

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 translocationizations.
- (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 ester¹² 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

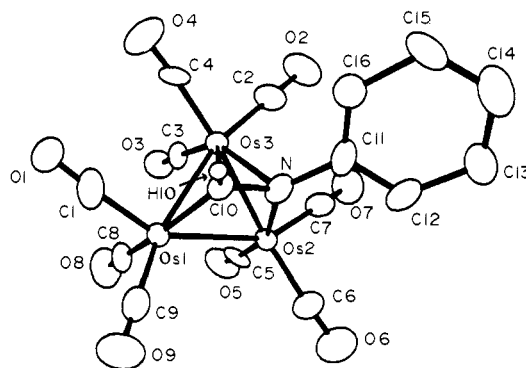


Figure 1. An ORTEP diagram of $(\mu_3\text{-CHNC}_6\text{H}_5)(\mu\text{-H})\text{Os}_3(\text{CO})_9$ showing 50% probability ellipsoids.

In the belief that an insertion reaction is the first step in the known catalytic activity of the cluster compound $\text{Os}_3(\text{CO})_{12}$,^{1a,b} we have examined the reaction of the closely related $\text{H}_2\text{Os}_3(\text{CO})_{10}$ with phenyl isocyanide. The initial reaction product, **I**,² has the formula $\text{H}_2\text{Os}_3(\text{CO})_{10}(\text{CNC}_6\text{H}_5)$ which is formally analogous to the previously reported compounds $\text{H}_2\text{Os}_3(\text{CO})_{10}\text{L}$.³ This complex probably has a structure analogous to those of $\text{H}_2\text{Os}_3(\text{CO})_{11}$ ⁴ and $\text{H}_2\text{Os}_3(\text{CO})_{10}\text{P}(\text{C}_6\text{H}_5)_3$ ⁵ since the infrared spectrum clearly shows the presence of a terminally coordinated isocyanide ligand, $\nu(\text{CN})$ 2190 cm^{-1} , and the ¹H 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 $\text{HOs}_3(\text{CO})_9(\text{CHNC}_6\text{H}_5)$ 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 ¹H 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.

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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.

