with stirring. The alcohol **18** was then transformed into the 2-methoxy-2-propyl ether **19** (76% overall from 17) by reaction with 2-methoxypropene[16] in CCl_4 in the presence of a trace of phosphorus oxychloride and exposed to 3 equiv of lithium acetylide–ethylenediamine complex in dimethyl sulfoxide at 25 °C for 36 h. After workup and stirring with Amberlite IRC-50 resin in methanol, the acetylenic diol **20** could be obtained as major product (90% yield) contaminated by a small amount (~10% yield) of the position isomeric 1,3-diol resulting from the alternative cleavage of the 3-membered ring in **19**; the mixture was used for the remaining steps since purification at a later stage was advantageous.[17] The pure acetylenic alcohol **21**, $[\alpha]^{22}_{D}$ +32.4° (CH_3OH), was obtained in 75% overall yield from the mixture by (1) conversion to the primary mesitylsulfonate (1.05 equiv of mesitylenesulfonyl chloride in dry pyridine at −20 °C for 12 h) and (2) coupling[18] with dimethylcopperlithium (excess) in ether at −15 to −20 °C for 20 h, and (3) chromatography on silica gel (pentane–ether for elution).[19] The alcohol **21** was then silylated[20] (*tert*-butyldimethylsilyl chloride–imidazole–DMF, 18 h at 25 °C) and methylated (1.1 equiv of lithium diisopropylamide in THF followed by 3 equiv of CH_3I at −78 to 25 °C over 1 h and 25 °C for 2 h) to afford in 88% overall yield the protected acetylene **22**. Sequential hydrozirconation[21] of **22** with dicyclopentadienylchlorohydridozirconium (1 equiv) in benzene under argon at 43 °C for 2 h and iodination (addition to a small excess of iodine in CCl_4 at 25 °C) afforded in 84% yield a single isomeric iodo olefin, the required intermediate **4**,[22] $[\alpha]^{20}_{D}$ +24.9° ($CHCl_3$).

With the successful synthesis of intermediates **3** and **4** the stage was thus set for the elaboration of the structure of erythronolide B as described in the following publication.[23,24]

References and Notes

(1) (a) Part 1: E. J. Corey, K. C. Nicolaou, and L. S. Melvin, Jr., *J. Am. Chem. Soc.*, **97**, 654 (1975). (b) Part 2: E. J. Corey, L. S. Melvin, Jr., and M. F. Haslanger, *Tetrahedron Lett.*, 3117 (1975).

(2) For reviews on structure, chemistry, and stereochemistry of erythromycins, see (a) T. J. Perun in "Drug Action and Drug Resistance in Bacteria", Vol. I, S. Mitsuhashi, Ed., University of Tokyo Press, Tokyo, 1971, pp 123–152; (b) W. D. Celmer, *Pure Appl. Chem.*, **28**, 413 (1971); and (c) W. Keller-Schierlein, *Prog. Chem. Org. Nat. Prod.*, **30**, 314 (1973).

(3) For a review of the biosynthesis of erythromycins, see N. L. Oleinick in "Antibiotics", Vol. III, J. W. Corcoran and F. E. Hahn, Ed., Springer-Verlag, New York, N.Y., 1975, pp 396–419.

(4) Of the synthetic challenge R. B. Woodward has written "Erythromycin, with all our advantages, looks at present hopelessly complex, particularly in view of its plethora of asymmetric centers . . ." (in "Perspectives in Organic Chemistry", A. Todd, Ed., Interscience Publishers, New York, N.Y., 1956, p 160).

(5) For recent reviews on the synthesis of macrocyclic lactones, see (a) K. C. Nicolaou, *Tetrahedron*, **33**, 683 (1977); and (b) S. Masamune, G. S. Bates, and J. W. Corcoran, *Angew. Chem., Int. Ed. Engl.*, **16**, 585 (1977).

