over $MgSO_4$, filtered through a plug of flash silica gel (5 × 15 mm), and evaporated to give a yellow oil that was nearly tin free by ^1H NMR spectroscopy. Purification of this material by flash chromatography (15 × 150 column; 1.25:1 hexanes/Et_2O) afforded a clear, glassy oil (39 mg, 48%): $[\alpha]^{21}_D = -52.9°$ (c 1.95, $CHCl_3$); IR (thin film) 2959, 1690, 1455, 1244, 1147 cm^{-1}; ^1H NMR δ 1.11–1.18 (m, 1), 1.14 (s, 3), 1.28 (s, 3), 1.33 (s, 3), 1.27–1.46 (m, 6), 1.79 (d, 1, $J = -12.9$), 2.11–2.17 (m, 2), 2.91 (d, 1, $J = -14.2$), 3.04 (d, 1, $J = -13.9$), 3.06 (dd, 1, $J = -13.6$, 1.4), 3.81–3.87 (m, 1), 3.96 (dd, 1, $J = -13.6$, 2.3), 4.50 (d, 1, $J = 1.9$), 4.74 (d, 1, $J = 1.8$), 7.21–7.25 (m, 2), 7.41–7.46 (m, 1), 7.54–7.60 (m, 1); ^{13}C NMR δ 24.17, 26.40, 30.03, 30.47, 33.27, 37.40, 41.55, 44.01, 46.63, 47.14, 51.64, 56.10, 106.60, 110.48, 119.83, 124.23, 124.64, 128.63, 141.03, 150.43, 152.31, 170.05, 176.06, 177.78; MS calcd for $C_{25}H_{30}N_2O_5$ 406.2256, found 406.2256.

***cis*-2-[(Phenylseleno)methyl]cyclopentanecarboxylic Acid (28).** This procedure is based on that of Smith and co-workers.[26] A solution of diphenyl diselenide (312 mg, 1.00 mmol) in DMF (5 mL) was purged with Ar for 20 min and then $NaBH_4$ (85 mg, 2.25 mmol) was added. The solution was slowly heated in an oil bath to 100 °C, and the lactone **27**[27] (225 mg, 1.78 mmol) in DMF (1.0 mL) was added by syringe. The temperature of the bath was raised to 120 °C and maintained at this temperature for 4 h. The mixture was cooled, diluted with Et_2O (100 mL), washed with 1 M HCl and brine (25 mL each), dried over $MgSO_4$, and evaporated to give a yellow-orange oil (640 mg). Flash chromatography of this oil (20 × 150 mm column, 2:1 hexanes/EtOAc) yielded a pale yellow oil (278 mg, 55%) that crystallized upon standing. ^1H NMR analysis of this material indicated contamination with ~5% of the starting lactone **27**. An analytical sample of **28** was prepared by trituration of the solid with pentane to give a white solid: mp 70–71 °C. IR (thin film) 2953, 1698, 733, 689 cm^{-1}; ^1H NMR δ 1.57–1.72 (m, 2), 1.79–2.07 (m, 4), 2.39–2.51 (m, 1), 2.88 (AMX, 1, $J_{AM} = -12.0$, $J_{AX} = 9.6$), 2.91–3.00 (m, 1), 3.16 (AMX, 1, $J_{AM} = -12.0$, $J_{MX} = 6.0$), 7.23–7.29 (m, 3), 7.48–7.52 (m, 2); ^{13}C NMR δ 23.49, 28.51, 29.22, 31.55, 43.68, 47.79, 126.79, 129.04, 130.22, 132.49, 181.49; MS calcd for $C_{13}H_{17}O_2Se$ 284.0316, found 284.0316.

Authentic Mixture of Diastereomers of 25. To a stirred solution of the acid **28** (21 mg, 0.075 mmol) in Et_2O (0.5 mL) at 0 °C was added Et_3N (15 μL, 11 mg, 0.11 mmol) and isobutyl chloroformate (10 μL, 10.5 mg, 0.077 mmol) by syringe. After 0.75 h, the mixture was filtered through Celite to remove the $Et_3N{\cdot}HCl$. The solid was washed with a small portion of dry Et_2O, and the combined filtrates were concentrated. In a separate flask, a solution of *rac*-**5** (22 mg, 0.075 mmol) in THF (0.5 mL) at −78 °C was treated with n-BuLi (46 μL, 1.8 M, 0.08 mmol) and allowed to stir for 0.5 h at −78 °C. A solution of the above mixed anhydride in THF (0.3 mL) was then added, and the mixture was maintained at −78 °C for 0.5 h and at 0 °C for 0.5 h. The reaction was quenched with saturated aqueous NH_4Cl (10 drops) and concentrated. The residue was partitioned between Et_2O (10 mL) and saturated aqueous $NaHCO_3$ (3 mL). The layers were separated, and the organic layer was washed with saturated aqueous $NaHCO_3$ and brine (3 mL each), dried over $MgSO_4$, and evaporated to give a clear glass (37 mg, 88%) that was used without further purification.

The material was dissolved in THF (1.0 mL), cooled to 0 °C, and 30% H_2O_2 (20 μL, 0.20 mmol) was added. The cold bath was removed and the reaction was allowed to stand for 23 h at ambient temperature. The reaction mixture was partitioned between Et_2O (10 mL) and H_2O (3 mL), the layers were separated, and the aqueous layer was extracted with Et_2O (5 mL). The combined organic layers were washed with brine (3 mL), dried over $MgSO_4$, and evaporated to give a clear oil (30 mg). Purification of this oil by flash chromatography (10 × 160 mm column, 5:2 hexanes/EtOAc) afforded **25** as a clear oil (6 mg, 10%) that consisted of a 2:1 mixture of diastereomers. The minor diastereomer corresponds to the major diastereomer obtained in the radical annulation: ^1H NMR (major diastereomer) δ 1.14–1.21 (m, 1), 1.17 (s, 3), 1.30 (s, 3), 1.35 (s, 3), 1.30–1.49 (m, 6), 1.79 (d, 1, $J = -12.9$), 2.14–2.20 (m, 2), 2.94 (d, 1, $J = -14.2$), 3.07 (d, 1, $J = -14.5$), 3.12 (d, 1, $J = -13.8$), 3.23 (d, 1, $J = 1.7$), 3.68–3.74 (m, 1), 3.92 (dd, 1, $J = -13.7$, 2.2), 4.41 (d, 1, $J = 1.4$), 7.22–7.26 (m, 2), 7.43–7.48 (m, 1), 7.57–7.62 (m, 1); ^1H NMR (minor diastereomer) δ 1.14–1.21 (m, 1), 1.17 (s, 3), 1.30 (s, 3), 1.35 (s, 3), 1.30–1.49 (m, 6), 1.79 (d, 1, $J = -12.9$), 2.09–2.15 (m, 2), 2.94 (d, 1, $J = -14.2$), 3.07 (d, 1, $J = -13.9$), 3.09 (d, 1, $J = -13.6$), 3.83–3.89 (m, 1), 3.98 (dd, 1, $J = -13.6$, 2.3), 4.50 (d, 1, $J = 1.9$), 4.74 (d, 1, $J = 1.8$), 7.22–7.26 (m, 2), 7.43–7.48 (m, 1), 7.57–7.62 (m, 1).

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Supplementary Material Available: Full details for the modified preparation of Kemp's triacid, a complete summary of the crystal structure determination of (S)-**6**, and a tabulation of the results of MM2 calculations on **7** (24 pages); tables of observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.

Regioselective Synthesis of Piperidinones by Metal Catalyzed Ring Expansion–Carbonylation Reactions. Remarkable Cobalt and/or Ruthenium Carbonyl Catalyzed Rearrangement and Cyclization Reactions

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Abstract: Carbonylation of pyrrolidines, catalyzed by cobalt carbonyl, results in the formation of piperidinones. The reaction is regiospecific in most cases, and the yield of product is increased when ruthenium carbonyl is present as a second catalyst. The dual catalytic system $[Co_2(CO)_8/Ru_3(CO)_{12}]$ is useful for the novel rearrangement of heterocyclic nitrogen ketones $[\overline{(CH_2)_nN}CH_2COR$, $n = 4$–$7]$ to lactams in 72–93% yields. An unusual metal catalyzed cyclization reaction of 2,6-dimethylpiperidinyl ketones afforded 5,6,7,8-tetrahydroindolizines in 86–94% yields.

Carbonylation based methodologies for the construction of lactams have attracted considerable interest in recent years.[1,2] Both stoichiometric and catalytic processes have been developed including, among others, the photochemical reaction of carbene chromium complexes with imines to give β-lactams in good yields[3] and the cyclization of N-alkyl-2-bromophenethylamines with carbon monoxide to form tetrahydroisoquinol-1-ones, a reaction catalyzed by palladium acetate in the presence of triphenylphosphine.[4]

(1) Colquhoun, H. M.; Thompson, D. G.; Twigg, M. V. *Carbonylation*; Plenum Press: New York, 1991; pp 191–203.
(2) Barrett, A. G. M.; Sturgess, M. A. *Tetrahedron* **1988**, *44*, 5615.
(3) Hegedus, L. S.; Imwinkelreid, R.; Alarid-Sargent, M.; Dvorak, D.; Satoh, Y. *J. Am. Chem. Soc.* **1990**, *112*, 1109.
(4) Mori, M.; Chiba, K.; Ban, Y. *J. Org. Chem.* **1978**, *43*, 1684.

