N,*N*-dimethylethanolamine (3)[15] in CH$_2$Cl$_2$ under N$_2$. After the mixture was stirred overnight at ambient temperature, the solvent was evaporated off under reduced pressure. The white solid thus obtained was repeatedly washed with anhydrous ether to remove any unreacted starting materials and then vacuum pumped overnight to give a 91% yield of the extremely hygroscopic ester hydrochloride 4: IR (CDCl$_3$) ν_{CO} 1740 (s), ν_{+NH} 2200 (s), 2250 (s), 2400 (br s) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.1 (s, CH$_3$CO), 2.94 (s, CH$_3$N$^+$CH$_3$), 3.43 (dist t, CH$_2$N), 4.48 (dist t, CH$_2$O). This ester hydrochloride was used as such without further purification considering its extreme hygroscopic behavior.

To obtain 1, solid Et$_4$NBH$_4$[15] (50% mol excess) was slowly added to a stirred solution of 4 in CH$_2$Cl$_2$. Vigorous evolution of H$_2$ gas took place initially. After the reaction had subsided, it was refluxed for 3 h, cooled, and washed 3 times with H$_2$O. The organic portion was dried over MgSO$_4$ and the solvent removed under reduced pressure to give an 85% yield of 1 (pure by ^{1}H and ^{11}B NMR spectra); vacuum distillation of the crude product yielded a colorless oil: bp 89–90 °C (0.4 torr); IR (CH$_2$Cl$_2$) ν_{CO} 1740 (s), ν_{BH} 2380 (s), 2310 (sh), 2270 (m) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.03 (s, CH$_3$CO), 2.62 (s, CH$_3$NCH$_3$), 2.98 (t, *J* = 6 Hz, CH$_2$N), 4.38 (t, *J* = 6 Hz, CH$_2$O); ^{11}B NMR (CDCl$_3$, BF$_3$/Et$_2$O) δ –9.42 (q, J_{BH} = 98 Hz). Anal. Calcd for C$_6$H$_{16}$BNO$_2$: C, 49.70; H, 11.12; N, 9.66; B, 7.46. Found: C, 49.63; H, 10.93; N, 9.32; B, 7.25.

When the reaction of 4 was carried out with NaBH$_4$[15] (100% molar excess) for 1 day in refluxing THF, the yield of 1 after workup was only 19%. However, the yield of 1 could be increased up to 74% by carrying out the reaction for 6 days under identical reaction conditions.

In view of the important roles played by acetylcholine and its analogues in the transmission of the nerve impulse, the conformation of these compounds has been extensively studied. It has been postulated that acetylcholine is capable of existence in several conformations. On the basis of various X-ray[16–18] and NMR[19–23] studies, it has been concluded that the predominant conformation of acetylcholine is gauche in solution as well as in the crystalline state.

By contrast, in the ^{1}H NMR spectrum[24] of 1 in CDCl$_3$, an apparently perfect A$_2$X$_2$ system, was observed for the CH$_2$CH$_2$ moiety as evidenced by the symmetrical 1:2:1 intensity distribution of the CH$_2$ multiplets with coupling constant *J* = 6 Hz. This implies that the two "A" protons are magnetically equivalent and, likewise, the two "X" protons. No observable difference exists in the free energy of the gauche and trans conformations.[25] This conclusion is supported by the fact that the spectrum of 1 did not change upon decreasing the temperature to –60 °C.

This boron analogue, like other tertiary amine–boranes, is thermally and hydrolytically stable (no hydrolysis of B–H bond

in pure H$_2$O). Also, since amine–boranes do not normally reduce esters,[26] this possible decomposition mode has not presented any difficulties.

The foregoing synthetic route readily lends itself to the preparation of substituted acetylcholines and a number of these, together with 1, have been prepared. Additional efforts are under way involving the synthesis of analogues with boron in other positions of substitution. An LD$_{50}$ > 750 mg/kg (male mice) for 1 has been obtained indicating a relatively nontoxic compound.[27] Investigation in various biological activity studies is under way.

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Synthesis and Structural-Magnetic Study of a New Type of High-Nuclearity Metal Carbonyl Cluster Possessing an 11-Atom Rh$_5$Ni$_6$ Core: Formation of a Heterometallic Core via Nickel Capping of a Pentarhodium Trigonal-Bipyramidal Kernel

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In connection with our extensive exploratory studies[2] of the chemistry of the [Ni$_6$(CO)$_{12}$]$^{2-}$ dianion,[3] we report herein the preparation and characterization of the [Rh$_5$Ni$_6$(CO)$_{21}$H$_x$]$^{3-}$ trianion (1). This cluster, which represents the third example[4] of an 11-atom heterometallic species,[5] possesses a heretofore unknown close-packed 11-vertex D_{3h} polyhedron which has not been theoretically predicted[6] and which is geometrically and