(6) (a) E. J. Corey and K. C. Nicolaou, *J. Am. Chem. Soc.*, **96**, 5614 (1974) (method); (b) E. J. Corey, D. J. Brunelle, and P. J. Stork, *Tetrahedron Lett.*, 3405 (1976) (method); (c) E. J. Corey and D. J. Brunelle, *ibid.*, 3409 (1976) (method); (d) E. J. Corey, K. C. Nicolaou and T. Toru, *J. Am. Chem. Soc.*, **97**, 2287 (1975) (vermiculine synthesis); (e) E. J. Corey, P. Ulrich, and M. Fitzpatrick, *ibid.*, **98**, 222 (1976) (recifeiolide synthesis); (f) E. J. Corey and R. H. Wollenberg, *Tetrahedron Lett.*, 4701, 4705 (1976) (brefeldin A synthesis); (g) E. J. Corey, R. H. Wollenberg, and D. R. Williams, *ibid.*, 2243 (1977) (brefeldin A synthesis); and (h) E. J. Corey and S. Bhattacharyya, *ibid.*, 3919 (1977) (enterobactin synthesis).

(7) For conformational studies on the erythronolide system, see (a) D. R. Harris, S. G. McGeachin, and H. H. Mills, *Tetrahedron Lett.*, 679 (1965); (b) T. J. Perun, *ibid.*, 4501 (1969); (c) R. S. Egan, T. J. Perun, J. R. Martin, and L. A. Mitscher, *Tetrahedron*, **29**, 2525 (1973); (d) E. J. Corey and L. S. Melvin, Jr., *Tetrahedron Lett.*, 929 (1975); and (e) W. D. Celmer, *Antimicrob. Agents Chemother.*, 144 (1965).

(8) B. Miller, *J. Am. Chem. Soc.*, **92**, 6246 (1970).

(9) Satisfactory infrared, proton magnetic resonance, and mass spectral data were obtained for each synthetic intermediate using purified and chromatographically homogeneous samples. All chemical reactions were conducted under an inert atmosphere unless otherwise indicated.

(10) The stereochemistry of this substance is clear from the NMR spectrum which unambiguously indicates that the proton at the newly created stereocenter is axial.

(11) Prepared from Ni–Al alloy and aqueous sodium hydroxide at 75–80 °C (temperature is critical) followed by washing to neutrality, activation using a small amount of hydrazine, and further washing with a few small portions of dimethoxyethane (air free). The stereoselectivity of the reduction of **12** is quite sensitive to the conditions used for preparation of the catalyst.

(12) The single-crystal x-ray crystallographic analysis was kindly carried out by Professor Jon Bordner, Department of Chemistry, North Carolina State University, Raleigh, N.C., in 1976. Details of the analysis will be published in *Cryst. Struct. Commun.*

(13) G. B. Payne and P. H. Williams, *J. Org. Chem.*, **24**, 54 (1959).

(14) K. Harada and J. Oh-hashi, *Bull. Chem. Soc. Jpn.*, **39**, 2311 (1966).

(15) The optical rotation of fully resolved salt was found to be $[\alpha]^{22}_{D}$ +11.8° (CH_3OH). The acid **17** was recovered quantitatively from the salt by treatment with 1.0 equiv of methanesulfonic acid in ether, washing with a small amount of saturated Na_2SO_4, and evaporation of ether.

(16) M. S. Newman and M. C. Vander Zwan, *J. Org. Chem.*, **38**, 2910 (1973).

(17) The selectivity of formation of **20** is due to the presence of the bulky ether group in the starting oxide **19**. Use of the epoxy alcohol **18** in the acetylide displacement yielded much inferior selectivity.

(18) E. J. Corey and G. H. Posner, *J. Am. Chem. Soc.*, **90**, 5615 (1968).

(19) The optically active alcohol **21** was identical chromatographically and spectroscopically with racemic alcohol obtained by reaction of *trans*-2-pentene oxide with sodium acetylide.

(20) E. J. Corey and A. Venkateswarlu, *J. Am. Chem. Soc.*, **94**, 6190 (1972).

(21) (a) D. W. Hart, T. F. Blackburn, and J. Schwartz, *J. Am. Chem. Soc.*, **97**, 679 (1975); (b) J. Schwartz and J. A. Labinger, *Angew. Chem., Int. Ed. Engl.*, **15**, 333 (1976).