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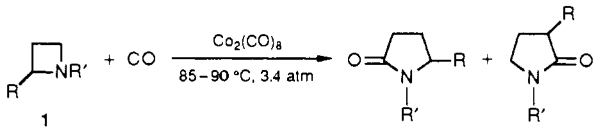
A different strategy for the synthesis of lactams involves the metal catalyzed "stitching" of carbon monoxide into a nitrogen heterocycle. Aziridines react in a stereospecific and enantiospecific manner with carbon monoxide and a rhodium(I) catalyst to give β-lactams in excellent yields.[5] This reaction occurs when a substituent having π-electrons (e.g., phenyl) is located at the 2-position of the aziridine ring, but not with simple alkylaziridines. In contrast, pyrrolidinones are obtained by cobalt carbonyl catalyzed carbonylation of alkyl, aryl, and other substituted azetidines with the regiospecificity in the case of alkylazetidines being opposite to that of arylazetidines. For example, the pyrrolidinone (*2*, R = CH_3, R′ = $C(CH_3)_3$) was isolated in 83% yield by $Co_2(CO)_8$ catalyzed carbonylation of **1** (R = CH_3, R′ = $C(CH_3)_3$) while the related phenyl containing azetidine **1** (R = Ph, R′ = CH_3) afforded **3** (R = Ph, R′ = CH_3) in 90% yield and traces of isomer **2**.[6]

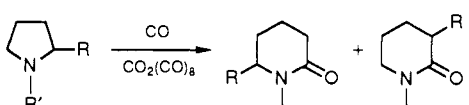


1 2 3

Azametallacycles are believed to be involved in the cobalt and rhodium catalyzed reactions. It was interesting to learn whether pyrrolidines could experience expansion to piperidinones since azametallacycloheptanes are potential intermediates, assuming an analogous mechanistic pathway. We now wish to report that use of $Co_2(CO)_8$ results in catalysis of the carbonylation of a series of pyrrolidines, with excellent regiochemical control being realized in nearly all cases. During this investigation, a remarkable rearrangement process was discovered which occurs with appropriately substituted pyrrolidines and other nitrogen heterocycles, using catalytic quantities of *both* cobalt and ruthenium carbonyls. A novel cyclization reaction was also observed during pursuit of mechanistic information for the rearrangement reaction.

Results and Discussion

Reaction of 1-methyl-2-phenylpyrrolidine (**4a**, R = Ph, R′ = CH_3) with carbon monoxide and cobalt carbonyl in dry benzene, for 72 h at 220 °C and 54 atm, afforded 1-methyl-3-phenylpiperidin-2-one (**6a**) in 56% yield of analytically pure material. The structure of **6a** was assigned on the basis of analytical and

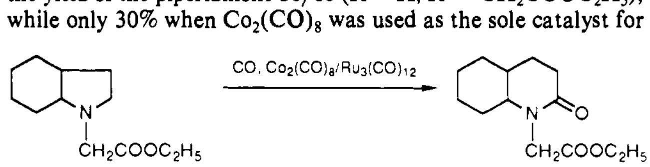


4a–f 5a–f 6a–f

a, R = Ph, R′ = CH_3; **b**, R = CH_2Ph, R′ = CH_3; **c**, R = CH_2OCH_3, R′ = $CH_2COOC_2H_5$; **d**, R = CH_2OCH_3, R′ = $CH_2COC(CH_3)_3$; **e**, R = H, R′ = $CH_2COOC_2H_5$; **f**, R = H, R′ = $CH_2COC(CH_3)_3$

spectral data (see Experimental Section). Nuclear magnetic resonance (NMR) results were especially helpful for assigning structure, e.g., the proton NMR gave a triplet at δ 3.63 due to the methine proton at C3. If isomer **5a** was formed, the signal for the methine proton at the 6-position would occur at lower field.

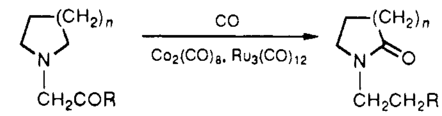
When the benzyl analog **4b** was employed as the substrate, **5b** and **6b** were isolated in a ratio of 1.5/1.0. The process is regiospecific for two pyrrolidines having a methoxymethyl substituent at the 2-position (i.e., **4c** or **4d**), with insertion occurring solely into the least substituted ring C–N bond. The observed regiochemistry is in accord with that found for the analogous azetidines.[6] Also consistent with previous findings, for a bicyclic azetidine, the perhydroindole **7** underwent regiospecific carbonylation to **8** in 46% yield. However, it was gratifying to find that the yield of **8** increased appreciably (to 79%) using a dual catalytic system consisting of cobalt and ruthenium carbonyls. Similarly, the yield of the piperidinone **5e/6e** (R = H, R′ = $CH_2COOC_2H_5$), while only 30% when $Co_2(CO)_8$ was used as the sole catalyst for



7 8

the carbonylation of **4e**, rose to 67% with $Co_2(CO)_8/Ru_3(CO)_{12}$. Such a dual catalytic system was shown to be effective for the conversion of oxetanes and thietanes to lactones and thiolactones, respectively.[7] Normal ring expansion occurred when 1-pyrrolidinyl-3,3-dimethyl-2-butanone (**4f**) was carbonylated in the presence of $Co_2(CO)_8$, affording **5f** in 42% yield. However, a remarkable rearrangement took place when the reaction was repeated with both $Co_2(CO)_8$ and $Ru_3(CO)_{12}$ as catalysts. In this case, 1-(3,3-dimethyl-1-butyl)pyrrolidinone (**10a**, R = $C(CH_3)_3$, *n* = 1) was isolated in 72% yield, with none of the ring expansion product (**5/6**) formed in the reaction. No reaction occurs with $Ru_3(CO)_{12}$ as the only catalyst.

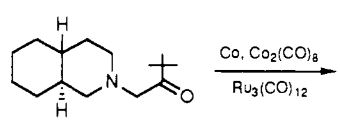
The novel rearrangement reaction is of general utility, being applicable to heterocycles containing either aliphatic or aromatic ketone side chain groups (i.e., **9a–i**). The results demonstrate the applicability of the reaction to 5–8-membered-ring nitrogen



9a–i 10a–i

a, *n* = 1, R = $C(CH_3)_3$; **b**, *n* = 2, R = $C(CH_3)_3$; **c**, *n* = 2, R = Ph; **d**, *n* = 2, R = *n*-C_6H_{13}; **e**, *n* = 2, R = 2-$C_{10}H_7$; **f**, *n* = 3, R = $C(CH_3)_3$; **g**, *n* = 3, R = Ph; **h**, *n* = 4, R = $C(CH_3)_3$; **i**, *n* = 4, R = Ph

heterocycles affording rearranged products in excellent yields. The structure of **10** was supported by analytical and spectral data with, for example, the carbon atom α to the carbonyl group showing the same trend in going from 5–8-membered-ring heterocycles as that found for the parent (i.e. NH) systems.[8] Furthermore, the process shows considerable site selectivity when two different sites are available for the rearrangement. Specifically, the perhydroisoquinoline **11**, on exposure to $Co_2(CO)_8$ and $Ru_3(CO)_{12}$ under carbon monoxide, gave the perhydroisoquinolin-3-one (**12**) in 90% yield, with isomeric perhydroisoquinolin-1-one (**13**) isolated



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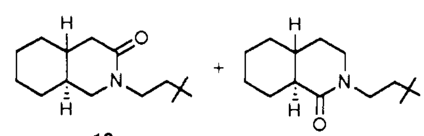

12 13

in 9% yield. While X-ray quality crystals of **12** could not be obtained, excellent crystals of **13** were grown and an X-ray structure determination confirmed the structure assigned on the basis of spectral results. (See supplementary material for ORTEP and relevant data.)

The rearrangement reaction is a process of considerable potential. The present method complements the nice work by Kuehne and Parsons[9] on the photochemical or thermal rearrangement of oxaziridines as a route for the synthesis of alkaloids.

(5) Calet, S.; Urso, F.; Alper, H. *J. Am. Chem. Soc.* **1989**, *111*, 931.
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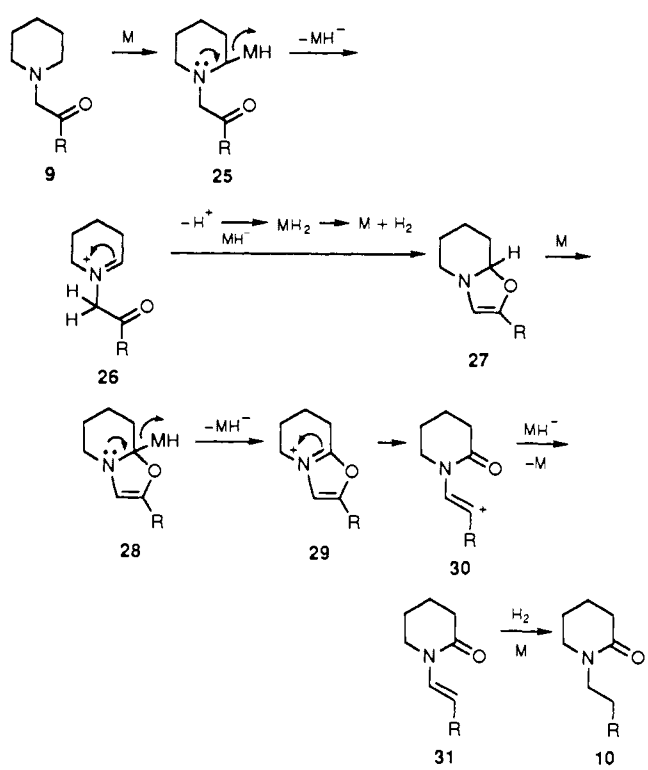
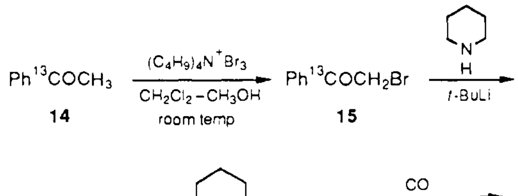
(7) Wang, M. D.; Calet, S.; Alper, H. *J. Org. Chem.* **1989**, *54*, 20.
(8) Williamson, K. L.; Roberts, J. D. *J. Am. Chem. Soc.* **1976**, *98*, 5082.
(9) Kuehne, M. E.; Parsons, W. H. *Tetrahedron* **1983**, *39*, 3763.

