The same holds for the spectra of sitosterol acetate (3) (Figure 1B) and (4) (not shown in the figure) isolated from peas germinated in ^1H_2O. These spectra were recorded on several samples at different concentrations and the differences in the peak heights were always observed. The signals of the acetate, C-10 and C-13 methyls were integrated by weighing the cut-out traces of these peaks. Throughout, all integrations were carried out on expanded spectra (4:1). Since the acetate methyl most certainly contains three ^1H atoms it was accepted as an internal standard. The ratios of the C-10 and C-13 methyls to the acetate methyl were 1:1, respectively.

The spectra of the samples of sitosterol acetate (1) and (2) biosynthesized in deuterium oxide are given in (Figure 1C) and (Figure 1D). It is clear that in both cases the signals for the C-10 methyls at 1.03 ppm relative to those at 0.84 ppm are significantly smaller. Although a slight decrease of the methyl multiplets at 0.84 ppm due to deuteration at C-26 (etc.) was anticipated, it is obvious that the singlets for the C-19 hydrogen atoms decreased to a much greater extent. Integration of the area for the C-10 methyl of (1) (Figure 1C) revealed that it corresponds to 85% of the area of the acetate peak. This would indicate the incorporation of 0.45 atom of deuterium at C-19. Similarly the C-10 peak of (2) (Figure 1D) corresponded to 87% of the acetate peak and this is equivalent to the incorporation of 0.40 atom of deuterium at C-19. In contrast deuterium was not incorporated into the C-13 methyls of (1) and (2) as evidenced by the fact that the ratios of the integrated peaks for the C-13 methyls of (1) and (2) to the acetate methyls remained unchanged (1:1). This constitutes proof that in the germination experiment of 15 days duration, deuterated acetyl CoA, if formed endogenously, was not incorporated in detectable amounts into the sitosterol.

Our results show that a proton from the medium was incorporated at C-19 of (1) and (2). This is consistent with the presence of an "anionic terminus" at this carbon in a precursor of this phytosterol. This electron-rich center could be formed through the cleavage of the C-9(19) bond of the cyclopropane ring as discussed above. The relatively high incorporation of deuterium at C-19 (0.4-0.45 atom) is in accord with the view that cycloartenol is an important key intermediate in the biosynthesis of sitosterol in the pea.

The absence of deuterium at C-18 of sitosterol is of added importance. It may be recalled that the formation of cycloartenol involves a backbone rearrangement of the C-20 protosterol cation.[11] During the rearrangement the 13α and 17β hydrogen atoms of the protosterol cation migrate to the 17α and 20 positions and the 14β and 8α methyls migrate to the 13β and 14α positions, respectively. Then, following the shift of the 9β hydrogen to 8β position and the loss of a C-19 hydrogen, cycloartenol is formed.[11] Our results show that in the course of the methyl migration to the 13β position, the hydrogens of this methyl were not exchanged. The same can be inferred for the backbone rearrangement leading to lanosterol in rat livers.[12,13] This therefore poses the interesting question of whether the migration of the methyls in the elaboration of cycloartenol and lanosterol proceeds with retention, inversion, or racemization of the hydrogens of the migrating carbons. According to the Woodward-Hoffman rules, if applicable to biological systems, the migration should occur with retention of configuration of the hydrogens.[14]

Note Added in Proof. Clifford and Phillips[15] have now reported that in the biosynthesis of lanosterol in rat livers, the methyl migrating to C-13, indeed retained its chirality. This was proven by the degradation of the biosynthesized cholesterol and isolation of the C-13 methyl as acetic acid ($C^{18}H_3C^{13}OOH$).

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Synthesis and Structural Characterization of a New Type of Homonuclear Metal Carbonyl, $[Ni_5(CO)_9(\mu_2\text{-}CO)_3]^{2-}$. A Trigonal Bipyramidal Metal Cluster System[1]

Sir:

We wish to report the isolation and stereochemical analysis of the $[Ni_5(CO)_9(\mu_2\text{-}CO)_3]^{2-}$ dianion which represents the first known example of a pentanuclear metal carbonyl with 12 ligands and of a homonuclear metal cluster possessing a bonding trigonal bipyramidal architecture.[2-4] Unlike the vast majority of nontransient polynuclear metal carbonyls which comply to the conceptually localized electron-pair mode of metal-metal bonding, this pentanickel carbonyl dianion necessitates a delocalized metal cluster bonding description which thereby provides a possible analogy between discrete metal clusters and one-dimensional metallic materials. This work was a direct result of continuing research effort in the area of the nickel and platinum carbonyl anions[5,6] for the purpose of unequivocally establishing their highly unusual structures coupled with an elucidation of their physicochemical properties and intriguing bonding behavior. The results further support our premise that the $Ni_3(CO)_3(\mu_2\text{-}CO)_3$ fragment, which was also found[6] to be the structural basis for the $[Ni_3(CO)_3(\mu_2\text{-}CO)_3]_2{}^{2-}$ dianion, is a fundamental building block for the nickel carbonyl anions.