(22) The location of iodine in **4** is clear from the ^1H NMR spectrum (e.g., sharp CH_3 singlet at 2.38 ppm), and the stereochemistry about the double bond follows from the cis addition course of hydrozirconation. The formation of only one position isomer in hydrozirconation, though not unexpected, is noteworthy.

(23) This work was assisted financially by a grant from the National Institutes of Health.

(24) We are deeply indebted to Dr. Jon Bordner[12] for his important assistance to this work by x-ray analysis of the bromo lactone **10**. Mr. Istvan Székely helped in the preparation of some of the synthetic intermediates.

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Total Synthesis of Erythromycins. 4. Total Synthesis of Erythronolide B[1]

Sir:

Described herein is the first total synthesis of an aglycone of the erythromycin family of antibiotics, erythronolide B (**1**), a naturally occurring substance which is the biosynthetic progenitor of all the erythromycins.[2] This work makes use of key intermediates described in the foregoing paper,[1] the keto acid **2** and the unsaturated iodide **3**.

Although both **2** and **3** are available in optically active form of the required absolute configuration, the initial demonstration of the approach as here outlined involved the use of racemic **2** and optically active **3** and the chromatographic separation of an unnatural diastereomer during the course of synthesis.

Baeyer–Villiger reaction of the keto acid (±)-**2** was surprisingly slow using customary procedures and required forcing conditions. The desired lactone **4** could be obtained, however, in ~70% yield by treatment with excess 25% peracetic acid in ethyl acetate (Union Carbide Co.) for 6 days at 55–58 °C after chromatographic removal of unchanged keto acid **2**.[3,4] Treatment of the lactone with 1.1 equiv of 2,2′-dipyridyl disulfide and 1.2 equiv of triphenylphosphine in THF at 20 °C[5] afforded, after removal of solvent and chromatography at +5 °C on silica gel, 65% of the pure thio ester **5** which was coupled[6] with the iodide **3** via a Grignard reaction. The dextrorotatory iodide **3**, $[\alpha]^{25}_{D}$ +24.9°, in THF at −78 °C was lithiated by treatment with 2 equiv of *tert*-butyllithium in pentane (−78 °C for 0.5 h and −50 °C for 0.5 h)[7] and, after addition of 1.0 equiv of anhydrous magnesium bromide in THF at −50 °C (from 1,2-dibromoethane and magnesium metal

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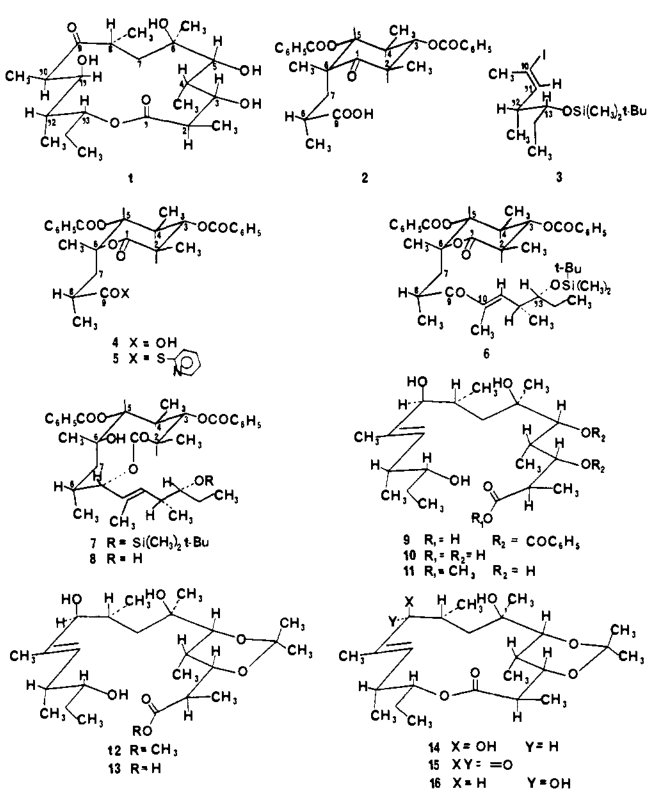