Scheme I



The rearrangement process involves a net oxidation at a ring carbon bonded to nitrogen. A number of such oxidation reactions, including electrochemical process, have been reported in the literature.[10]

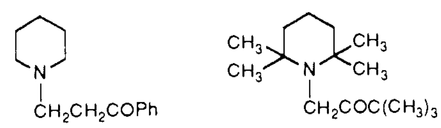
Several labeling experiments were undertaken to probe the mechanism of the rearrangement reaction. First, use of labeled carbon monoxide (i.e., ^{13}CO) in the reaction of **9b** results in no incorporation of the label in the product (**10b**). Nevertheless, carbon monoxide is required for the reaction since use of nitrogen as the atmosphere results in less than 5% rearrangement. Apparently, carbon monoxide is required to stabilize one of the reaction intermediates. In order to determine whether the rearrangement involves transposition of methylene and carbonyl groups or positional exchange of one oxygen and two hydrogen atoms, the piperidinylacetophenone (**16**) was obtained from commercially available acetophenone (**14**) labeled at the carbonyl carbon. Treatment of **14** with tetrabutylammonium tribromide[11] afforded labeled 2-bromoacetophenone (**15**) in 91% yield, and reaction of the latter was piperidine and *tert*-butyllithium in ether gave **16** in 89% yield. When **16** was subjected to rearrangement using conditions identical with those for **9**, (n = 2, R = Ph), the rearranged product **17** was obtained in 90% yield, with the label remaining at the carbon atom adjacent to the phenyl group. This result provides evidence for the positional exchange of the oxygen and two hydrogen atoms.



14 15

16 17

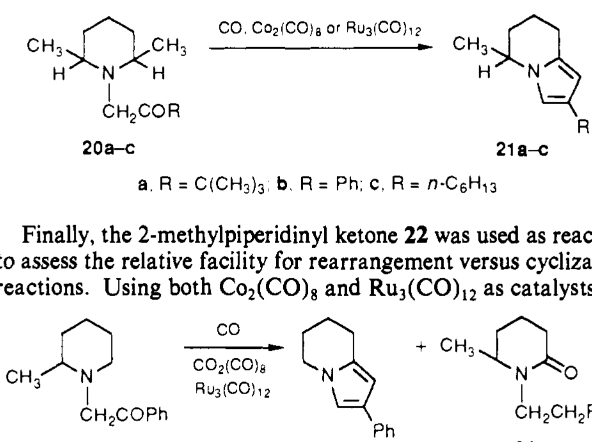
No rearrangement takes place if another carbon atom is placed between the nitrogen atom and the carbonyl group (i.e., **18**). Also, replacing all of the hydrogen atoms at the α-carbon atoms of the



18 19

heterocycle (**19**) results in recovery of starting material on attempted carbonylation with cobalt and ruthenium carbonyls.

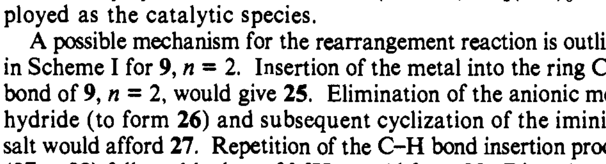
A unique cyclization reaction occurs when only one of the hydrogen atoms at an α-carbon atom is replaced by an alkyl group. Deprotonation of commercially available 2,6-dimethylpiperidine by *tert*-butyllithium, followed by reaction with an α-halo ketone, gives **20a–c**. Exposure of **20a** to the reaction conditions utilized for rearrangement resulted in cyclization to form the 5,6,7,8-tetrahydroindolizine **21a** in 86% yield (see Experimental Section for spectral data). Further experiments revealed that the conversion of **20a** to **21a** proceeds with $Co_2(CO)_8$ *or* $Ru_3(CO)_{12}$ in contrast to the rearrangement process which requires *both* metal carbonyls as catalysts. This unusual metal catalyzed cyclization reaction is applicable to other 2,6-dimethylpiperidinyl ketones to obtain **21** in excellent yields (i.e., **21b**, 94% (84% using $Ru_3(CO)_{12}$ as the only catalyst); **21c**, 91% yield). Appropriately substituted tetrahydroindolizine and related octahydroindolizine alkaloids (e.g., δ-coniceine) are of considerable pharmacological interest.[12,13]



20a–c 21a–c

a, R = C(CH$_3$)$_3$; b, R = Ph; c, R = n-C$_6$H$_{13}$

Finally, the 2-methylpiperidinyl ketone **22** was used as reactant to assess the relative facility for rearrangement versus cyclization reactions. Using both $Co_2(CO)_8$ and $Ru_3(CO)_{12}$ as catalysts for



22 23 24

the reaction of **22** under carbon monoxide results in 10:1 selectivity (77% yield) for cyclization to **23**, compared with rearrangement to **24**. Only cyclization occurs when (47% **23**) $Co_2(CO)_8$ is employed as the catalytic species.

A possible mechanism for the rearrangement reaction is outlined in Scheme I for **9**, n = 2. Insertion of the metal into the ring C–H bond of **9**, n = 2, would give **25**. Elimination of the anionic metal hydride (to form **26**) and subsequent cyclization of the iminium salt would afford **27**. Repetition of the C–H bond insertion process (**27** to **28**) followed by loss of MH^- would form **29**. Ring cleavage of **29** to the vinyl cation **30** and then reaction with MH^- would afford the enamide **31**. The product would then result by metal catalyzed hydrogenation of **31**, the hydrogen having been generated during the conversion of **26** to **27**.

Evidence for this pathway comes from the $Ru_3(CO)_{12}$ catalyzed reaction of **9b**. While, as noted previously, no reaction usually occurs with $Ru_3(CO)_{12}$ as the only metal catalyst in the rearrangement reaction, **9b** did react to a limited extent, affording **31** (R = C(CH$_3$)$_3$) in 13% yield.

The initial step (**20** to **32**) in the conversion of piperidines to 5,6,7,8-tetrahydroindolizines (Scheme II) likely is the same as that for the rearrangement process. Hydrogen transfer from the

(10) Shono, T. *Tetrahedron* **1984**, *40*, 811 and references cited therein.
(11) Kajigaeshi, S.; Kakinami, T.; Okamoto, T.; Fujisaki, S. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 1159.
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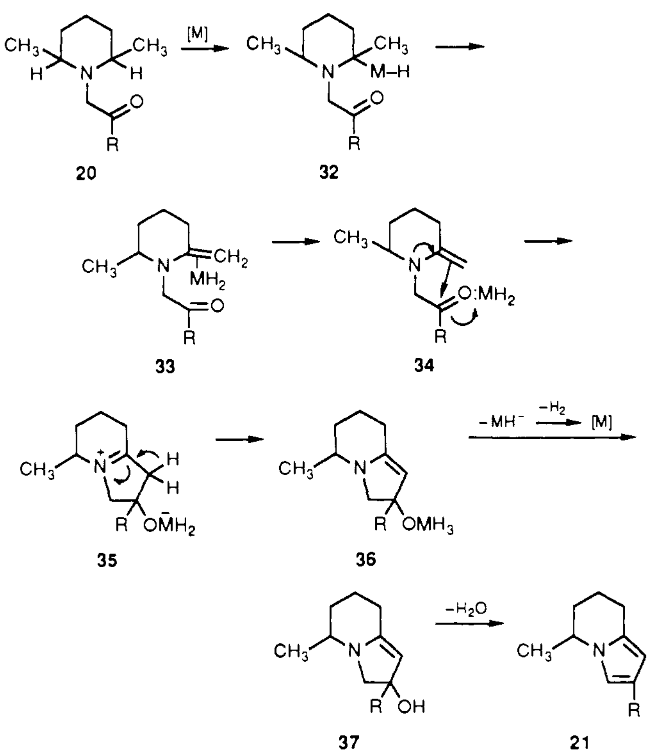
(13) Rajeswari, S.; Chandrasekharan, S.; Govindachari, T. R. *Heterocycles* **1987**, *25*, 659.

Scheme II



methyl group to the metal would form **33** which can collapse to the monodentate complex **34**. Cyclization to **35** followed by conversion to **36** and subsequent reductive elimination of MH_2 would result in the formation of **37**. The 5,6,7,8-tetrahydroindolizines would then be produced by dehydration. Note that **33** can alternatively undergo decomplexation to give the enamino ketone (uncomplexed analog of **34**) which can, by an analogous reaction sequence, be converted to the 5,6,7,8-tetrahydroindolizines.

It is important to note that neither of the proposed mechanisms account for the role of the metal, i.e. what is the function of $Ru_3(CO)_{12}$ in the rearrangement process and why does the cyclization reaction occur with either cobalt or ruthenium carbonyls? Nevertheless, the schemes do provide a rationale for the observed transformations and, in the case of the rearrangement process, are consistent with the results of the labeling experiments.

In conclusion, pyrrolidines can be converted into piperidinones by metal catalyzed carbonylation. Furthermore, this investigation has resulted in the discovery of several novel, intriguing, and useful metal catalyzed rearrangement and cyclization reactions.

Experimental Section

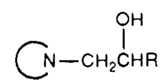
General. Spectral data were obtained by use of the following instrumentation: Bomem MB-100 (FT-IR), Varian XL300 or Gemini 200 (NMR), VG 7070E (MS). Elemental analyses were carried out by MHW Laboratories, Phoenix, AZ. Organic solvents were dried and distilled prior to use. Cobalt and ruthenium carbonyls as well as ethyl 1-pyrrolidineacetate were purchased from commercial firms and used as received.

Pyrrolidines: **4a** was prepared in 65% yield from cyclopropyl phenyl ketone and *N*-methylformamide, following the procedure of Blake and Gillies;[14] bp 56–58 °C (0.8 mmHg) (lit.[14] bp 52–54 °C (0.7 mmHg)). **4b** was obtained in 72% yield from benzyl cyclopropyl ketone and *N*-methylformamide, following the literature procedure; bp 94–97 °C (0.9 mmHg) (lit.[14] bp 70 °C (0.1 mmHg)).

