(3-methyl-3-butenyl)amine]carbonylrhodium(I) Chloride (24). Reaction of 124.5 mg (1.1 mmol) of amine 10 and 194.4 mg of 3 gave 271.2 mg (97%) of complex 24 as a light yellow solid: mp 162 °C; IR ($CHCl_3$) 3010, 2920, 2040, 1470, 1180, 1080 cm^{-1}; ^1H NMR δ 1.78 (s, 3 H), 1.81 (m, 1 H), 2.25 (dd, 1 H, J = 4.5 Hz, J = 12 Hz), 2.4 (s, 3 H), 2.4 (m, 1 H), 2.6 (s, 3 H), 2.6 (m, 1 H), 3.26 (s, 1 H), 3.4 (s, 1 H); MS (EI), m/e (relative intensity) 279 (34, M^+), 251 (33), 215 (76), 213 (62), 211 (100), 144 (22), 112 (12), 103 (16), 58 (53). Anal. Calcd for $C_8H_{15}NORhCl$: C, 34.37; H, 5.41. Found: C, 34.35; H, 5.78.

Trans α-β-Unsaturated Ester Complex 25. Addition of 92.6 mg (0.5 mmol) of amine 11 to 97.2 mg (0.25 mmol) of 3 gave complex 25 (170.3 mg, 98%) as a dark red oil: IR ($CHCl_3$) 3280, 3200, 3020, 2980, 2950, 2050, 1740, 1500, 1470, 1440, 1300, 1280, 1160, 1080, 1020 cm^{-1}. ^1H NMR δ 0.98 (t, 3 H, J = 7 Hz), 1.4 (sex., 2 H, J = 8 Hz), 1.6 (m, 2 H), 1.97 (d, 1 H, J = 17 Hz), 2.21 (dq, 1 H, J = 5 Hz, J = 12 Hz), 2.71 (m, 2 H), 2.97 (m, 2 H), 3.63 (s, 1 H), 3.73 (s, 3 H), 3.86 (dd, 1 H, J = 3 Hz, J = 12 Hz), 5.07 (d, 1 H, J = 12 Hz); MS (EI), m/e (relative intensity) 351 (1, M^+), 323 (14), 287 (16), 245 (10), 216 (6), 185 (2), 142 (7), 113 (7), 110 (8), 103 (2), 86 (100), 68 (3), 57 (10), 55 (11).[19]

[*N*-(3-Cyclohexenyl)*n*-butylamine]carbonylrhodium(I) Chloride (26). Reaction of 124.2 mg (0.81 mmol) of amine 12 and 155.5 mg (0.4 mmol) of 3 gave 250.8 mg (98%) of complex 26 as a yellow solid: mp 155 °C; IR ($CHCl_3$) 3280, 3010, 2980, 2950, 2030, 1460, 1230, 1090, 1040, 970 cm^{-1}; ^1H NMR δ 0.97 (t, 3 H, J = 7 Hz), 1.33 (m, 2 H), 1.5 (m, 2 H), 1.86 (m, 2 H), 2.05 (d, 1 H, J = 16 Hz), 2.4 (m, 3 H), 3.25 (m, 2 H), 3.4 (p, 1 H, J = 6.5 Hz), [4.3 (b s, major), 4.46 (b s; minor), 4.62 (b s, major)], 2 H (major/minor = ca. 5:1); MS (EI), m/e (relative intensity) 319 (1, M^+), 291 (1), 253 (8), 153 (16), 110 (21), 103 (3), 99 (37), 84 (100), 70 (15), 56 (67).[19]