Previously it has been reported[7] that the reduction of $Ni(CO)_4$ with lithium or sodium amalgam gives rise to the formation of nickel carbonyl dianions of formulas $[Ni_3(CO)_8]^{2-}$ and $[Ni_4(CO)_9]^{2-}$. We have found, however, that $Ni(CO)_4$ is reduced by alkali metals or alkali amal-

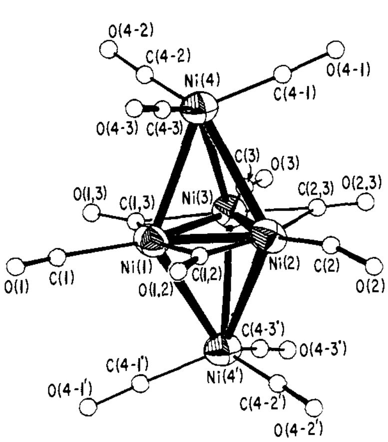

Figure 1. The configuration of the $[Ni_5(CO)_9(\mu_2\text{-}CO)_3]^{2-}$ dianion. This trigonal bipyramidal metal cluster is comprised of a planar $Ni_3(CO)_3(\mu_2\text{-}CO)_3$ residue which is capped by Ni-Ni interactions to two apical $Ni(CO)_3$ groups.

gams in THF as well as by alkali hydroxides in methanol to give a mixture of the $[Ni_6(CO)_{12}]^{2-}$ and $[Ni_5(CO)_{12}]^{2-}$ dianions. The final composition of the solution greatly depends on the experimental conditions, but in all cases $[Ni_5(CO)_{12}]^{2-}$ is the species which prevails at the end of the reaction. Initial failures to isolate this dianion may be ascribed to its transformation via a hydrolysis reaction of probable stoichiometry (eq 1).

$$3[Ni_5(CO)_{12}]^{2-} + 2H_2O \rightarrow 2[Ni_6(CO)_{12}]^{2-} + H_2 + 2OH^- + 3Ni(CO)_4 \quad (1)$$

The redox condensation equilibrium (2), which is shifted to the left under anhydrous conditions and atmospheric pressure of carbon monoxide, provides a reliable method for the isolation of the $[Ni_5(CO)_{12}]^{2-}$ dianion.

$$[Ni_5(CO)_{12}]^{2-} + Ni(CO)_4 \rightleftarrows [Ni_6(CO)_{12}]^{2-} + 4CO \quad (2)$$

Crystals of the bis(triphenylphosphine)iminium salt were obtained by dissolving $[PPN]_2[Ni_6(CO)_{12}]$ in anhydrous THF under dry carbon monoxide, evaporating the resulting solution to dryness, redissolving the residue in dry THF under CO, and then precipitating with dry, CO-saturated toluene. An infrared spectrum of the PPN salt in THF revealed carbonyl absorption bands at 1970 (vs), 1915 (w), and 1770 (ms) cm^{-1}. Analytical data indicated a nickel:cation ratio of 2.39; both the stoichiometry and structure of $[PPN]_2[Ni_5(CO)_{12}]$ were ascertained by an X-ray diffraction examination[8-10] which expectedly revealed discrete cations and anions with normal interionic separations. The PPN^+ counterion possesses the usual bent geometry[11] rather than the linear one recently uncovered by Wilson and Bau[12] from a structural analysis of the ionic $[PPN][V(CO)_6]$.

The configuration (Figure 1) of the $[Ni_5(CO)_{12}]^{2-}$ dianion may be described as a trigonal bipyramidal cluster of transition metal atoms in which a planar $Ni_3(CO)_3(\mu_2\text{-}CO)_3$ fragment of $D_{3h}\text{-}\bar{6}2m$ symmetry is symmetrically capped by Ni-Ni interactions to two identical apical $Ni(CO)_3$ groups of localized $C_{3v}\text{-}3m$ site symmetry. The entire anion ideally possesses a C_{3v} geometry which is reduced to an approximate C_3 one by a twisting of the apical carbonyls by ca. 10° relative to those on the $Ni_3(CO)_3(\mu_2\text{-}CO)_3$ fragment. This twisting deformation apparently reduces steric strain between the carbonyls attached to the apical Ni(4) and Ni(4′) atoms and the carbonyls of the $Ni_3(CO)_3(\mu_2\text{-}CO)_3$ moiety.