General Procedure for the Preparation of Heterocycles Containing CH_2COR (R = $C(CH_3)_3$, Ph, C_6H_{13}, OC_2H_5) Groups. (a) The first procedure involved deprotonation of the parent heterocycle and subsequent alkylation of a halide. To 20 mmol of the heterocycle in 75 mL of ether at 0 °C (N_2 atmosphere) was added, drop-by-drop, a 10% molar excess of a solution of *n*-butyl or *tert*-butyl lithium (2.5 M) in hexane. After being stirred at room temperature for 4 h, this solution was added dropwise to a cold (0 °C) ether (50 mL) solution of 21 mmol of the α-bromo ketone or ester. The reaction mixture was stirred overnight at room temperature, washed with water (2 × 25 mL), dried (K_2CO_3), and concentrated by rotary evaporation. Pure product was obtained by distillation of the crude material at reduced pressure.

(b) The second procedure involved deprotonation and reaction with an epoxide followed by oxidation (used for the preparation of **9d** and **20c**.

After generation of the anion as described in procedure a above, the solution was added dropwise to a solution of 21 mmol of 2-phenyl- or 2-*n*-hexyloxirane in ether (50 mL). Workup as described for procedure a afforded the alcohol



R = Ph, *n*-C_6H_{13}

Oxidation of the alcohol to the requisite ketone was effected by known methodology with chromium trioxide[15] for **9d** and pyridinium dichromate[16] for **20c**.

Yields and Characterization Data for Reactants Prepared by Procedure a. 4c: 57% yield; bp 56–58 °C (0.45 mmHg); IR ($CHCl_3$) ν(CO) 1735 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.28 (t, 3 H, CH_3CH_2O), 1.82 (m, 4 H, CH_2CH_2), 2.38 (m, 2 H, NCH_2 ring), 2.79 (m, 1 H, $CHCH_2OCH_3$), 3.34 (s, 3 H, OCH_3), 3.46 (m, 4 H, CH_2OCH_3 and $COOCH_2CH_3$), 3.98 (m, 2 H, NCH_2CO); MS, *m/e* 201 [M]$^+$. Anal. Calcd for $C_{10}H_{19}NO_3$: C, H.

4d: 85% yield; bp 43–45 °C (0.35 mmHg); IR ($CHCl_3$) ν(CO) 1720 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.09 (s, 9 H, $C(CH_3)_3$), 1.81 (m, 4 H, CH_2CH_2), 2.32 (m, 2 H, NCH_2 ring), 2.82 (m, 1 H, $CHCH_2OCH_3$), 3.24 (s, 3 H, OCH_3), 3.34 (m, 2 H, CH_2O), 3.74 (m, 2 H, NCH_2CO); MS, *m/e* 168 [M − CH_2OCH_3]$^+$. Anal. Calcd for $C_{12}H_{23}NO_2$: C, H.

4f (or **9a**): 84% yield; bp 34–36 °C (0.3 mmHg); IR($CHCl_3$) ν(CO) 1712 cm^{-1}; ^{1}H NMR ($CDCl_3$)δ 1.13 (s, 9 H, $C(CH_3)_3$), 1.79 (m, 4 H, CH_2CH_2), 2.64–2.81 (m, 4 H, NCH_2 ring), 3.59 (s, 2 H, NCH_2CO); ^{13}C NMR ($CDCl_3$) δ 23.67 (C3, C4), 26.53 [$(CH_3)_3C$], 43.34 [$(CH_3)_3C$], 53.94 (C2, C5), 59.76 (NCH_2CO), 211.82 (CO); MS, *m/e* 169 [M]$^+$. Anal. Calcd for $C_{10}H_{19}NO$: C, H.

7: 79% yield; bp 94–96 °C (0.8 mmHg); IR ($CHCl_3$) ν(CO) 1733 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.20 (t, 3 H, CH_2CH_3), 1.49–1.60 (m, 8 H, protons at C4–C7), 1.82 (m, 2 H, protons at C3), 2.05 (m, 1 H, proton at C9), 2.63 (m, 2 H, NCH_2 ring), 3.13 (m, 1 H, NCH), 3.18, 3.37 (d each, 2 H, *J* = 16 Hz, NCH_2COO), 4.19 (q, 2 H, OCH_2); MS *m/e* 211 [M]$^+$. Anal. Calcd for $C_{12}H_{21}NO_2$: C, H.

9b: 88% yield; bp 100–102 °C (1.0 mmHg); IR ($CHCl_3$) ν(CO) 1715 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.02 (s, 9 H, $C(CH_3)_3$), 1.31 (m, 2 H, protons at C4), 1.49 (m, 4 H, protons at C3,C5), 2.28 (m, 4 H, protons at C2,C6), 3.21 (s, 2 H, NCH_2CO); MS, *m/e* 183 [M]$^+$. Anal. Calcd for $C_{11}H_{21}NO$: C, H.

9c: 94% yield; bp 110–112 °C (0.4 mmHg); IR ($CHCl_3$) ν(CO) 1686 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.43 (m, 2 H, protons at C4 of piperidine), 1.61 (m, 4 H, protons at C3,C5 of piperidine), 2.49 (m, 4 H, protons at C2,C6 of piperidine), 3.72 (s, 2 H, NCH_2CO), 7.43 (m, 3 H, meta and para protons), 7.90 (m, 2 H, ortho protons); MS, *m/e* 203 [M]$^+$. Anal. Calcd for $C_{13}H_{17}NO$: C, H.

9e: 85% yield; bp 160–162 °C (0.4 mmHg); IR ($CHCl_3$) ν(CO) 1677 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.56 (m, 2 H, protons at C4 of piperidine), 1.71 (m, 4 H, protons at C3,C5 of piperidine), 2.65 (m, 4 H, protons at C2,C6 of piperidine), 3.96 (s, 2 H, NCH_2CO), 7.51–8.40 (m, 7 H, $C_{10}H_7$); MS, *m/e* 253 [M]$^+$. Anal. Calcd for $C_{17}H_{19}NO$: C, H.

9f: 91% yield; bp 115–117 °C (4 mmHg); IR ($CDCl_3$) ν(CO) 1712 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.10 (s, 9 H, $C(CH_3)_3$), 1.50–1.75 (m, 8 H, protons at C3–C6), 2.72 (m, 4 H, protons at C2,C7), 3.59 (s, 2 H, NCH_2CO); MS, *m/e* 197 [M]$^+$. Anal. Calcd for $C_{12}H_{23}NO$: C, H.

9g: 93% yield; bp 118–120 °C (0.4 mmHg); IR ($CHCl_3$) ν(CO) 1680 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.49–1.72 (m, 8 H, protons at C3–C6 of azepine), 2.78 (m, 4 H, protons at C2,C7 of azepine), 3.95 (s, 2 H, NCH_2CO), 7.38 (m, 3 H, meta and para protons of C_6H_5), 8.01 (m, 2 H, ortho protons of C_6H_5); MS, *m/e* 217 [M]$^+$. Anal. Calcd for $C_{14}H_{19}NO$: C, H.

9h: 91% yield; bp 118–119 °C (3.5 mmHg); IR ($CHCl_3$) ν(CO) 1710 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.06 (s, 9 H, $C(CH_3)_3$), 1.53–1.68 (m, 10 H, protons at C3–C7), 2.63 (m, 4 H, protons at C2,C8), 3.59 (s, 2 H, NCH_2CO); MS, *m/e* 211 [M]$^+$. Anal. Calcd for $C_{13}H_{25}NO$: C, H.

9i: 91% yield; bp 135–136 °C (0.4 mmHg); IR ($CHCl_3$) ν(CO) 1675 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.50–1.68 (m, 10 H, protons at C3–C7 of heterocycle), 2.68 (m, 4 H, protons at C2,C8 of heterocycle), 3.87 (s, 2 H, NCH_2CO), 7.36 (m, 3 H, meta and para protons of C_6H_5), 7.95 (m,

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(15) *Org. Synth.* **1965**, *45*, 28, 77.

2 H, ortho protons of phenyl); MS, m/e 231 [M]$^+$. Anal. Calcd for $C_{15}H_{21}NO$: C, H.

11: 87% yield; bp 112–114 °C (0.45 mmHg); IR ($CHCl_3$) ν(CO) 1714 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.90–1.65 (m, 19 H, protons at C4,C5–C8 of perhydroisoquinoline, and $C(CH_3)_3$), 1.97 (m, 2 H, ring juncture protons), 2.69 (m, 2 H, C3 protons), 2.84 (m, 2 H, C1 protons), 3.28 (s, 2 H, NCH_2CO); MS, m/e 237 [M]$^+$. Anal. Calcd for $C_{15}H_{27}NO$: C, H, N.

19: 89% yield; bp 50–51 °C (0.25 mmHg); IR ($CHCl_3$) ν(CO) 1717 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.10 (s, 9 H, $C(CH_3)_3$), 1.19, 1.21 (s, 12 H, CH_3), 1.21–1.40 (m, 6 H, CH_2 ring), 4.07 (s, 2 H, NCH_2CO); MS, m/e 239 [M]$^+$.

20a: bp 60–61 °C (0.1 mmHg); IR ($CHCl_3$) ν(CO) 1710 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.98 (d, 6 H, CH_3), 1.12 (s, 9 H, $C(CH_3)_3$), 1.18–1.65 (m, 6 H, ring CH_2), 3.05 (m, 2 H, CHN), 3.81 (s, 2 H, NCH_2CO); MS, m/e 211 [M]$^+$. Anal. Calcd for $C_{13}H_{25}NO$: C, H.

22: 63% yield; bp 114–116 °C (0.45 mmHg); IR ($CHCl_3$) ν(CO) 1683 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.31 (d, 3 H, CH_3), 1.23–1.83 (m, 6 H, protons at C3–C5 of piperidine ring), 2.79 (m, 2 H, NCH_2 ring), 3.40 (m, 1 H, $CHCH_3$), 4.00 (m, 2 H, NCH_2CO), 7.35 (m, 3 H, meta and para protons of Ph), 8.01 (m, 2 H, ortho protons of Ph); MS, m/e 112 [M − PhCO]$^+$, 105 [PhCO]$^+$. Anal. Calcd for $C_{14}H_{19}NO$: C, H.