(15) CH$_3$COCl, Me$_2$NCH$_2$CH$_2$OH, and NaBH$_4$ were obtained commercially from Aldrich Chemical Co. and used without further purification. Et$_4$NBH$_4$ was prepared from NaBH$_4$ and Et$_4$NOH by a standard method described previously: Gibson, D. H.; Ahmed, F. U.; Phillips, K. R. *J. Organomet. Chem.* **1981**, *218*, 325.
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(25) The conformational behavior of metocloramide and its protonated analogues was investigated recently by NMR spectroscopy (Anker, L.; Lauterwein, J.; Van de Waterbeemd, H.; Testa, B. *Helv. Chim. Acta* **1984**, *67*, 706). For these compounds with their protonated aminoethyl side chain, the gauche and trans rotamers have observable identical energies in D$_2$O as well as in CDCl$_3$ solutions and an apparently perfect A$_2$X$_2$ system was observed for the CH$_2$CH$_2$ moiety (e.g., 1:2:1 symmetrical triplet for CH$_2$ resonance, *J* = 6 Hz). These studies are very similar to what we have observed for 1.

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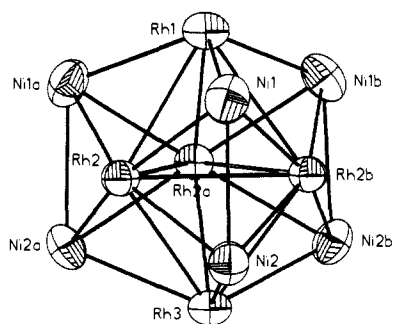
Communications to the Editor

Figure 1. 11-vertex Rh_5Ni_6 core in the paramagnetic $[Rh_5Ni_6(CO)_{21}H_x]^{3-}$ trianion (1) of crystallographic C_3-3 site symmetry. The idealized D_{3h}-$\bar{6}2m$ metal architecture suggests that this heterometallic core is formed by nickel capping of a trigonal-bipyramidal rhodium kernel.

electronically related to the known *pentacapped* trigonal-prismatic polyhedron.[7,8] The Rh_5Ni_6 core is also of particular interest in providing a clear-cut illustration on a molecular level of a segregated bimetallic phase; a similar model has been previously postulated from surface-science studies[9-13] to describe the nature of a number of heterogeneous bimetallic catalysts and immiscible alloys.

The Rh_5Ni_6 cluster 1 was obtained from the equimolar reaction $[PPh_3Me]_2^+[Ni_6(CO)_{12}]^{2-}$ (1.0 g, 1.66 mmol) and $Rh_2(CO)_4Cl_2$ (0.33 g, 1.66 mmol) in Me_2SO (75 mL) at ambient temperature for 36 h. Addition of water to the resulting reaction mixture gave a brown precipitate containing 1. After repeated washings with water followed by washings with Et_2O and THF, the $[PPh_3Me]^+$ salt of 1 was extracted into acetone and isolated as a brown powder in 50–70% yields. Its formulation is based on elemental, spectroscopic, magnetic, and single-crystal X-ray diffraction analyses.[14,15]

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(15) $[PPh_3Me]_3^+[Rh_5Ni_6(CO)_{21}H_x]^{3-}\cdot^1/_2Me_2CO$: Rhombohedral, $R\bar{3}$. Structure based on a triply primitive hexagonal unit cell with $a = b = 21.904$ (2) Å, $c = 32.827$ (5) Å, $V = 13\,640$ Å³; ρ(calcd) = 1.67 g/cm³ for $Z = 6$. The crystal structure (with the independent unit consisting of one monocation, one-third of the trianion, and one-sixth of a centrosymmetrically disordered acetone molecule) was determined by direct methods (SHELXTL) followed by successive Fourier and difference syntheses. Anisotropic least-squares refinement converged at $R_1(F) = 5.16\%$ and $R_2(F) = 5.59\%$ for 4840 independent absorption-corrected reflections ($F \geq 3.0\sigma(F)$) obtained at room temperature via a Nicolet P3F diffractometer with Mo $K\alpha$ radiation.
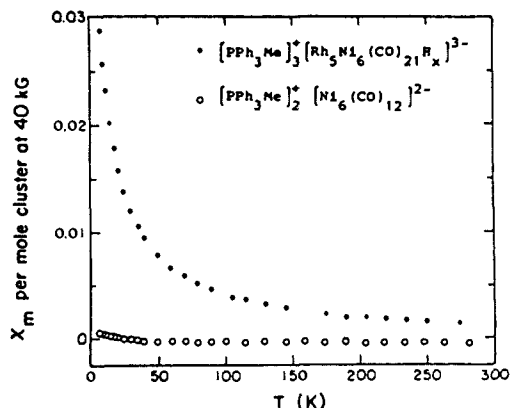

Figure 3. Temperature dependence of the molar magnetic susceptibility at 40 kG for the $[PPh_3Me]^+$ salts of the $[Rh_5Ni_6(CO)_{21}H_x]^{3-}$ trianion (1) and its precursor, the antiprismatic $[Ni_6(CO)_{12}]^{2-}$ dianion.