[*N*-(4-Methyl-3-cyclohexenyl)*n*-butylamine]carbonylrhodium(I) Chloride (27). Reaction of 133.7 mg (0.8 mmol) of amine 13 and 155.5 mg (0.4 mmol) of 3 gave 222.2 mg (95%) of complex 27 as a dark yellow solid: mp 158 °C; IR ($CHCl_3$) 3280, 3010, 2980, 2950, 2020, 1460, 1390, 1090, 1060, 1040 cm^{-1}; ^1H NMR δ 0.97 (t, 3 H, J = 7 Hz), 1.4 (m, 2 H), 1.5 (m, 2 H), 1.71 (s, 3 H), 1.83 (m, 1 H), 2.1 (m, 2 H), 2.25 (d, 1 H, J = 16 Hz), 2.5 (m, 3 H), 3.1 (d, 1 H, J = 21 Hz), 3.46 (m, 1 H), [4.19 (b s, minor), 4.43 (b s, major)], 1 H (major/minor = 4:1); MS (EI), m/e (relative intensity) 333 (1, M^+), 305 (1), 267 (8), 167 (19), 124 (15), 120 (18), 103 (1), 99 (30), 84 (100), 70 (12), 57 (50). Anal. Calcd for $C_{12}H_{21}NORhCl$: C, 43.20; H, 6.34. Found: C, 43.23; H, 6.23.

[*N*-(3-Methyl-3-cyclohexenyl)*n*-butylamine]carbonylrhodium(I) Chloride (28). Addition of 133.7 mg (0.8 mmol) of amine 14 to 155.5 mg (0.4 mmol) of 3 resulted in the formation of complex 28 (258.4 mg, 97%) as a brownish yellow solid: mp 184 °C; IR ($CHCl_3$) 3280, 3010, 2980, 2950, 2100, 2030, 1460, 1380, 1060 cm^{-1}; ^1H NMR δ 0.93 (t, 3 H, J = 7 Hz), 1.33 (m, 2 H), 1.45 (m, 2 H), 1.75 (m, 2 H), 1.82 (s, 3 H), 1.87 (m, 1 H), 2.41 (m, 3 H), 3.09 (m, 1 H), 3.33 (m, 2 H), [4.13 (b s, major), 4.27 (b s, minor)], 1 H (major/minor = 6/1); MS (EI), m/e (relative intensity) 333 (1, M^+), 305 (2), 267 (13), 167 (37), 124 (19), 120 (19), 103 (10), 99 (27), 95 (21), 91 (22), 84 (100), 70 (13), 57 (54), 56 (61). Anal. Calcd for $C_{12}H_{21}NORhCl$: C, 43.20; H, 6.34. Found: C, 43.41; H, 6.37.

[*N*-(3-Cyclopentenyl)*n*-butylamine]carbonylrhodium(I) Chloride (29). Reaction of 30.6 mg (0.22 mmol) of amine 15 and 38.9 mg (0.10 mmol) of 3 gave complex 29 (58 mg, 98%) as an orange-yellow solid: mp 139 °C; IR ($CHCl_3$) 3290, 3010, 2980, 2950, 2040, 1470, 1290, 1230, 1090, 1040 cm^{-1}; ^1H NMR δ 0.93 (t, 3 H, J = 7.5 Hz), 1.35 (m, 2 H), 1.54 (m, 2 H), 1.61 (d, 1 H, J = 15 Hz), 1.83 (d, 1 H, J = 15 Hz), 2.39 (dd, 1 H, J = 9 Hz, J = 15 Hz), 3.11 (s, 2 H), 3.19 (m, 1 H), 4.44 (s, 1 H), 4.48 (s, 1 H); MS (EI), m/e (relative intensity) 305 (17, M^+), 277 (51), 239 (100), 237 (55), 178 (22), 168 (37), 139 (4), 138 (17), 131 (18), 103 (13), 67 (13). Anal. Calcd for $C_{10}H_{17}NORhCl$: C, 39.30; H, 5.61; N, 4.58. Found: C, 39.35; H, 5.90; N, 4.13.