Yields and Characterization Data for Reactants Prepared by Procedure b. **9d** was prepared via 1-piperidinyl-2-octanol, obtained in 95% yield from 2-*n*-hexyloxirane and lithium piperidide. Properties of the alcohol: bp 116–118 °C (0.4 mmHg); IR ($CHCl_3$) ν(OH) 3413 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.82 (t, 3 H, CH_3), 1.17–1.57 (m, 16 H, $CH_3(CH_2)_5$, protons at C3–C5 of ring), 2.39 (m, 4 H, protons at C2,C6 of ring), 2.54 (m, 2 H, NCH_2), 3.61 (m, 1 H, $CHOH$); MS, m/e 213 [M]$^+$. Data for the ketone **9d**: 67% yield; bp 115–117 °C (8 mmHg); IR ($CHCl_3$) ν(CO) 1718 cm^{-1}; NMR ($CDCl_3$) δ 0.81 (t, 3 H, CH_3), 1.18–1.57 (m, 14 H, $CH_3(CH_2)_4$, protons at C3–C5 of ring), 2.20 (t, 2 H, $COCH_2C_5H_{11}$), 2.32 (m, 4 H, protons at C2,C6 of ring), 3.08 (s, 2 H, NCH_2CO); MS, m/e 211[M]$^+$. Anal. Calcd for $C_{13}H_{25}NO$: C, H.

20c was prepared via 1-(2,6-dimethylpiperidinyl)-2-octanol, obtained in 80% yield from 2-*n*-hexyloxirane and lithium 2,6-dimethylpiperidide. Properties of the alcohol: bp 103–106 °C (0.4 mmHg); IR ($CHCl_3$) ν(OH) 3385 cm^{-1}; NMR ($CDCl_3$) δ 0.85 (t, 3 H, CH_3), 1.01 (d, 6 H, CH_3 at C2,C6), 1.20–1.60 (m, 16 H, $CH_3(CH_2)_5$, protons at C3–C5 of ring), 2.49 (m, 4 H, NCH_2 and 2 NCH), 3.49 (m, 1 H, $CHOH$); MS, m/e 241 [M]$^+$. Data for the ketone **20c**: 90% yield; bp 108–109 °C (0.3 mmHg), IR ($CHCl_3$) ν(CO) 1712 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.83 (t, 3 H, CH_3CH_2), 0.98 (d, 6 H, CH_3), 1.23–1.54 (m, 14 H, $CH_3(CH_2)_4$ and C3–C5 of ring), 2.39 (t, 2 H, $COCH_2CH_2$), 2.72 (m, 2 H, protons at C2,C6 of ring), 3.39 (s, 2 H, NCH_2CO); MS, m/e 224 [M − CH_3]$^+$. Anal. Calcd for $C_{15}H_{29}NO$: C, H, N.

20b was prepared via 1-phenyl-2-(2,6-dimethylpiperidinyl)ethanol, obtained in 85% yield from 2-phenyloxirane and lithium 2,6-dimethylpiperidide. Properties of the alcohol: bp 125–128 °C (0.4 mmHg); IR ($CHCl_3$) ν(OH) 3385 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.16 (d, 6 H, CH_3 at C2,C6), 1.30–1.72 (m, 6 H, protons at C3–C5), 2.61 (m, 4 H, NCH_2 and 2 NCH), 4.56 (m, 1 H, CHPh), 7.27 (m, 5 H, Ph); MS, m/e 215 [M − H_2O]$^+$. Data for the ketone **20b**: 69% yield; IR ($CHCl_3$) ν(CO) 1689 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.03 (d, 6 H, CH_3), 1.28–1.53 (m, 6 H, protons at C3–C5), 3.03 (m, 2 H, $NCHCH_3$), 4.20 (s, 2 H, NCH_2CO), 7.45 (m, 3 H, meta and para protons of Ph), 7.93 (m, 2 H, ortho protons of Ph); MS, m/e 231 [M]$^+$. Anal. Calcd for $C_{15}H_{21}NO$: C, H.

Phenyl β-piperidinoethyl ketone (18) was prepared in 68% yield by dehydrochlorination of the hydrochloride. The latter was obtained in 86% yield by Mannich reaction of acetophenone, paraformaldehyde, and piperidine hydrochloride.[16] Properties of **18**: mp 27–29 °C; IR ($CHCl_3$) ν(CO) 1681 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.42–1.55 (m, 6 H, protons at C3–C5 of pyridine ring), 2.41 (t, 4 H, NCH_2 ring), 2.75 (t, 2 H, CH_2COPh), 3.12 (t, 2 H, $NCHCH_2CO$), 7.44 (m, 3 H, protons at meta and para positions of Ph), 7.95 (m, 2 H, protons at ortho positions of Ph); CI-MS, m/e 218 [M + 1]$^+$. Anal. Calcd for $C_{14}H_{19}NO$: C, H.

General Procedure for the Carbonylation and Ring Expansion of Pyrrolidines. A mixture of the pyrrolidine (**4** or **7**, 1.32 mmol), cobalt carbonyl (0.103 g, 0.30 mmol), and benzene (10 mL) was placed in an autoclave containing a glass liner and a stirring bar. The autoclave was purged several times with carbon monoxide and pressurized to 54 atm. The reaction mixture was stirred at 200–220 °C for 3 days. The cooled autoclave was opened, and after standing in air, the mixture was filtered through Celite and the filtrate was concentrated by rotary evaporation. Purification of the resulting crude material was effected using alumina preparative thin-layer chromatography with hexane–acetone as the developer. Yields and characterization data for the products follow.

6a: 56% yield; IR (C_6H_6) ν(CO) 1640 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.60–2.10 (m, 4 H, CH_2CH_2), 2.99 (s, 3 H, NCH_3), 3.40 (m, 2 H, CH_2N), 3.63 (t, 1 H, CHPh), 7.11–7.33 (m, 5 H, Ph); ^{13}C NMR ($CDCl_3$) δ 20.51, 30.33 (CH_2CH_2), 34.84 (NCH_3), 48.36 (CHPh), 50.13 (CH_2N), 126.41, 128.26, 128.42, 147.12 (aromatic), 170.83 (CO); MS, m/e 189 [M]$^+$. Anal. Calcd for $C_{12}H_{15}NO$: C, H, N.

5b: 24% yield; IR (C_6H_6) ν(CO) 1645 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.28–1.84 (m, 4 H, CH_2CH_2), 2.33 (dd, 2 H, CH_2Ph), 2.60 (m, 2 H, CH_2CO), 2.93 (s, 3 H, CH_3), 3.65 (m, 1 H, CHN), 7.10–7.30 (m, 5 H, Ph); ^{13}C NMR, ($CDCl_3$) δ 17.31, 25.66 (CH_2CH_2), 31.97 (CH_2CO), 34.10 (NCH_3), 38.97 (CH_2Ph), 60.60 (CHN), 128.43, 128.56, 129.00, 137.91 (aromatic), 170.10 (CO); MS, m/e 204 [M + 1]$^+$ (CI). Anal. Calcd for $C_{13}H_{17}NO$: C, H, N.

6b: 15% yield; IR (C_6H_6) ν(CO) 1642 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.50–2.10 (m, 4 H, CH_2CH_2), 2.32 (m, 2 H, $PhCH_2$), 2.98 (s, 3 H, CH_3), 3.11 (m, 1 H, CH), 3.38 (m, 2 H, CH_2N), 7.10–7.32 (m, 5 H, Ph); ^{13}C NMR ($CDCl_3$) δ 21.90, 29.92 (CH_2CH_2), 32.92 (NCH_3), 38.24 (CH_2Ph), 42.09 (CHCO), 52.18 (NCH_2), 128.22, 128.32, 129.21, 137.40 (aromatic), 169.70 (CO); MS, m/e 203 [M]$^+$. Anal. Calcd for $C_{13}H_{17}NO$: C, H, N.

5c: 49% yield; IR (C_6H_6) ν(CO) 1645, 1735 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.18 (t, 3 H, CH_3CH_2), 1.55–1.80 (m, 4 H, CH_2CH_2), 2.28 (m, 2 H, CH_2CO), 3.10 (m, 1 H, CHN), 3.15 (s, 3 H, OCH_3), 3.30 (dd, 2 H, CH_2O), 4.21, 4.35 (d each, 2 H, J = 18 Hz, NCH_2CO); MS, m/e 156 [M − $COOC_2H_5$]$^+$. Anal. Calcd for $C_{11}H_{19}NO_4$: C, H, N.

5d: 61% yield; IR (C_6H_6) ν(CO) 1647, 1720 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.10 (s, 9 H, $C(CH_3)_3$), 1.60–1.82 (m, 4 H, CH_2CH_2), 2.35 (m, 2 H, CH_2CON), 3.20 (s, 3 H, OCH_3), 3.25 (m, 1 H, CHN), 3.35 (m, 2 H, OCH_2), 4.19, 4.63 (d each, 2 H, J = 18 Hz, NCH_2CO); ^{13}C NMR ($CDCl_3$) δ 18.18, 25.75 (CH_2CH_2), 26.45 ($C(CH_3)_3$), 31.76 (CH_2CO), 43.14 ($C(CH_3)_3$), 51.20 (NCH_2), 57.45 (CHN), 58.90 (OCH_3), 75.42 (CH_2O), 170.48 (NCO), 209.66 (CO); MS, m/e 156 [M − $COC(CH_3)_3$]$^+$. Anal. Calcd for $C_{13}H_{23}NO_3$: C, H, N.