The idealized D_{3h}-$\bar{6}2m$ configuration of the Rh_5Ni_6 core (Figure 1) is reduced to C_{3h}-$3/m$ upon inclusion of the 21 carbonyl ligands (Figure 2, supplementary material), of which six are terminally coordinated to the six nickel atoms, 12 are doubly bridging between 12 of the 18 Rh–Ni bonds, and three are triply bridging to triangular $RhNi_2$ faces. The Rh_5Ni_6 core may be viewed as a Rh_5 trigonal bipyramid penetrating a Ni_6 trigonal prism. The pentarhodium trigonal bipyramid[16,17] has *six* bonding Rh(ax)–Rh(eq) distances (2.900 Å (av)) and *three* nonbonding (or weakly bonding) Rh(eq)–Rh(eq) distances (3.103 (1) Å); conversely, the hexanickel trigonal prism has *six* nonbonding intratriangular (horizontal edge) Ni–Ni distances (4.316 Å (av)) and *three* bonding intertriangular(vertical edge) Ni–Ni distances (2.702 (1) Å). All 18 Rh–Ni distances (2.629 Å (av)) correspond to strong interfacial bonding interactions.[18,19] A *formal* interconversion of the observed D_{3h} polyhedron of the Rh_5Ni_6 core into an isomeric *pentacapped* trigonal-prismatic D_{3h} polyhedron[7] (in which five *nonbonding* rhodium atoms would cap the faces of an edge-bridged nickel trigonal prism) primarily involves the concomitant breakage of the *six* Rh(ax)–Rh(eq) bonds in 1 and formation of *six* intratriangular (horizontal edge) Ni–Ni bonds.

That the Rh_5Ni_6 core exists as an unprecedented D_{3h} polyhedron instead of a *pentacapped* trigonal-prismatic D_{3h} polyhedron is attributed to the Rh(ax)–Rh(eq) bonding interactions being considerably stronger than the intratriangular Ni–Ni bonding interactions of the trigonal prism. The structure of 1 has a deltahedral core which minimizes total energy by maximizing both the degree of skeletal bond delocalization and the contribution of the various relative bond energies in the heterometallic cluster. The Rh_5Ni_6 core may be considered as a segregated bimetallic phase, where the central part (or kernel) of the core is composed of an aggregate of rhodium atoms (which possess substantially stronger metal–metal bonds) with surface coverage by the nickel atoms. This same model will also account for the observed core geometries in other heterometallic clusters, e.g., the $[Pd_6Fe_6(CO)_{24}H]^{3-}$ trianion[20] and the $[Pt_6Ni_{38}(CO)_{52}H_x]^{4-x}$ anions.[21] A similar interpretation involving surface coverage of kernels of the metal that has the higher heat of sublimation by the metal with the lower heat of sublimation has been invoked from surface-science studies[9-13] for a number of heterogeneous bimetallic

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catalysts and immiscible alloys.

A temperature-variable investigation of the solid-state magnetic properties of this high-nuclearity heterometallic cluster was undertaken because the even-electron decametal cluster $H_2Os_{10}C$-$(CO)_{24}$ was found to exhibit Curie-like behavior below 70 K with a magnetic moment of 0.62 μ_B which was attributed to "quantum-size" effects.[22] Magnetic susceptibility measurements of the $[PPh_3Me]^+$ salts of 1 and the $[Ni_6(CO)_{12}]^{2-}$ dianion were carried out with a SHE SQUID magnetometer (5 K < *T* < 280 K) in magnetic fields from 1 to 40 kG. The magnetic data[23] (Figure 3) expectedly showed the $[Ni_6(CO)_{12}]^{2-}$ dianion to be diamagnetic but surprisingly revealed 1 to be paramagnetic with an effective magnetic moment of 2.08 μ_B indicative of one unpaired electron. This paramagnetism was substantiated by powder EPR measurements (10 K < *T* < 300 K; 9.243 GHz) with a spectrum (Figure 4, supplementary material) at 10 K exhibiting a line shape expected for an axially symmetric spin-$^1/_2$ system ($g_\parallel$ = 2.279; $g_\perp$ = 2.027).