General Procedure B: Preparation of [*N*-(4-Pentenyl)*n*-butylamine]carbonylrhodium(I) Chloride (31). To a stirred solution of 3 (194.4 mg, 0.5 mmol) in 15 mL of hexane was added 148.2 mg (1.05 mmol) of amine 17 in 2 mL of hexane over 1–2 min. After 30 min, the solvent was removed in vacuo, then 7 mL of chloroform ($CHCl_3$) and 7 mL of hexane were added, and again the solvent was removed in vacuo. This was repeated twice more, then 30 mL of $CHCl_3$ was added to the resulting brown oil, and the mixture was heated at 60 °C for 24 h. Then, the solvent was removed in vacuo at 25 °C, and the resulting brown solid was filtered through 2 in. of silica gel with hexane/EtOAc (1:1) to give 304.6 mg (99%) of an orange solid after solvent removal: mp 83 °C; IR ($CHCl_3$) 3250, 3010, 2980, 2950, 2040, 1460, 1230, 1130, 1080, 1030 cm^{-1}; ^1H NMR δ 0.96 (t, 3 H, J = 7.5 Hz), 1.46 (sex., 2 H, J = 7.5 Hz), 1.67 (m, 3 H), 1.93 (m, 1 H), 2.31 (m, 3 H), 2.69 (m, 2 H), 2.93 (m, 1 H), 3.11 (d, 1 H, J = 13 Hz), 3.44 (d, 1 H, J = 8 Hz), 4.69 (m, 1 H): MS (EI), m/e (relative intensity) 307 (3, M^+), 279 (4), 241 (24), 141 (2), 140 (14), 103 (4), 98 (86), 86 (100), 70 (20), 69 (20), 57 (18), 56 (17).[19]

[*N*-(*cis*-3-Pentenyl)*n*-butylamine]carbonylrhodium(I) Chloride (30). Following procedure B, 70.6 mg (0.5 mmol) of amine 16 and 97.2 mg (0.25 mmol) of 3 refluxed for 12 h gave 152.6 mg (99%) of a dark yellow solid: mp 107 °C; IR ($CHCl_3$) 3280, 3010, 2980, 2950, 2030, 1470, 1080, 1010 cm^{-1}; ^1H NMR δ 0.93 (t, 3 H, J = 7.5 Hz), 1.35 (p, 2 H, J = 7 Hz), 1.5 (m, 2 H), 1.83 (d, 3 H, J = 6.5 Hz), 2.22 (m, 1 H), 2.43 (m, 1 H), 2.65 (m, 2 H), 3.11 (m, 1 H), 3.25 (m, 1 H), 3.44 (s, 1 H), 4.15 (dq, 1 H, J = 7 Hz, J = 7 Hz), 4.61 (d, 1 H, J = 5.5 Hz); MS (EI), m/e (relative intensity) 307 (1, M^+), 279 (2), 241 (9), 141 (1), 140 (4), 103 (2), 100 (10), 98 (11), 86 (100), 69 (18), 57 (24).[19]

[*N*-[2-(1-Cyclohexenyl)ethyl]*n*-butylamine]carbonylrhodium(I) Chloride (32). Addition of 181.1 mg (1 mmol) of amine 18 to 194.4 mg (0.5 mmol) of complex 3, following procedure B, and refluxing in $CHCl_3$ for 6 h gave 316.7 mg (91%) of a brown-yellow solid: mp 168 °C; IR ($CHCl_3$) 3280, 3010, 2980, 2950, 2020, 1450, 1240, 1080, 1010, 930 cm^{-1}; ^1H NMR δ 0.93 (t, 3 H, J = 7 Hz), 1.35 (m, 4 H), 1.59 (m, 4 H), 1.89 (d, 1 H, J = 17 Hz), 2.19 (m, 2 H), 2.5 (m, 2 H), 2.8 (p, 1 H, J = 6 Hz), 3.0 (m, 2 H), 4.35 (s, 1 H); MS (EI), m/e (relative intensity) 347 (1, M^+), 319 (0.2), 277 (9), 181 (6), 136 (9), 103 (0.2), 86 (100), 67 (4), 57 (12). Anal. Calcd for $C_{13}H_{23}RhClNO$: C, 44.91; H, 6.67. Found: C, 44.95; H, 6.67.