1, **2**, **3**, **4** X = OH, **5** X = S-2-pyridyl, **6**, **7** R = Si(CH$_3$)$_2$t-Bu, **8** R = H, **9** R$_1$ = H, R$_2$ = COC$_6$H$_5$, **10** R$_1$ = R$_2$ = H, **11** R$_1$ = CH$_3$, R$_2$ = H, **12** R = CH$_3$, **13** R = H, **14** X = OH, Y = H, **15** XY: =O, **16** X = H, Y = OH

in ether at 20 °C, followed by evaporation and addition of THF), the resulting vinylmagnesium reagent was allowed to react with the 2-pyridinethiol ester (±)-**5** at −20 °C for 10 min to give, after quenching with pH 7 buffer, extractive isolation, and chromatography, the keto lactone diester **6** (90%).[8] The next step, reduction of the ketonic function in the coupling product **6**, turned out to be unexpectedly challenging owing to the surprisingly similar reactivity of the keto and ϵ-lactone carbonyls toward most reducing agents and the propensity of the enone unit to undergo conjugate (1,4) hydride addition. However, success was achieved using zinc borohydride (4.5 molar equiv) in dimethoxyethane-ether (2:1) at 5 °C for 3 days, which converted **6** to the 10-membered lactone **7**[8a] by a combination of carbonyl reduction and translactonization[9] (70% yield after chromatography). Remarkably, the addition of hydride to the carbonyl group of **6** was effectively stereospecific generating only one of the two possible configurations at C(9). The 10-membered cyclic structure of **7** follows unambiguously from spectral data and the stereochemistry at C(9) is based on conversion (see below) to a 9-hydroxy erythronolide derivative whose configuration at C(9) is indicated by the evidence presented below. Removal of the silyl protecting group in **7** was readily accomplished (acetic acid–water–THF, 3:1:1, at 55 °C for 24 h) to form the alcohol **8**[8a] (92%).

Hydrolysis of the lactone function in **8** could not be effected cleanly using aqueous alkali–organic solvent combinations; however, clean saponification was accomplished with THF, 30% hydrogen peroxide, and 1 N aqueous lithium hydroxide (15:2.5:1) at 20 °C for 5 h[10] to afford after isolation carboxylic acid **9**[8a] (85% yield after chromatography on silica gel using 10% CH_3OH in CH_2Cl_2).[11] Treatment of **9** with excess potassium hydroxide (0.07 N) in 2.5:1 dimethoxyethane-water at 45 °C for 20 h resulted in complete saponification of the benzoate groups to give, after isolation of the acid **10** and treatment with excess diazomethane, an 86% yield of the methyl ester **11** and its diastereomer.[8a] These could be separated by preparative thin layer chromatography on silica gel, the R_f values of **11** and the diastereomer being 0.66 and 0.62 (five developments using 10% CH_3OH in CH_2Cl_2). The product of higher R_f (**11**), $[\alpha]^{20}{}_D$ +8.5° ($CHCl_3$), was identical in all respects with a sample of **11** obtained by an unambiguous series of transformations (outlined below) starting from naturally occurring erythronolide B; infrared, ^{1}H NMR, ultraviolet, and mass spectra were superimposable and the optical rotation and chromatographic behavior of the two samples corresponded within experimental limits. Treatment of synthetic **11** with 2-methoxypropene (excess) and 0.5 equiv of dry hydrogen bromide in methylene chloride at 0 °C for 16 h and subsequent selective methanolysis of the isolated product with Amberlite IRC-50 in methanol at 20 °C for 12 h yielded (75%), after workup and chromatography on silica gel, the acetonide ester **12**, $[\alpha]^{20}{}_D$ +11.8° ($CHCl_3$), identical in all respects with an authentic sample made from erythronolide B. Treatment of the methyl ester **12** with 0.1 N potassium hydroxide in 3:1 methanol–water at 45 °C for 12 h afforded in 95% yield the acetonide acid **13**. Cyclization of **13** to the 14-membered lactone **14** could be effected in 50% yield via the thiol ester with 4-*tert*-butyl-*N*-isopropyl-2-mercaptoimidazole[12] by heating in dry toluene at reflux.[13]