5e/6e: 30% yield (67% using $Co_2(CO)_8/Ru_3(CO)_{12}$); IR (C_6H_6) ν(CO) 1648, 1740 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.26 (t, 3 H, CH_3CH_2), 1.71–1.86 (m, 4 H, CH_2CH_2), 2.41 (m, 2 H, CH_2CO), 3.34 (m, 2 H, NCH_2 ring), 4.10 (q, 2 H, OCH_2), 4.08, 4.17 (d each, 2 H, J = 16 Hz, NCH_2CO); ^{13}C NMR ($CDCl_3$) δ 14.23 (CH_3), 21.40 (CH_2CH_2CO), 23.21 (CH_2CH_2N), 32.11 (CH_2CO), 48.67 (NCH_2 ring), 54.23 (NCH_2CO), 61.13 (OCH_2), 169.00, 170.31 (CO); MS, m/e 185 [M]$^+$. Anal. Calcd for $C_9H_{15}NO_3$: C, H, N.

5f/6f: 42% yield; IR (C_6H_6) ν(CO) 1650, 1722 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.18 (s, 9 H, $C(CH_3)_3$), 1.60–1.85 (m, 4 H, CH_2CH_2), 2.39 (m, 2 H, $NCOCH_2$ ring), 3.22 (m, 2 H, NCH ring), 4.29 (s, 2 H, NCH_2CO); ^{13}C NMR, ($CDCl_3$) δ 21.49, 23.22 (CH_2CH_2), 26.32 ($C(CH_3)_3$), 32.07 (CH_2CO), 43.40 ($C(CH_3)_3$), 49.21 (NCH_2 ring), 52.78 (NCH_2CO), 170.11 (NCO), 209.62 (CO); MS, m/e 197 [M]$^+$. Anal. Calcd for $C_{11}H_{19}NO_2$: C, H, N.

8: 46% yield (79% using $Co_2(CO)_8/Ru_3(CO)_{12}$); IR (C_6H_6) ν(CO) 1650, 1740 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.20 (t, 3 H, CH_3), 1.10 (m, 10 H, protons at C4–C8), 2.40 (m, 2 H, $NCOCH_2$), 2.47 (m, 1 H, H4′), 2.96 (m, 1 H, H8′), 4.12 (q, 2 H, OCH_2), 4.00, 4.32 (d each, 2 H, J = 18 Hz, NCH_2COO); ^{13}C NMR, ($CDCl_3$) δ 14.20 (CH_3), 24.95, 25.30, 30.27, 27.80, 31.23, 32.10 (C4–C8), 32.50 (CH_2CON), 40.91 (C4′), 53.70 (NCH_2CO), 61.00 (OCH_2), 62.30 (C8′), 169.60, 171.22 (CO); MS, m/e 239 [M]$^+$. Anal. Calcd for $C_{13}H_{21}NO_3$: C, H, N.

General Procedure for the $Co_2(CO)_8/Ru_3(CO)_{12}$ Catalyzed Rearrangement Reaction of Nitrogen Heterocyclics with Ketone Groups. The previous reaction was repeated in the presence of 0.14 mmol of $Ru_3(CO)_{12}$. Workup was carried out by column chromagoraphy (alumina) with CH_2Cl_2/hexane and then ethyl acetate as the eluant. Yields and characterization data for the products follow.

10a: 72% yield; IR ($CDCl_3$) ν(CO) 1656 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.92 (s, 9 H, $C(CH_3)_3$), 1.39 (m, 2 H, $CH_2C(CH_3)_3$), 2.00 (m, 2 H, protons at C-4), 2.35 (t, 2 H, CH_2CO), 3.26 (m, 2 H, NCH_2), 3.35 (t, 2 H, NCH_2 ring); ^{13}C NMR ($CDCl_3$) δ 17.93 (C4), 29.33 ($C(CH_3)_3$), 29.80 ($C(CH_3)_3$), 31.22 (C3), 39.17 (NCH_2), 40.45 ($CH_2C(CH_3)_3$), 47.06 (C5), 174.56 (CO); MS, m/e 169 [M]$^+$. Anal. Calcd for $C_{10}H_{19}NO$: C, H, N.

10b: 86% yield; IR ($CDCl_3$) ν(CO) 1630 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.91 (s, 9 H, $C(CH_3)_3$), 1.40 (m, 2 H, $CH_2C(CH_3)_3$), 1.74 (m, 4 H, protons at C-4 and C-5), 2.33 (t, 2 H, CH_2CO), 3.22 (t, 2 H, NCH_2 ring), 3.33 (m, 2 H, NCH_2); ^{13}C NMR ($CDCl_3$) δ 21.19 (C5), 23.07 (C4), 29.03 ($C(CH_3)_3$), 29.49 ($C(CH_3)_3$), 32.16 (C3), 39.90 ($CH_2C(CH_3)_3$), 45.53 (NCH_2), 47.38 (C6), 169.29 (CO); MS, m/e 183 [M]$^+$. Anal. Calcd for $C_{11}H_{21}NO$: C, H, N.

10c: 91% yield; IR ($CDCl_3$) ν(CO) 1626 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.67 (m, 4 H, protons at C4, C5), 2.34 (t, 2 H, CH_2CO), 2.84 (t, 2 H, CH_2Ph), 3.07 (t, 2 H, NCH_2 ring), 3.56 (t, 2 H, NCH_2), 7.23 (m, 5 H, Ph); ^{13}C NMR ($CDCl_3$) δ 21.01 (C4), 22.95 (C5), 32.09 (C3), 33.32

(16) Corey, E. J.; Schmidt, G. *Tetrahedron Lett.* **1979**, 399.
(17) *Org. React.* **1942**, *1*, 329.

(CH_2Ph), 48.60 (C6), 49.31 (NCH_2), 126.33, 128.40, 128.82, 139.31 (aromatic), 169.99 (CO); MS, *m/e* 203 $[M]^+$. Anal. Calcd for $C_{13}H_{17}NO$: C, H, N.

10d: 79% yield; IR ($CDCl_3$) ν(CO) 1624 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.84 (t, 3 H, CH_3), 1.15–1.50 (m, 12 H, $CH_3(CH_2)_6$), 1.74 (m, 4 H, protons at C4, C5), 2.33 (t, 2 H, CH_2CO), 3.23 (t, 2 H, NCH_2 ring), 3.30 (m, 2 H, NCH_2); ^{13}C NMR ($CDCl_3$) δ 13.99 (CH_3), 21.34, 22.55, 23.22, 26.86, 26.97, 29.13, 29.31 (C4, C5, and $CH_3(CH_2)_5$), 32.25 (C3), 37.71 (NCH_2CH_2), 47.11 (NCH_2), 47.70 (C6), 169.37 (CO); MS, *m/e* 211 $[M]^+$. Anal. Calcd for $C_{13}H_{25}NO$: C, H, N.

10e: 88% yield; IR ($CDCl_3$) ν(CO) 1630 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.67 (m, 4 H, protons at C4,C5), 2.37 (t, 2 H, CH_2CO), 3.02 (t, 2 H, $CH_2C_{10}H_7$), 3.08 (t, 2 H, NCH_2 ring), 3.62 (t, 2 H, NCH_2), 7.45–7.80 (m, 7 H, aromatic); ^{13}C NMR ($CDCl_3$) δ 21.12 (C4), 23.15 (C5), 32.35 (C3), 33.67 ($CH_2C_{10}H_7$), 48.75 (C6), 49.29 (NCH_2), 125.31, 127.11, 127.38, 127.54, 127.88, 127.93, 127.96, 132.11, 133.51, 138.77 (aromatic), 169.67 (CO); MS, *m/e* 253 $[M]^+$. Anal. Calcd for $C_{17}H_{19}NO$: C, H, N.

10f: 85% yield; IR ($CDCl_3$) ν(CO) 1628 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90 (s, 9 H, $C(CH_3)_3$), 1.34–1.65 (m, 8 H, protons at C4–C6 and $CH_2C(CH_3)_3$), 2.46 (t, 2 H, CH_2CO), 3.27 (t, 2 H, NCH_2 ring), 3.34 (t, 2 H, NCH_2); ^{13}C NMR ($CDCl_3$) δ 23.18 (C4), 28.56 (C5), 29.06 ($C(CH_3)_3$), 29.45 ($C(CH_3)_3$), 29.80 (C6), 37.15 (C3), 41.01 ($CH_2C(CH_3)_3$), 44.73 (NCH_2), 49.30 (C6), 175.35 (CO); MS, *m/e* 197 $[M]^+$. Anal. Calcd for $C_{12}H_{23}NO$: C, H, N.

10g: 93% yield; IR ($CDCl_3$) ν(CO) 1626 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.48–1.62 (m, 6 H, protons at C4–C6), 2.35 (t, 2 H, CH_2CO), 2.78 (t, 2 H, CH_2Ph), 3.24 (m, 2 H, NCH_2 ring), 3.54 (t, 2 H, NCH_2), 7.24 (m, 5 H, Ph); ^{13}C NMR ($CDCl_3$) δ 23.33 (C5), 28.54 (C6), 29.89 (C4), 34.49 (CH_2Ph), 37.51 (C3), 50.41 (C7), 50.61 (NCH_2), 126.19, 128.37, 128.77, 139.26 (aromatic), 175.58 (CO); MS, *m/e* 217 $[M]^+$. Anal. Calcd for $C_{14}H_{19}NO$: C, H, N.

10h: 87% yield; IR ($CDCl_3$) ν(CO) 1622 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.86 (s, 9 H, $C(CH_3)_3$), 1.38–1.72 (m, 10 H, protons at C4–C7 and $CH_2C(CH_3)_3$), 2.40 (t, 2 H, CH_2CO), 3.23 (m, 2 H, NCH_2), 3.36 (t, 2 H, NCH_2 ring); ^{13}C NMR ($CDCl_3$) δ 24.14 (C6), 25.99 (C5), 28.36 (C4), 28.46 (C7), 29.02 ($C(CH_3)_3$), 29.18 ($C(CH_3)_3$), 33.81 (C3), 40.69 ($CH_2C(CH_3)_3$), 41.82 (NCH_2), 46.73 (C8), 174.44 (CO); MS, *m/e* 211 $[M]^+$. Anal. Calcd for $C_{13}H_{25}NO$: C, H, N.