Effective magnetic moments indicative of one unpaired electron have been found in several other high-nuclearity metal clusters.[24] We rationalize that the existence of an odd electron in 1 necessitates the presence of either one hydrido (x = 1) or three hydrido (x = 3) atoms. Our formulation of 1 as a monohydrido $[Rh_5Ni_6(CO)_{21}H_x]^{3-}$ trianion (with x = 1) is consistent with an analysis which indicates that the hydrogen atom could occupy *one* of the two tetrahedral Rh_4 cavities with reasonable, equivalent Rh(ax)–H and Rh(eq)–H distances of 1.85 Å; in fact, the calculated hydrogen position is in the near vicinity of a residual density peak found from a difference map. Attempts to isolate deprotonated species of 1 have been unsuccessful.

A detailed bonding description of 1 will be deferred until the presence of the hydrogen atom(s) is ascertained from a planned neutron diffraction investigation. Current research involves reactions of the $[Ni_6(CO)_{12}]^{2-}$ dianion with a number of ruthenium, osmium, rhodium, and iridium carbonyl clusters with the hope of nickel plating the metal polyhedral cores.

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(23) Samples were loaded into kel-f containers and sealed under dry argon. The χ_M values were corrected for the diamagnetism of the kel-f containers and for trace amounts of ferromagnetic impurities (<0.2%). For 1, the χ_M values over 5 K < *T* < 280 K obey the equation $\chi_M = C/(T - \theta) + \chi_0$, where the first term represents the Curie-Weiss temperature-dependent behavior and the second term is a temperature-independent constant; parameters obtained from a data fitting are C = 0.515 K mol⁻¹, θ = −11.0 K, and χ_0 = −8.0 × 10⁻⁴ mol⁻¹.

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Epoxy Silyl Ether Rearrangements: A New, Stereoselective Approach to the Synthesis of β-Hydroxy Carbonyl Compounds

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Reported herein is a new method for the synthesis of β-hydroxy carbonyl compounds which is stereospecific, simple, and highly efficient. The new process depends on the site-specific 1,2-rearrangement as represented by Scheme I.[1,2]

The rearrangement of epoxy silyl ether 1 giving the aldol adduct 2 is effected by the use of titanium tetrachloride. Some examples are given in Table I. The typical experimental procedure is provided by the synthesis of 2-butyl-2-methyl-1-hydroxy-3-heptanone (3) from epoxy silyl ether 4 (entry 2). To a solution of 4 (272 mg, 1 mmol) in CH_2Cl_2 was added at −78 °C a 1 M CH_2Cl_2 solution of $TiCl_4$ (1.1 mL, 1.1 mmol). The mixture was stirred at −78 °C for 10 min, poured into aqueous HCl, and extracted with CH_2Cl_2. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated. The residual oil was chromatographed on silica gel (ether/hexane, 1:1 as eluant) to give 3 (150 mg, 75% yield) as a colorless oil.

The characteristics of the new method follow. (1) The starting epoxy silyl ethers can be readily prepared stereo- and enantioselectively from a wide variety of simple precursors such as allylic alcohols or α,β-epoxy carbonyl compounds. (2) Of all the Lewis acids examined, $TiCl_4$ has proved to be the most efficacious. (3) The facile migration of the alkyl group was observed in the reaction of α,α,β-trisubstituted derivative 1 (entries 1–6 and 20–22). Here the aryl group migrates preferentially, leaving the alkyl group intact (entry 6). (1) In the case of β-nonsubstituted derivative 1, only aryl and alkenyl groups participated in the selective 1,2-migration, reflecting the low migratory aptitude of the alkyl group (entries 7–15).[3] The rearranged α-alkenyl aldols were already

(1) This process represents the potential synthetic equivalent of stereoselective aldol methodologies. For recent reviews of the stereoselective aldol condensations, see: Evans, D. A.; Nelson, J. V.; Taber, T. R. *Top. Stereochem.* **1982**, 13. Mukaiyama, T. *Org. React.* **1982**, *28*, 203. Heathcock, C. H. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1984; Vol. 3B, p 111. Heathcock, C. H. In *Comprehensive Carbanion Chemistry*; Buncel, E., Durst, T., Eds.; Elsevier: New York, 1984; Vol. 5B, p 177. For related approaches to aldol adducts, see: Schreiber, S. L.; Hoveyda, A. H.; Wu, H.-J. *J. Am. Chem. Soc.* **1983**, *105*, 660. Curran, D. P. *Ibid.* **1983**, *105*, 5826. Fujita, M.; Hiyama, T. *Ibid.* **1985**, *107*, 8294.

(2) For another type of the epoxy alcohol rearrangement with Ti(O-*i*-Pr)₄, see: Morgans, D. J., Jr.; Sharpless, K. B.; Traynor, S. G. *J. Am. Chem. Soc.* **1981**, *103*, 462.