Authentic **14** and also reference samples of intermediates **11**, **12**, and **13** were synthesized from the known erythronolide B derived ketone **15**[14] as follows. Whereas reduction of **15** with sodium borohydride in ethanol, lithium triethylborohydride in THF, or a number of other standard reagents affords stereospecifically the less polar (R_f 0.28 in 1:1 Et_2O–hexane) of two epimeric 9-alcohols, the other epimer (R_f 0.15) is obtained as major product (65% yield) using 3 molar equiv of lithium *n*-butylborohydride (prepared from borane-dimethyl sulfide complex in toluene with 1 equiv of *n*-butyllithium in hexane at 0 °C) in toluene solution at 70 °C for 60 s (with subsequent rapid cooling in an ice bath, quenching with pH 7 buffer, extractive isolation, and chromatography) along with only 20% of the epimer of R_f 0.28. The two epimers of R_f 0.15 and 0.28 can reasonably be assigned as **14** and **16** respectively based on ^{1}H NMR data and chemical studies.[15] The chemical shift values for C(9) H (δ in $CDCl_3$) and coupling constants $J_{8,9}$ for the two epimers were determined as δ 3.45 ($J_{8,9}$ = 10.5 Hz) for the isomer of R_f 0.15 and δ 3.75 ($J_{8,9}$ = 0 Hz) for the isomer of R_f 0.28. Based on the Perun–Celmer conformation[16] for the erythronolide ring and study of CPK models these data lead to formulation of the more polar epimer as **14** (9β-OH) and the less polar epimer as **16** (9α-OH). This formulation is further supported by the observation that the reaction of the more polar epimer (9β-OH) with *m*-chloroperbenzoic acid leads to an epoxy alcohol which is oxidized (CrO_3–pyridine) to the known[14] 10,11β-oxido-9 ketone,[17] whereas the same sequence applied to the less polar epimer (9α-OH) leads to the isomeric 10,11α-oxido-9 ketone.[18] The more polar 9-alcohol **14** (derived from erythronolide B) was converted to the hydroxy acid **13** by treatment with 2.3 N sodium hydroxide in dimethyl sulfoxide–water (4:3) at 115 °C for 7 h and, from this reference sample, the ester **12** was obtained by reaction with diazomethane. From erythronolide-derived **12** a reference sample of the pentahydroxy ester **11** was prepared by exposure to THF–1 HCl (1:1) at 20 °C for 12 h.

The conversion of the alcohol **14** to erythronolide B which completes the present synthesis follows the route previously described:[14] (1) oxidation of **14** to the ketone **15** (MnO_2 in CH_2Cl_2 at 25 °C for 3 h), (2) epoxidation of the 10,11 double bond (H_2O_2–OH^-), (3) hydrogenolysis of the oxido function at C-10 (H_2/Pd/C, CH_3OH), (4) epimerization at C-10 (catalytic K_2CO_3 in CH_3OH), and (5) removal of the 3,5-isopropylidene group (1:1 THF–1 N HCl at 20 °C).

These studies are being continued along several lines which include (1) modifications in the synthesis of erythronolide B, (2) synthesis of erythronolide A, and (3) synthesis of the erythromycins.[19,20]