Rhodium(I) Dimeric Complexes from Table II. General Procedure: Preparation of Bis(μ-chloro)bis[*N*-(3-butenyl)*n*-butylamine]dirhodium(I) (39). Amine 7 (16.4 mg, 0.129 mmol) was added, in 0.5 mL of Et_2O, to a stirred solution of complex 4 (25 mg, 0.65 mmol) in Et_2O (2 mL) at 25 °C. After 20 min, the solvent was removed in vacuo at 25 °C, and the resulting oil was filtered through Celite with Et_2O giving 33.6 mg (98%) of a dark orange oil after solvent removal in vacuo at 25 °C: IR ($CHCl_3$) 3280, 3010, 2980, 2950, 1610, 1460, 1220, 1140, 1080, 910 cm^{-1}; ^1H NMR δ 0.97 (t, 3 H, J = 7 Hz), 1.36 (sex, 2 H, J = 8 Hz), 1.53 (d, 1 H, J = 8 Hz), 1.6 (m, 1 H), 2.26 (m, 1 H), 2.47 (m, 1 H), 2.83 (m, 3 H), 3.03 (m, 1 H), 3.2 (dd, 1 H, J = 4 Hz, J = 10 Hz), 3.43 (m, 1 H), 3.71 (m, 1 H), MS (EI), m/e (relative intensity) 530 (0.12, M^+), 392 (6), 293 (20), 265 (53), 227 (100), 185 (35), 171 (17), 158 (23), 140 (23), 127 (18), 126 (61), 103 (15). Complexes 38–43 were synthesized by using this procedure.[19]

Bis(μ-chloro)bis[*N*-(*trans*-3-pentenyl)*n*-butylamine]dirhodium(I) (38). Addition of amine 5 (18.2 mg, 0.129 mmol) to complex 4 (25 mg, 0.065 mmol) yielded 36.5 mg (99%) of a dark orange oil: IR ($CHCl_3$) 3280, 3010, 2980, 2950, 1470, 1230, 1100, 1040, 1020 cm^{-1}; ^1H NMR δ 0.76 (d, 3 H, J = 4 Hz), 0.85 (t, 3 H, J = 7.5 Hz), 1.26 (m, 3 H), 1.57 (m, 1 H), 1.71 (dd, 1 H, J = 4 Hz, J = 16 Hz), 2.12 (dq, 1 H, J = 4.5 Hz, J = 11.5 Hz), 2.53 (m, 2 H), 2.97 (m, 1 H), 3.12 (d, 1 H, J = 9 Hz), 3.33 (m, 2 H); MS (NCI), m/e (relative intensity) 558 (1, M^+), 254 (5), 417 (8), 304 (9), 279 (100), 176 (58), 174 (91), 168 (32), 166 (94), 142 (1), 140 (4).[19]

Bis(μ-chloro)bis[*N*-(*cis*-3-pentenyl)*n*-butylamine]dirhodium(I) (40). Addition of amine 16 (18.2 mg, 0.129 mmol) to complex 4 (25 mg, 0.065 mmol) yielded 36.6 mg (99%) of an orange oil: IR ($CHCl_3$) 3280, 3010, 2980, 2950, 1470, 1370, 1230,

Table III. Fractional Atomic Coordinated (×10⁴) for the Non-Hydrogen Atoms with Estimated Standard Deviations in Parentheses