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- I is formed by adding phenyl isocyanide dropwise to a concentrated solution of $\text{H}_2\text{Os}_3(\text{CO})_{10}$ in pentane until the solution turns yellow (1–2 min). Vigorous stirring induces precipitation (< 10 min) of I. With cooling (-20°C) the yield becomes essentially quantitative.
- (a) J. R. Shapley, J. B. Keister, M. R. Churchill, and B. G. DeBoer, *J. Am. Chem. Soc.*, **97**, 4145 (1975); (b) A. J. Deeming and S. Hasso, *J. Organomet. Chem.*, **114**, 313 (1976).
- M. R. Churchill and B. G. DeBoer, *Inorg. Chem.*, **16**, 878 (1977).
- M. R. Churchill and B. G. DeBoer, *Inorg. Chem.*, **16**, 2397 (1977).
- Satisfactory elemental analysis have been obtained. Variable-temperature ^1H NMR spectra indicate that I exists as mixture of two isomers and is also fluxional (i.e., bridging and terminal hydride ligands are rapidly interconverting at room temperature).
- The reaction is characterized by a purple coloration which develops and disappears within the first 10–15 min, and proceeds to completion over a period of ~ 2 h. At completion, II is formed in up to 70% yield. The isolation and characterization of intermediates in the transformation $\text{I} \rightarrow \text{II}$ is now being carried out. II was isolated by chromatography over alumina/6% H_2O and crystallized from hexane solvent: IR ν (CO) 2090 (m), 2065 (s), 2035 (s), 2010 (s), 2000 (s), 1990 (s), 1970 (m) cm^{-1} .
- II crystallizes in the monoclinic space group $P2_1/n$; $a = 8.518$ (3) Å, $b = 8.095$ (2) Å, $c = 30.141$ (4) Å, $\beta = 93.85$ (2) $^\circ$. Diffraction data were collected on a CAD-4 automatic diffractometer; 2468 reflections ($F^2 > 3.0\sigma(F^2)$) were used in the structure solution and refinement. The structure was solved by the heavy-atom method. All programs used were those of the Enraf-Nonius structure determination program library, and all calculations were done on a PDP 11/45 computer. Final residuals were $R = 0.034$ and $R_w = 0.040$.
- $\text{Os}(1)-\text{Os}(2) = 2.956$ (1), $\text{Os}(1)-\text{Os}(3) = 2.797$ (1), $\text{Os}(2)-\text{Os}(3) = 2.740$ (1), $\text{Os}(1)-\text{C}(10) = 2.03$ (1), $\text{Os}(2)-\text{N} = 2.12$ (1), $\text{Os}(3)-\text{C}(10) = 2.27$ (1), $\text{Os}(3)-\text{N} = 2.22$ (1), $\text{C}(10)-\text{N} = 1.415$ (11), $\text{N}-\text{C}(11) = 1.478$ (13) Å.
- Kaesz^{1d} has recently discussed a structurally similar compound which was observed as an intermediate in the cluster catalyzed reduction of organonitriles. An analogous structure has been proposed for the compound, $\text{HOs}_3(\text{CO})_9(\text{CHNCH}_3)_3$, which was prepared by the reaction of $\text{Os}_3(\text{CO})_{12}$ with trimethylamine.¹¹
- C. C. Yin and A. J. Deeming, *J. Organomet. Chem.*, **133**, 123 (1977).
- E. L. Muetterties, *Bull. Soc. Chim. Belg.*, **85**, 451 (1976).
- There have been previous reports of isocyanide insertions into metal-hydride bonds.¹⁴
- (a) D. F. Christian, G. R. Clark, W. R. Roper, J. M. Waters, and K. R. Whittle, *J. Chem. Soc., Chem. Commun.*, 458 (1972); (b) D. F. Christian, H. C. Clark, and R. F. Stepaniak, *J. Organomet. Chem.*, **112**, 209 (1976); (c) D. F. Christian and W. R. Roper, *J. Chem. Soc., Dalton Trans.*, 2556 (1975); (d) D. F. Christian and W. R. Roper, *J. Organomet. Chem.*, **80**, C35 (1974).
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Tetrametallic Nickel-Boron Clusters, $(\eta^5\text{-C}_5\text{H}_5)_4\text{Ni}_4\text{B}_4\text{H}_4$ and $(\eta^5\text{-C}_5\text{H}_5)_4\text{Ni}_4\text{B}_5\text{H}_5$. Synthesis of Metalloboron Cluster Systems by Transition Metal Aggregation on a Small Borane Framework

Sir:

The reaction¹ of B_5H_8^- ion with CoCl_2 and C_5H_5^- in cold tetrahydrofuran (THF) generates, among other products, a series of polyhedral cobalt-boron clusters having a high metal content, e.g., $(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}_2\text{B}_4\text{H}_6$, $(\eta^5\text{-C}_5\text{H}_5)_3\text{Co}_3\text{B}_3\text{H}_5$, $(\eta^5\text{-C}_5\text{H}_5)_3\text{Co}_3\text{B}_4\text{H}_4$, and $(\eta^5\text{-C}_5\text{H}_5)_4\text{Co}_4\text{B}_4\text{H}_4$, all of which have been crystallographically characterized.² The major cobaltaborane product of the reaction is the square-pyramidal complex $2\text{-}(\eta^5\text{-C}_5\text{H}_5)\text{CoB}_4\text{H}_8$, a B_5H_9 analogue; further addition of cobalt to the bridge-deprotonated anion of that species, $(\eta^5\text{-C}_5\text{H}_5)\text{CoB}_4\text{H}_7^-$, produces the same metal-rich clusters.³

The formation of these metalloboron cages can be envisioned as a stepwise aggregation of cyclopentadienylcobalt units onto a borane substrate, which thereby serves as a nucleation center.

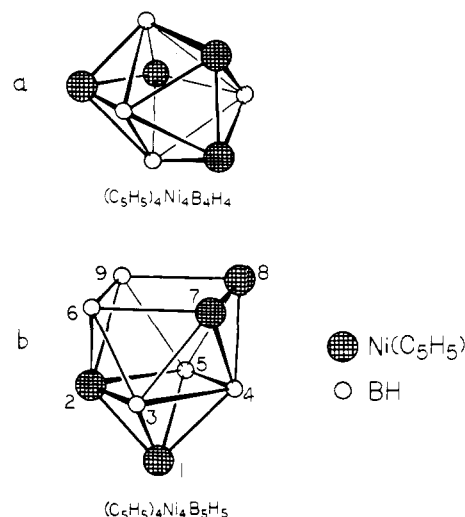


Figure 1. (a) Structure of $(\eta^5\text{-C}_5\text{H}_5)_4\text{Ni}_4\text{B}_4\text{H}_4$ (I). (b) Proposed structure of $(\eta^5\text{-C}_5\text{H}_5)_4\text{Ni}_4\text{B}_5\text{H}_5$ (II). The molecule is bisected by a mirror plane through Ni(1), Ni(2), and B(4).