References and Notes

(1) Part 3: E. J. Corey, E. J. Trybulski, L. J. Melvin, Jr., K. C. Nicolaou, J. A. Secrist, R. Lett, P. W. Sheldrake, J. R. Falck, D. J. Brunelle, M. F. Haslanger, S. Kim, and S. Yoo, *J. Am. Chem. Soc.*, proceeding paper in this issue.
(2) N. L. Oleinick in "Antibiotics", Vol. III, J. W. Corcoran and F. E. Hahn, Ed., Springer-Verlag, New York, N.Y., 1975, pp 396–419.
(3) Some starting material was recovered under these conditions and the yield given here is corrected for such recovery (usually ~35%). Less satisfactory results were obtained with longer times or more strongly acidic peracid reagents. The product **4** is accompanied by minor amounts of an isomeric ϵ-lactone which is removed in the next step. Further studies are planned on the conversion of 2 to **4** inter alia by an internal Baeyer–Villiger reaction. The use of wet peracid reagent promotes rearrangement of **4** to the isomeric γ-lactone carboxylic acid.
(4) Satisfactory infrared, proton magnetic resonance, and mass spectral data were obtained on purified, chromatographically homogeneous samples of each stable intermediate. All reactions were conducted under an inert atmosphere.
(5) (a) T. Mukaiyama, R. Matsueda, and M. Suzuki, *Tetrahedron Lett.*, 1901 (1970); (b) T. Mukaiyama, R. Matsueda, and H. Marayama, *Bull. Chem. Soc. Jpn.*, **43**, 1271 (1970).
(6) T. Mukaiyama, M. Araki, and H. Takai, *J. Am. Chem. Soc.*, **95**, 4763 (1973).
(7) E. J. Corey and D. J. Beames, *J. Am. Chem. Soc.*, **94**, 7210 (1972).
(8) (a) This product was obtained as a mixture of two diastereomers as expected from the coupling of racemic **5** and dextrorotatory **3**; (b) R_f values on diastereomers (ratio ~1:1) on silica gel plates using 2% acetone in CH_2Cl_2 with two developments, 0.78 and 0.76.
(9) See E. J. Corey, D. J. Brunelle, and K. C. Nicolaou, *J. Am. Chem. Soc.*, **99**, 7359 (1977), for other examples of such translactonizations.
(10) See E. J. Corey, J. S. Bindra, A. Grodski, and T. K. Schaaf, *J. Am. Chem. Soc.*, **95**, 7522 (1973), for another case of peroxide accelerated lactone hydrolysis under mildly basic conditions.
(11) That no epimerization (e.g., α to carbonyl) occurs during the hydrolysis of **8** to **9** was demonstrated by conversion of **9** to the 4-*tert*-butyl-*N*-isopropyl-2-mercaptoimidazole thiol ester[12] and cyclization by heating in toluene at reflux which afforded the lactone **8** in high yield. Although no appreciable amount of 14-membered lactone could be detected (by careful TLC analysis), we plan to study further this possibility for forming the erythronolide system.
(12) E. J. Corey and D. J. Brunelle, *Tetrahedron Lett.*, 3409 (1976).
(13) The thiol ester was prepared from azeotropically dried (toluene) hydroxy acid **13** by the disulfide–phosphine method[5,12] (in toluene at 20 °C for 30 min) and (at +5 °C) added slowly (over 12 h by motor-driven syringe) to dry toluene at reflux under argon.
(14) E. J. Corey, K. C. Nicolaou, and L. S. Melvin, Jr., *J. Am. Chem. Soc.*, **97**, 654 (1975).
(15) Since this configurational assignment is based on interpretation rather than formal proof, the configuration assigned with respect to C(9) in intermediates **7–14** and **16** is regarded as provisional and further study of this point is planned.
(16) See (a) W. D. Celmer, *Antimicrob. Agents Chemother.*, 144 (1965); (b) T. J. Perun, *Tetrahedron Lett.*, 4501 (1969); (c) R. S. Egan, T. J. Perun, J. R. Martin, and L. A. Mitscher, *Tetrahedron*, **29**, 2525 (1973); (d) D. R. Harris, S. G. McGeachin, and H. H. Mills, *Tetrahedron Lett.*, 679 (1965), and (e) E. J. Corey and L. S. Melvin, Jr., *ibid.*, 929 (1975).
(17) That is, the 10(*R*),11(*S*) oxide.
(18) For stereochemical control of epoxidation by allylic hydroxyl orientation, see G. Berti, *Top. Stereochem.*, **7**, 130 (1973). Examination by CPK molecular models indicates that suitable geometry can be attained in the transition state for hydroxyl assisted epoxidation within the Perun–Celmer conformational limits for either epimeric alcohol **14** or **16**. The rates of oxidation of the two alcohols differ only by a factor of ~2.
(19) We are grateful to a number of individuals for their help in the successful completion of the project. Drs. W. D. Celmer and F. Sciavolino (Chas. Pfizer Co.) and Dr. Thomas J. Perun (Abbott Co.) generously provided advice, encouragement, and samples of erythronolide B. Drs. J. A. Secrist, M. F. Haslanger, and I. Székely made experimental contributions to the early part of the synthesis.
(20) This research was assisted financially by the National Institutes of Health.