atom	x/a	y/b	z/c
Rh(1)	8768.6 (5)	4743 (1)	2542.7 (4)
Cl(1)	8465 (2)	2448 (3)	1777 (2)
N(1)	8754 (5)	6111 (10)	1641 (4)
C(2)	8773 (7)	7859 (13)	1786 (6)
C(3)	8337 (8)	8130 (14)	2246 (7)
C(4)	8697 (7)	7037 (14)	2948 (6)
C(5)	9560 (7)	6534 (14)	3336 (6)
C(6)	10048 (11)	6109 (18)	4189 (7)
C(7)	9370 (7)	5621 (15)	1375 (7)
C(8)	9099 (8)	6153 (18)	577 (7)
C(9)	8301 (9)	5228 (20)	-56 (8)
C(10)	8070 (12)	5566 (25)	-860 (8)
C(11)	8705 (8)	3690 (15)	3293 (6)
O(12)	8599 (7)	3015 (15)	3730 (5)
Rh(2)	6138.2 (5)	4536 (1)	1301.1 (4)
Cl(2)	8465 (2)	2448 (3)	1777 (1)
N(1′)	6288 (5)	2480 (11)	784 (5)
C(2′)	6243 (7)	1053 (14)	1188 (7)
C(3′)	6526 (8)	1426 (15)	1981 (7)
C(4′)	6120 (8)	2878 (15)	2065 (6)
C(5′)	5250 (7)	3298 (16)	1534 (6)
C(6′)	4674 (8)	4282 (21)	1749 (8)
C(7′)	5790 (7)	2357 (16)	-69 (6)
C(8′)	6017 (8)	1009 (17)	-419 (7)
C(9′)	6883 (9)	1153 (20)	-361 (9)
C(10′)	7130 (9)	-245 (23)	-692 (8)
C(11′)	6158 (7)	6310 (14)	1857 (5)
O(12′)	6198 (7)	7375 (12)	2200 (5)

1080, 1050, 1010, 910 cm^{-1}; ^{1}H NMR δ 0.80 (t, 3 H, J = 7 Hz), 1.2 (m, 2 H), 1.53 (d, 3 H, J = 7 Hz), 1.7 (m, 2 H), 2.36 (m, 2 H), 2.65 (m, 1 H), 2.97 (m, 1 H), 3.3 (m, 2 H), 3.48 (b s, 1 H), 3.7 (b s, 1 H); MS (NCI), m/e (relative intensity) 558 (0.3, M$^+$), 417 (5), 304 (7), 279 (100), 176 (11), 174 (14), 168 (36), 166 (98), 142 (3), 140 (9).[19]

Bis(μ-chloro)bis[*N*-(4-pentenyl)*n*-butylamine]dirhodium(I) (41). Addition of amine **17** (18.2 mg, 0.129 mmol) to complex **4** (25 mg, 0.65 mmol) yielded 33.6 mg (93%) of an orange oil: IR ($CHCl_3$) 3280, 3010, 2980, 2950, 1470, 1440, 1230, 1130, 1080, 1030 cm^{-1}; ^{1}H NMR δ 0.97 (t, 3 H, J = 7 Hz), 1.47 (m, 3 H), 1.75 (m, 1 H), 1.86 (d, 1 H, J = 18 Hz), 2.12 (d, 1 H, J = 8 Hz), 2.25 (m, 2 H), 2.57 (d, 1 H, J = 12.5 Hz), 2.78 (m, 1 H), 2.83 (d, 1 H, J = 12 Hz), 3.0 (m, 1 H), 3.2 (s, 1 H), 3.3 (s, 1 H), 3.85 (s, 1 H); MS (NCI) m/e (relative intensity) 558 (1.6, M$^+$), 417 (13), 304 (19), 280 (100), 176 (15), 174 (21), 168 (24), 166 (41), 142 (5), 140 (13).[19]