Moreover, since in each of the polyhedral cobalt-boron clusters the metal atoms show a distinct propensity to adopt adjacent vertices in the cage framework,² it appears that the presence of one or more cobalt centers in the cage promotes the further addition of cobalt.⁴ That this phenomenon is not limited to cobalt is suggested by the preparation from CB_5H_9 of a trimetallic $(\eta^5\text{-C}_5\text{H}_5)_3\text{Ni}_3\text{CB}_5\text{H}_6$ complex containing two Ni-Ni interactions,⁵ and the synthesis of a $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ni}_2\text{B}_{10}\text{H}_{10}$ complex which is proposed to have adjacent metal atoms, from the $\text{B}_{10}\text{H}_{10}^{2-}$ ion.⁶ Moreover, in the closely related metallocarborane family there are numerous examples of di- and trimetallic species in which the metals kinetically adopt vicinal locations in the polyhedron (although in some cases they migrate at elevated temperature to nonvicinal positions).⁷

In this communication we report a major extension of this pattern with the synthesis of two tetranickel species which are the second and third examples (after $(\eta^5\text{-C}_5\text{H}_5)_4\text{Co}_4\text{B}_4\text{H}_4$ ^{1b,c}) of metalloboron polyhedra containing four metal atoms, and are new representatives of "hybrid" cages¹ linking the borane and metal cluster families. The treatment of 22 mmol of $\text{Na}^+\text{B}_5\text{H}_8^-$ (prepared from B_5H_9 and NaH) with 34 mmol of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ni}$ and sodium amalgam containing 36 mmol of Na in THF at -30°C , with subsequent stirring at 0°C and finally at room temperature, gave a dark green solution. Removal of solvent in vacuo, extraction with hexane followed by CH_2Cl_2 , and separation by preparative-scale liquid chromatography on silica afforded two major components as crystalline, air-stable solids: brown $(\eta^5\text{-C}_5\text{H}_5)_4\text{Ni}_4\text{B}_4\text{H}_4$ (I) (0.817 g (18% yield based on $(\text{C}_5\text{H}_5)_2\text{Ni}$ consumed), R_f 0.60) and green $(\eta^5\text{-C}_5\text{H}_5)_4\text{Ni}_4\text{B}_5\text{H}_5$ (II) (0.465 g (10%), R_f 0.49). The mass spectra of I and II exhibited strong parent groupings with intensity patterns conforming to the compositions indicated above. Exact mass determinations: for I, calculated for $^{60}\text{Ni}_4^{12}\text{C}_{20}^{11}\text{B}_4^1\text{H}_{24}^+$ 547.9578, found 547.9576; for II, calculated for $^{60}\text{Ni}_4^{12}\text{C}_{20}^{11}\text{B}_5^1\text{H}_{25}^+$ 559.9750, found 559.9743.

The 100-MHz ^1H FT NMR spectrum of I in CDCl_3 exhibited a single C_5H_5 resonance at δ 5.34 ppm¹⁰ relative to $(\text{CH}_3)_4\text{Si}$, and an H-B singlet (^{11}B decoupled) at δ 8.22; the ^1H spectrum of II contained C_5H_5 singlets at δ 5.45, 5.35, and 5.29 with relative areas of 5:10:5, and H-B resonances (^{11}B decoupled) at δ 8.80, 7.25, and 4.70 with relative areas of 2:1:2. The 32-MHz ^{11}B FT NMR spectrum of I exhibited one doublet at δ 56.2 ppm¹⁰ relative to $\text{BF}_3\cdot\text{O}(\text{C}_2\text{H}_5)_2$ ($J_{\text{BH}} = 156$ Hz), which collapsed to a singlet on ^1H decoupling. The ^{11}B spectrum of II exhibited doublets at δ 64.7 ($J = 156$ Hz, area 2),