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Isocyanide Insertion Reactions. The Role of Isocyanide Insertions in the Metal Assisted Hydrogenation of Isocyanides

Sir:

Several recent reports have described the first examples of the homogeneous hydrogenation of heteronuclear triple bonds.[1]

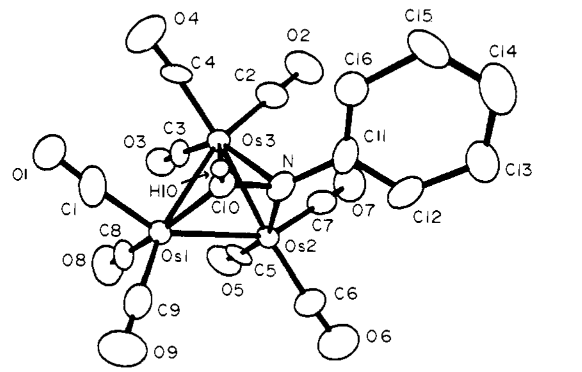

Figure 1. An ORTEP diagram of (μ_3-$CHNC_6H_5$)(μ-H)$Os_3(CO)_9$ showing 50% probability ellipsoids.

In the belief that an insertion reaction is the first step in the known catalytic activity of the cluster compound $Os_3(CO)_{12}$,[1a,b] we have examined the reaction of the closely related $H_2Os_3(CO)_{10}$ with phenyl isocyanide. The initial reaction product, I,[2] has the formula $H_2Os_3(CO)_{10}(CNC_6H_5)$ which is formally analogous to the previously reported compounds $H_2Os_3(CO)_{10}L$.[3] This complex probably has a structure analogous to those of $H_2Os_3(CO)_{11}$[4] and $H_2Os_3(CO)_{10}P(C_6H_5)_3$[5] since the infrared spectrum clearly shows the presence of a terminally coordinated isocyanide ligand, ν(CN) 2190 cm^{-1}, and the ^{1}H NMR spectrum shows both bridging and terminal hydride ligands.[6]

Upon refluxing in *n*-butyl ether,[7] I loses 1 mol of CO and is transformed into the new complex, II, of formula $HOs_3(CO)_9(CHNC_6H_5)$ which is believed to be a possible intermediate in the phenyl isocyanide reduction process.

The molecular structure of II was established by x-ray crystallographic methods, and is shown in Figure 1.[8] II contains a cluster of three osmium atoms and nine linear carbonyl groups, but the most important feature is an *N*-phenyl formimidoyl ligand which bridges the three osmium atoms.[9,10] Interestingly, the C(10)–N bond distance is very long at 1.415 (11) Å. We believe that this long distance indicates a high degree of reduction of the formimidoyl carbon–nitrogen double bond, and that this effect may, in turn, pave the way for further reduction processes.[12]

The formimidoyl hydrogen atom, H(10), was located crystallographically, and is attached solely to the formimidoyl carbon, C(10). The location of this hydrogen atom was also supported through the ^{1}H NMR spectrum which showed a characteristic singlet at τ −0.69 ppm. A second singlet at τ 27.45 ppm indicates that the remaining hydrogen atom is present as a bridging hydride ligand, but this was not located in the structure analysis.

The characterization of this formimidoyl ligand strongly indicates the occurrence of an insertion rearrangement involving the isocyanide ligand and a metal–hydrogen bond.[13] The fact that the ligand is bonded to three osmium atoms may be a very important and certainly a unique feature of cluster chemistry.[15] Although we have not yet obtained complete reduction of the isocyanide ligand, this has recently been achieved for a different cluster system.[1c] Our studies to date, however, do demonstrate the important first steps in the hydrogenation process and thoroughly reveal the manner in which this partially hydrogenated isocyanide is bonded to the cluster unit.

Acknowledgment. Support from the Division of Basic Energy Sciences, U.S. Department of Energy is gratefully acknowledged.

Supplementary Material Available: Tables of fractional coordinates, bond distances and angles, and structure factor amplitudes (21 pages). Ordering information is given on any current masthead page.