Bis(μ-chloro)bis[*N*-(4-methyl-3-cyclohexenyl)*n*-butylamine]dirhodium(I) (42). Addition of amine **14** (21.6 mg, 0.129 mmol) to complex **4** (25 mg, 0.065 mmol) yielded 38.1 mg (97%) of a yellow solid: mp 141 °C dec; IR ($CHCl_3$) 3290, 3020, 2990, 2950, 2900, 1470, 1390, 1150, 1090, 1050, 1030, 920 cm^{-1}; ^{1}H NMR δ 0.80 (s, 3 H), 0.92 (t, 3 H, J = 7 Hz), 1.47 (m, 6 H), 1.8 (m, 2 H), 2.35 (d, 1 H, J = 15.5 Hz), 2.52 (p, 1 H, J = 9 Hz), 3.0 (b s, 1 H), 3.13 (b s, 1 H), 3.47 (m, 2 H); MS (NCI), m/e (relative intensity) 610 (0.02, M$^+$), 307 (1.2), 305 (3.7), 203 (3), 201 (5), 176 (4), 174 (6), 170 (13), 168 (52), 166 (100).[19]

Bis(μ-chloro)bis[*N*,*N*-dimethyl(3-cyclohexenyl)amine]dirhodium(I) (43). Addition of amine **37** (16.1 mg, 0.129 mmol) to complex **4** (25 mg, 0.065 mmol) gave 33.9 mg (99%) of an orange-yellow solid: mp 143 °C dec; IR ($CHCl_3$) 3010, 2990, 2920, 1470, 1220, 1160, 1080, 1020, 970, 920 cm^{-1}; ^{1}H NMR δ 1.47 (m, 2 H), 1.9 (m, 1 H), 2.07 (dq, 2 H, J = 5 Hz, J = 19 Hz), 2.47 (m, 2 H), 2.53 (s, 3 H), 2.76 (s, 3 H), 3.17 (s, 2 H), 3.38 (s, 1 H); MS (NCI), m/e (relative intensity) 528 (0.1, M$^+$), 401 (4), 304 (39), 263 (17), 176 (38), 174 (53), 168 (69), 166 (100).[19]

Preparation of Triphenylphosphine Olefinic Amine Complex 44. Complex **39** was prepared in solution as described previously. To a stirred solution of 25 mg (0.065 mmol) of complex **4** in 2 mL of Et_2O was added 16.4 mg (0.13 mmol) of amine **7** in 0.5 mL of Et_2O at 25 °C. After 20 min, 33.8 mg (0.13 mmol) of triphenylphosphine in 0.5 mL of Et_2O was added and stirring continued for 1 h. The solvent was then removed to give 65.8 mg (97%) of a pale orange solid: mp 102 °C; IR ($CHCl_3$) 3080,

Table IV. Interatomic Bond Lengths (Å) and Valency Angles (deg) with Estimated Standard Deviations in Parentheses

	unprimed	primed
	(a) Bond Lengths	
Rh-Cl	2.363 (3)	2.379 (3)
Rh-N(1)	2.141 (9)	2.108 (9)
Rh-C(4)	2.130 (12)	2.091 (13)
Rh-C(5)	2.132 (12)	2.127 (13)
Rh-C(11)	1.804 (13)	1.860 (12)
N(1)-C(2)	1.50 (1)	1.48 (2)
N(1)-C(7)	1.50 (1)	1.49 (2)
C(2)-C(3)	1.49 (2)	1.45 (2)
C(3)-C(4)	1.53 (2)	1.47 (2)
C(4)-C(5)	1.39 (2)	1.41 (2)
C(5)-C(6)	1.53 (2)	1.54 (2)
C(7)-C(8)	1.49 (2)	1.50 (2)
C(8)-C(9)	1.55 (2)	1.48 (2)
C(9)-C(10)	1.48 (2)	1.52 (2)
C(11)-O(12)	1.14 (2)	1.11 (2)
	(b) Bond Angles	
Cl-Rh-N(1)	89.3 (2)	89.6 (3)
Cl-Rh-C(4)	163.2 (3)	164.3 (4)
Cl-Rh-C(5)	156.6 (3)	155.1 (3)
Cl-Rh-C(11)	93.0 (4)	90.7 (4)
N(1)-Rh-C(4)	81.8 (4)	82.2 (4)
N(1)-Rh-C(5)	88.6 (4)	89.7 (4)
N(1)-Rh-C(11)	175.2 (5)	172.5 (4)
C(4)-Rh-C(5)	38.0 (5)	39.0 (5)
C(4)-Rh-C(11)	94.9 (5)	95.7 (5)
C(5)-Rh-C(11)	91.0 (5)	93.1 (5)
Rh-N(1)-C(2)	112.1 (6)	110.2 (7)
Rh-N(1)-C(7)	117.1 (7)	118.6 (7)
C(2)-N(1)-C(7)	113.1 (8)	114.4 (9)
N(1)-C(2)-C(3)	107.7 (9)	110.2 (10)
C(2)-C(3)-C(4)	112.1 (10)	112.9 (11)
Rh-C(4)-C(3)	105.7 (8)	106.5 (9)
Rh-C(4)-C(5)	71.1 (7)	71.9 (7)
C(3)-C(4)-C(5)	122.1 (11)	122.2 (11)
Rh-C(5)-C(4)	70.9 (7)	69.1 (7)
Rh-C(5)-C(6)	117.5 (9)	117.8 (10)
C(4)-C(5)-C(6)	122.9 (12)	123.3 (11)
N(1)-C(7)-C(8)	113.9 (10)	116.9 (11)
C(7)-C(8)-C(9)	113.4 (12)	114.4 (12)
C(8)-C(9)-C(10)	115.8 (14)	114.5 (14)
Rh-C(11)-O(12)	174.9 (13)	177.7 (12)