10i: 92% yield; IR ($CDCl_3$) ν(CO) 1622 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.41–1.75 (m, 8 H, protons at C4–C7), 2.46 (t, 2 H, CH_2CO), 2.85 (m, 2 H, CH_2Ph), 3.31 (t, 2 H, NCH_2 ring), 3.49 (m, 2 H, NCH_2), 7.22 (m, 5 H, Ph); ^{13}C NMR ($CDCl_3$) δ 24.21, 26.09, 28.59, 29.18, (C4–C7), 33.92 (C3), 34.14 (CH_2Ph), 47.60, 47.62 (C8 and NCH_2), 126.09, 128.30, 128.68, 139.42 (aromatic), 170.62 (CO); MS, *m/e* 231 $[M]^+$. Anal. Calcd for $C_{15}H_{21}NO$: C, H, N.

12: 90% yield; IR ($CDCl_3$) ν(CO) 1625 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90 (s, 9 H, $C(CH_3)_3$), 1.32–1.93 (m, 9 H, methylene protons of cyclohexyl ring and methine proton on carbon β to CO), 1.72 (t, 2 H, $CH_2C(CH_2)_3$), 2.38 (t, 2 H, CH_2CO), 2.88 (m, 1 H, proton at ring juncture β to nitrogen), 3.09 (t, 2 H, NCH_2), 3.28 (dd, 2 H, NCH_2 ring); ^{13}C NMR ($CDCl_3$) δ 25.18, 28.92, 29.33, 29.84 (methylene carbons of cyclohexane ring), 29.06 ($C(CH_3)_3$), 29.53 ($C(CH_3)_3$), 32.38 ($COCH_2$), 36.98, 38.23 (carbons at ring juncture), 39.87 ($CH_2C(CH_3)_3$), 43.29 (NCH_2), 53.46 (NCH_2 ring), 169.35 (CO); MS, *m/e* 237 $[M]^+$. Anal. Calcd for $C_{15}H_{27}NO$: C, H, N.

13: 9% yield; IR ($CDCl_3$) ν(CO) 1620 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.91 (s, 9 H, $C(CH_3)_3$), 1.30–2.14 (m, 13 H, methylene protons of cyclohexane ring, $CHCH_2CH_2N$ and $CH_2C(CH_3)_3$), 2.41 (m, 1 H, COCH), 2.96 (m, 2 H, NCH_2), 3.36 (m, 2 H, NCH_2 ring); ^{13}C NMR ($CDCl_3$) δ 25.38, 26.16, 27.14, 28.94 (methylene carbons of cyclohexane ring), 29.05 ($C(CH_3)_3$), 29.65 ($C(CH_3)_3$), 33.20 (NCH_2CH_2), 39.91 ($CH_2C(CH_3)_3$), 38.02, 46.92 (ring juncture carbons), 43.69 (NCH_2), 46.88 (NCH_2 ring), 171.39 (CO); MS, *m/e* 237 $[M]^+$. Anal. Calcd for $C_{15}H_{27}NO$: C, H, N.

$Ru_3(CO)_{12}$ Catalyzed Reaction of 9b. The previous reaction was repeated with 0.14 mmol of $Ru_3(CO)_{12}$ but in the absence of $Co_2(CO)_8$, affording **31** (R = $C(CH_3)_3$) in 13% yield: ^1H NMR ($CDCl_3$) δ 1.03 (s, 9 H, $C(CH_3)_3$), 1.79 (m, 4 H, $NCH_2CH_2CH_2$), 2.44 (t, 2 H, $COCH_2$), 3.33 (t, 2 H, NCH_2), 5.03 (d, 1 H, J = 15 Hz, $=CHC(CH_3)_3$), 7.33 (d, 1 H, J = 15 H, NCH=); ^{13}C NMR ($CDCl_3$) δ 20.54, 22.65 ($NCH_2CH_2CH_2$), 30.24 ($C(CH_3)_3$), 32.08 ($C(CH_3)_3$), 32.88 ($COCH_2$), 45.02 (NCH_2), 122.28 ($=CHC(CH_3)_3$), 123.38 (NCH=), 168.23 (CO); MS, *m/e* 181 $[M]^+$. Anal. Calcd for $C_{11}H_{19}NO$: C, H, N.

General Procedure for the Metal Catalyzed Cyclization of 2-Methylpiperidines (20a–c). Application of the "rearrangement" procedure to **20a–c** resulted in exclusive cyclization to **21a–c**, while **22** afforded the cyclized heterocycle **23** as the predominant product, with the rearranged ketone **24** obtained as a minor byproduct. Note that the cyclization of **20b** to **21b** occurs in almost as high yield using *only* $Co_2(CO)_8$ *or* $Ru_3(CO)_{12}$ rather than both metal catalysts. Yields and characterization data for the bicyclic heterocycles **21a–c** and **23**, as well as rearranged **24**, follow.

21a: 86% yield; ^1H NMR ($CDCl_3$) δ 1.19 ($CDCl_3$) δ (s, 9 H, $C(CH_3)_3$), 1.43 (d, 3 H, CH_3), 1.56–1.81 (m, 4 H, $CH_2CHCH_2CH_2$), 2.70 (m, 2 H, $CH_2C=$), 3.94 (m, 1 H, $CHCH_3$), 5.72 (d, 1 H, proton at C1), 6.39 (d, 1 H, NCH=); ^{13}C NMR ($CDCl_3$) δ 19.51, 23.53 ($CH_3CHCH_2CH_2$), 22.09 (CH_3), 29.63 ($C(CH_3)_3$), 30.46 ($C(CH_3)_3$), 32.06 ($CH_2C=$), 50.18 ($CHCH_3$), 102.76 (CCH), 111.69 (NCH=), 129.10 ($(CH_3)CC$), 134.85 (C=CH); MS, *m/e* 191 $[M]^+$. Anal. Calcd for $C_{13}H_{21}N$: C, H, N.

21b: 94% yield (84% using $Ru_3(CO)_{12}$); ^1H NMR ($CDCl_3$) δ 1.49 (d, 3 H, CH_3), 1.81–2.01 (m, 4 H, $CH_3CHCH_2CH_2$), 2.76 (m, 2 H, $CH_2C=$), 4.09 (m, 1 H, $CHCH_3$), 6.11 (d, 1 H, proton at C1), 6.92 (d, 1 H, NCH=), 7.28–7.46 (m, 5 H, Ph); ^{13}C NMR ($CDCl_3$) δ 19.69, 22.30 ($CH_3CHCH_2CH_2$), 22.31 (CH_3), 31.89 ($CH_2C=$), 50.56 ($CHCH_3$), 102.12 (C=CH), 113.64 (NCH=), 124.87, 125.00, 128.40, 129.05 (aromatic), 130.66 (PhC), 136.17 (C=CH); MS, *m/e* 211 $[M]^+$. Anal. Calcd for $C_{15}H_{17}N$: C, H, N.

21c: 91% yield, ^1H NMR ($CDCl_3$) δ 0.83 (t, 3 H, CH_3CH_2), 1.25–1.68 (m, 11 H, $CH_3(CH_2)_4$ and CH_3CH), 1.78–1.91 (m, 4 H, $CH_3CHCH_2CH_2$), 2.39 (t, 2 H, $CH_3(CH_2)_4CH_2$), 2.71 (m, 2 H, $CH_2C=$), 3.98 (m, 1 H, $CHCH_3$), 5.65 (d, 1 H, proton at C1), 6.56 (d, 1 H, NCH=); ^{13}C NMR ($CDCl_3$) δ 14.17 (CH_3CH_2), 19.99, 23.62 ($CH_3CHCH_2CH_2$), 22.30 (CH_3CH), 22.67, 27.29, 29.49, 31.23, 31.83 ($CH_3(CH_2)_5$), 32.13 ($CH_2C=$), 50.49 ($CHCH_3$), 104.08 (C=CH), 113.82 (NCH=), 124.27 (n-$C_6H_{13}C$), 129.34 (C=CH); MS, *m/e* 219 $[M]^+$. Anal. Calcd for $C_{15}H_{25}N$: C, H, N.

23: 70% yield; ^1H NMR ($CDCl_3$) δ 1.73–2.08 (m, 4 H, protons at C6,C7), 2.78 (m, 2 H, $CH_2C=$), 3.80 (m, 2 H, CH_2N), 6.15 (d, 1 H, proton at C1), 6.86 (d, 1 H, NCH=), 7.35 (m, 5 H, Ph); ^{13}C NMR ($CDCl_3$) δ 21.39, 23.30 (C6,C7), 29.26 ($CH_2C=$), 45.42 (NCH_2), 102.12 (C=CH), 115.45 (NCH=), 124.94, 125.21, 128.33, 128.77 (aromatic), 130.47 (PhC), 137.10 (C=CH); MS, *m/e* 197 $[M]^+$. Anal. Calcd for $C_{14}H_{15}N$: C, H, N.

24: 7% yield; IR ($CHCl_3$) ν(CO) 1628 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.35 (d, 3 H, CH_3CH), 1.69 (m, 4 H, protons at C4,C5), 2.32 (t, 2 H, CH_2CO), 2.81 (t, 2 H, CH_2Ph), 3.36 (t, 2 H, NCH_2), 3.81 (m, 1 H, $CHCH_3$), 7.28 (m, 5 H, Ph); MS, *m/e* 217 $[M]^+$.

Preparation of 16. The conversion of $Ph^{13}COCH_3$ (**14**) (Merck, Sharpe, and Dohme) to $Ph^{13}COCH_2Br$ (**15**) was effected using $(C_4H_9)_4N^+Br_3^-$[11]. The yield of **15** was 91%: IR ($CHCl_3$) ν (^{13}CO) 1648 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.02 (d, 2 H, $J_{HC\text{-}^{13}C}$ = 11.2 Hz, CH_2), 7.48–8.07 (m, 5 H, Ph); MS, *m/e* 106 $[M]^+$.