3020, 2980, 2960, 2900, 1660, 1490, 1450, 1130, 1110, 700 cm^{-1}; ^{1}H NMR δ 0.91 (m, 4 H), 1.26 (m, 3 H), 1.53 (m, 1 H), 1.97 (m, 1 H), 2.25 (m, 2 H), 2.63 (m, 1 H), 3.03 (m, 1 H), 3.76 (m, 1 H), 4.16 (d, 1 H, J = 10 Hz), 4.33 (s, 1 H), 7.4 (m, 10 H), 7.63 (m, 5 H); MS (EI) m/e (relative intensity) 527 (3, M$^+$), 287 (6), 286 (18), 285 (3), 284 (3), 278 (5), 277 (9), 263 (6), 262 (20), 185 (4), 184 (6), 183 (24), 154 (10), 152 (5), 127 (11), 126 (100), 103 (1), 86 (8), 84 (6), 78 (8), 55 (6).[19]

Crystal Data: $C_{10}H_{20}ClNORh$; M_r 308.6; monoclinic; a = 17.699 (5), b = 8.442 (1), c = 20.119 (5) Å; β = 120.19 (2)°; U = 2598.3 (9) Å^3, Z = 8, D_{calcd} = 1.578 g/cm^3, $F(000)$ = 1256; Mo Kα radiation (λ = 0.710 69 Å); μ = 1.5 cm^{-1}; space group $P2_1/c$ (C_{2h}^5) from systematic absences $0k0$ when $k \neq 2n$ and $h0l$ when $l \neq 2n$.

Collection and Reduction of X-ray Data. A crystal of dimensions 0.10 × 0.20 × 0.35 mm was mounted on a glass fiber and attached to an automated Syntex $P2_1$ diffractometer. Cell constants were obtained, at room temperature, from a least-squares fit of setting angles for 15 reflections. A quandrant of data ($h,k,\pm l$; $1.0° \leq 2\theta \leq 50°$) was measured. Of the 3586 independent reflections, 2432 were regarded as observed ($I \geq 3\sigma(I)$). Empirical absorption corrections were made to the data via a ψ scan using the 0,-2,0 reflection whose I/I(max) ranged from 0.77 to 1.0.

Structure Solution and Refinement. The structure was solved by Patterson and F_o Fourier methods. Hydrogen atom positions were calculated, and isotropic thermal parameters were assigned based on the thermal parameter of the atom to which each hydrogen was bonded. Full-matrix least-squares iterations on all positional parameters and anisotropic thermal parameters

for non-hydrogen atoms brought refinement to convergence at $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.052$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum|F_o|^2]^{1/2} = 0.061$. The least-squares weighting that was used was $w^{1/2} = 1$ for $|F_o| \leq 46.0$ and $w^{1/2} = 46.0/|F_o|$ for $|F_o| \geq 46.0$. The atomic scattering factors for the non-hydrogen atoms were those from Cromer and Waber;[22] those for hydrogen atoms were from Stewart.[23] Anomalous dispersion factors for the Rh atoms were from ref 24. All calculations were performed on a VAX 8650 computer or a μVAX-II.

There are two, very similar, independent molecules in the asymmetric unit. The atomic coordinates are recorded in Table III, and bond lengths and angles are given in Table IV.

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Registry No. **3**, 14523-22-9; **4**, 12081-16-2; **5**, 85288-96-6; **6**, 87156-72-7; **7**, 18903-55-4; **8**, 55831-89-5; **9**, 116669-56-8; **10**, 17945-72-1; **11**, 116669-57-9; **12**, 116669-58-0; **13**, 116669-59-1; **14**, 116669-60-4; **15**, 116669-61-5; **16**, 85288-95-5; **17**, 28031-49-4; **18**, 116669-62-6; **19**, 116698-91-0; **20**, 116698-92-1; **21**, 116698-93-2; **22**, 116698-94-3; **23**, 116698-95-4; **24**, 116698-96-5; **25**, 116698-97-6; **26** (isomer 1), 116699-08-2; **26** (isomer 2), 116836-58-9; **27** (isomer 1), 116699-09-3; **27** (isomer 2), 116781-94-3; **28** (isomer 1), 116836-57-8; **28** (isomer 2), 116699-10-6; **29**, 116698-98-7; **30**, 116781-92-1; **31**, 116698-99-8; **32**, 116699-00-4; **33** ($n = 1$, $R_1 = Me$, $R_2 = H$), 116699-01-5; **33** ($R_1 = R_2 = H$, $n = 3$), 116699-02-6; **33** ($R_1 = H$, $R_2 = (CH_2)_4-$, $n = 1$), 116699-03-7; **33** ($R_1 = R_2 = Me$, $n = 1$), 116699-07-1; **34**, 116669-63-7; **37**, 116599-60-1; **38**, 116699-04-8; **39**, 116699-05-9; **40**, 116781-93-2; **41**, 116724-43-7; **42**, 116724-44-8; **43**, 116747-04-7; **44**, 116699-06-0; $RhCl_3$, 10049-07-7.

Supplementary Material Available: Listings of anisotropic thermal parameters for non-hydrogen atoms and refined hydrogen atom positional parameters (3 pages); a listing of observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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Interesting Bonding between the Inverted Germanium Atoms in Pentagerma[1.1.1]propellane and Derivatives. A Theoretical Study

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The unique Ge–Ge central bonding in the title compounds are characterized by means of ab initio calculations and a π-complex model. It is found that electron-accepting substituents at the peripheral positions have an important effect on the bond lengths. Especially interesting is the trioxa substitution which leads to an unusual bond shortening.

Among strained compounds, [1.1.1]propellane having three three-membered rings fused to a common carbon–carbon bond is a most intriguing species because of its unusual structure with "inverted" tetrahedral configurations at the bridgehead carbon atoms;[1] the nature of the interesting interbridgehead C–C bonding has repeatedly been debated.[2] The structures and properties of the silicon analogues have been investigated in the last year.[3-6] We report now several interesting features of the germanium analogues pentagerma[1.1.1]propellane (1) and its derivatives by means of ab initio calculations. Our primary concern is on the characterization of the central Ge–Ge bridge bonding between the inverted tetracoordinate germanium atoms because of growing interest. Geometries were fully optimized at the Hartree–Fock (HF) level with the split-valence d-polarized 3-21G(d) and 3-21G(2d) basis sets.[7,8] For uniform comparison, all values cited here are

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