2-(1-Piperidinyl)acetophenone-^{13}C (**16**) was isolated in 89% yield from **15** following procedure (a) above for the unlabeled analog (i.e., **9**, n = 2, R = Ph); bp 105–107 °C (0.3 mmHg); IR ($CHCl_3$) ν (^{13}CO) 1656 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.43 (m, 2 H, protons at C4 of piperidine), 1.59 (m, 4 H, protons at C3,C5 of piperidine), 2.48 (m, 4 H, protons at C2,C6 of piperidine), 3.72 (d, 2 H, $J_{HC\text{-}^{13}C}$ = 10.1 Hz, NCH_2CO), 7.43 (m, 3 H, meta and para protons), 7.94 (m, 2 H, ortho protons); ^{13}C NMR ($CDCl_3$) δ 23.99 (C4 of piperidine), 25.79 (C3,C5 of piperidine), 51.84 (C2,C6 of piperidine), 65.27 ($NCH^{13}CO$), 128.08, 128.30, 128.47, 133.06 (aromatic), 196.82 (^{13}CO, intense signal); MS, *m/e* 204 $[M]^+$.

Rearrangement of 16 to 17. The general procedure described above was applied to the rearrangement of **16** affording **17** in 90% yield: mp 38–40 °C; IR ($CHCl_3$) ν(CO) 1626 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.67 (m, 4 H, protons at C4,C5 of piperidine), 2.32 (t, 2 H, CH_2CO), 2.88 (dd, 2 H, $^{13}CH_2Ph$), 3.08 (t, 2 H, NCH_2 ring), 3.54 (dd, 2 H, NCH_2), 7.25 (m, 5 H, Ph); ^{13}C NMR ($CDCl_3$) δ 21.07 (C4 of piperidinone), 23.09 (C5), 32.14 (CH_2CO), 33.44 ($^{13}CH_2Ph$, intense signal), 48.68 (NCH_2 ring), 49.38 (NCH_2), 126.22, 128.39, 128.80, 139.30 (aromatic), 169.92 (CO); MS, *m/e* 204 $[M]^+$.

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Registry No. **4a**, 938-36-3; **4b**, 4266-03-9; **4c**, 142438-90-2; **4d**, 142438-91-3; **4e**, 22041-19-6; **4f**, 30269-21-7; **5b**, 142438-99-1; **5c**, 142439-00-7; **5d**, 142439-01-8; **5e**, 22875-63-4; **5f**, 142439-02-9; **6a**, 20538-40-3; **6b**, 37129-04-7; **7**, 142438-92-4; **8**, 142439-03-0; **9b**, 30269-23-9; **9c**, 779-52-2; **9d**, 108656-79-7; **9e**, 119270-43-8; **9f**, 142438-93-5; **9g**, 111733-88-1; **9h**, 142438-94-6; **9i**, 115217-25-9; **10a**, 142439-04-1; **10b**, 142439-05-2; **10c**, 26209-66-5; **10d**, 15865-21-1; **10e**, 142439-06-3; **10f**, 21053-50-9; **10h**, 142439-08-5; **10i**, 89241-25-8; **11**, 142438-95-7; **12**, 142439-09-6; **13**, 142439-10-9; **16**, 779-52-2; **16**-^{13}C, 142439-16-5; **17**, 142439-17-6; **18**·HCl, 886-06-6; **18**, 73-63-2; **19**, 142438-96-8; **20a**, 142438-97-9; **20b**, 17721-98-1; **20c**, 142438-98-0; **21a**, 142439-12-1; **21b**, 142439-13-2; **21c**, 142439-14-3; **22**, 17721-98-1; **23**, 142439-15-4; **31** (R = $C(CH_3)_3$), 142439-11-0; $Ru_3(CO)_{12}$, 15243-33-1; 2-phenylpyrrolidine, 1006-64-0; 2-benzylpyrrolidine, 35840-91-6; pyrrolidine, 123-75-1; 2-(methoxymethyl)pyrrolidine, 135523-48-7; bromoacetic acid, 105-36-2; *tert*-butyl bromoacetate, 5292-43-3; octahydroindole, 4375-14-8; piperidine, 110-89-4; 1-bromo-3,3-dimethyl-2-butanone, 5469-26-1; 2-bromo-1-phenyl-1-ethanone, 70-11-1; 1-bromo-2-octanone, 26818-08-6; 2-bromo-1-(2-naphthyl)-1-ethanone, 613-54-7; decahydroisoquinoline, 6329-61-9; 2,2,6,6-tetraethylpiperidine, 768-66-1; 2,6-dimethylpiperidine, 504-03-0; 2-hexyloxirane, 2984-50-1; 2-phenyloxirane, 96-09-3; cobalt chloride, 34240-80-7.

Supplementary Material Available: Description of experimental procedures, listing of crystal data, bond lengths and angles, torsion angles, and atomic parameters, and ORTEP plots for **13** (10 pages); listing of observed and calculated structure factors for **13** (11 pages). Ordering information is given on any current masthead page.

A Room Temperature Synthesis of Perstanna[1.1.1]propellanes and the Structure/Property Relationships Revealed by a Comparison of Two Derivatives

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Abstract: Chemical reduction of hexakis(2,6-diethylphenyl)cyclotristannane (**2**) with 2.3 equiv of lithium metal in THF provides hexakis(2,6-diethylphenyl)pentastanna[1.1.1]propellane (**1**) (31% yield) and octakis(2,6-diethylphenyl)tetracyclo-[4.1.0.0^{1,5}.0^{2,6}]heptastannane (**4**) (~1% yield). With 1.2 equiv of lithium metal, the same procedure provides 1,2,2,3,3,4,4-heptakis(2,6-diethylphenyl)cyclotetrastannane (**3**) (85% yield) and tris(2,6-diethylphenyl)stannane (**5**) (103% yield). A proposed mechanism to account for the formation of **3** proceeds through the intermediacy of the monovalent tin species, $[R_2Sn]^-$ (R = 2,6-diethylphenyl) (**9**) and 1-lithio-1,2,2,3,3,4,4-heptakis(2,6-diethylphenyl)cyclotetrastannane (**14**). Evidence for the existence of **9** is provided by an ESR spectrum of a mixture of **2**, 0.5% potassium amalgam (1 equiv), and 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (crypt) (1 equiv) in THF which displays a single strong resonance centered at $g = 2.024$ [$a(^{119/117}Sn) = 152$ G]. Compound **14** has been synthesized separately by deprotonation of **3** with lithium diisopropylamide in THF, and it has been isolated as an orange microcrystalline material (43% yield). Reaction of **14** with an excess of lithium metal produces **1** in a 30% yield which supports the observation that this compound appears to be the key intermediate in the transformation of **2** to **1** and **4**. Single crystals of **4**, obtained from a toluene/acetonitrile solvent mixture at −40 °C, are, at 20 °C, monoclinic, space group $C2/c$–C^6_{2h} with $a = 27.968$ (7) Å, $b = 16.000$ (4) Å, $c = 38.510$ (11) Å, $\beta = 103.17$ (2)°, $V = 16780$ (8) Å^3, and $Z = 8$ {$d_{calcd} = 1.501$ g cm^{-3}; μ_a(Mo Kα) = 2.09 mm^{-1}}. The molecular structure of **4**, as obtained from crystallographic analysis ($R_1 = 0.047$ for 6189 independent reflections), reveals that the [1.1.1]propellane core of this compound is contracted relative to **1** with a mean Sn_{bh}–Sn_{br} bond length value of 2.845 (18) Å and a Sn_{bh}–Sn_{bh} distance of 3.348 (1) Å. On the basis of a correlation between the reduction of this latter value with an hypsochromic shift and increased intensity of an electronic transition, assumed to originate from the HOMO of perstanna[1.1.1]propellanes, in going from **1** to **4**, a significant bonding interaction between the two inverted tetrahedral tin atoms in this class of compounds is proposed. Cyclic voltammetry of **4** in THF shows two quasireversible one-electron reduction waves at $E_{1/2} = -1.35$ and -1.90 V (V vs NHE) which correspond to the [**4**]/[**4**]$^-$ and the [**4**]$^-$/[**4**]$^{2-}$ redox couples, respectively. Finally, chemical reduction of **4** can be achieved with 0.1% potassium amalgam in THF in the presence of crypt to generate, in situ, the complex [**4**]$^-$[K,crypt]$^+$, and the isotopic ESR spectrum (25 °C) of this species displays a single resonance centered at $g = 1.95$. Simulation of this spectrum can be accomplished by assuming hyperfine interactions with three sets of equivalent tin nuclei with the following parameters: $a(^{119/117}Sn) = 22$ G (2 Sn atoms); $a(^{119/117}Sn) = 50$ G (2 Sn atoms); $a(^{119/117}Sn) = 65$ G (3 Sn atoms); line width = 6.5 G.

Introduction

In 1989, we reported the isolation and characterization of the first, and to date, only, example of a heavy-atom group 14 [1.1.1]propellane, the pentastannane derivative, Sn_5R_6 (R = 2,6-diethylphenyl) (**1**), and have since explored the properties and chemical reactivity of this exceedingly stable molecule.[1] However, the low yield (ca. 15%) and the experimental difficulties encountered with the preparation of **1** through the thermolysis of hexakis(2,6-diethylphenyl)cyclotristannane (**2**) at 200 °C has severely limited its availability. Herein, we now report that **1** can be conveniently prepared through an alternative, low-temperature, higher-yielding procedure which also provides access to (1) the first example of a substitutionally-unsaturated cyclopolystannane, heptakis(2,6-diethylphenyl)cyclotetrastannane (**3**), and (2) the new perstanna[1.1.1]propellane derivative, octakis(2,6-diethylphenyl)tetracyclo[4.1.0.0^{1,5}.0^{2,6}]heptastannane (**4**). A comparison of the properties and molecular structure of this latter compound with those of **1** provides the first direct experimental evidence for a significant bonding interaction between the two bridgehead tin atoms in perstanna[1.1.1]propellanes.

Results and Discussion

Chemical Reduction of 2. In the course of studies directed toward the production of monovalent tin species, we made the

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