The resemblance of the $[Ni_5(CO)_9(\mu_2\text{-}CO)_3]^{2-}$ dianion with the Ruff $[M_2Ni_3(CO)_{13}(\mu_2\text{-}CO)_3]^{2-}$ dianions (M = Cr, Mo, W),[3] in which a central $Ni_3(CO)_3(\mu_2\text{-}CO)_3$ residue is capped by two apical $M(CO)_5$ groups, emphasizes that these complexes may be considered analogously to involve coordination of a given square pyramidal $M(CO)_5$ or trigonal $Ni(CO)_3$ group as a Lewis acid to a $[Ni_3(CO)_3(\mu_2\text{-}CO)_3]^{2-}$ fragment which thereby functions effectively as a two-electron-donating cyclopropenyl-like trinickel ring system that occupies one coordination site about each apical metal atom.[13,14] The average Ni-Ni distance of 2.36 Å within the $Ni_3(CO)_3(\mu_2\text{-}CO)_3$ fragment of the $[Ni_5(CO)_9(\mu_2\text{-}CO)_3]^{2-}$ dianion compares favorably with the corresponding *intra*triangular distance of 2.34 Å found in both the $[Mo_2Ni_3(CO)_{13}(\mu_2\text{-}CO)_3]^{2-}$ and $[W_2Ni_3(CO)_{13}(\mu_2\text{-}CO)_3]^{2-}$ dianions[3] and with that of 2.38 Å determined for the $[Ni_3(CO)_3(\mu_2\text{-}CO)_3]_2{}^{2-}$ dianion[6] which has a trigonal antiprismatic nickel arrangement. Although a distinct distortion of the trigonal bipyramidal metal core occurs in the molybdenum- and tungsten-nickel dianions in which the M_2Ni_3 cluster is lowered from an idealized D_{3h} to C_{3v} geometry through elongation of the three M-Ni bonds by 0.10 Å on one side of the trinickel plane, no analogous deformation of the Ni_5 core is observed in the $[Ni_5(CO)_9(\mu_2\text{-}CO)_3]^{2-}$ dianion. The three Ni-Ni bonds on one side are 2.773 (3), 2.865 (3), and 2.839 (3) Å, while those on the other side are 2.743 (3), 2.836 (3), and 2.798 (3) Å. The fact that the shortest distance on each side corresponds to that between the apical nickel atom and the same basal nickel atom, Ni(1), indicates that the large variation in these Ni-Ni distances may be attributed mainly to a translational distortion of the Ni_5 core from an idealized D_{3h} geometry toward a C_{2v} one.

A qualitative MO bonding description proposed[3] for the $[M_2Ni_3(CO)_{13}(\mu_2\text{-}CO)_3]^{2-}$ dianions corresponds to normal electron-pair nickel-nickel interactions within the $Ni_3(CO)_3(\mu_2\text{-}CO)_3$ fragment and delocalized, multicentered metal-metal interactions involving this trinickel fragment and the two $M(CO)_5$ groups. It is presumed from the close correlation of the corresponding distances and angles that the bonding in the $[Ni_5(CO)_9(\mu_2\text{-}CO)_3]^{2-}$ dianion parallels that in the $[M_2Ni_3(CO)_{13}(\mu_2\text{-}CO)_3]^{2-}$ dianions. Since nonparameterized (Fenske-Hall)-type molecular orbital calculations[15] are presently being carried out on the $[Ni_5(CO)_9(\mu_2\text{-}CO)_3]^{2-}$ dianion, a further discussion of its bonding properties will be reserved for a later publication which also will provide details of the results presented here. Additional investigations are presently underway on structural studies of other nickel carbonyl anions and on the preparation and characterization of new nickel carbonyl clusters containing other ligands.

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Supplementary Material Available. A listing of atomic parameters for $[((C_6H_5)_3P)_2N]_2[Ni_5(CO)_{12}]$ will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Business Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C., 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number JACS-75-5034.

References and Notes

(1) To be presented in part at the 170th National Meeting of the American Chemical Society, Chicago, Ill., Aug 1975.

(2) The only other examples (to our knowledge) of a cluster system of five transition metal atoms are the $[M_2Ni_3(CO)_{13}(\mu_2\text{-}CO)_3]^{2-}$ dianions (M = Mo, W),[3] which have a trigonal bipyramidal M_2Ni_3 core, and the unique $Fe_5(CO)_{15}(\mu_5\text{-}C)$ molecule,[4] which possesses a tetragonal pyramid with the carbide-like atom positioned slightly below the basal iron plane at essentially equal bonding distances from the five iron atoms.

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(10) For the computation of distances and bond angles, atomic coordinates will appear following these pages in the microfilm edition of this volume of the journal; see paragraph at end of paper regarding supplementary material.

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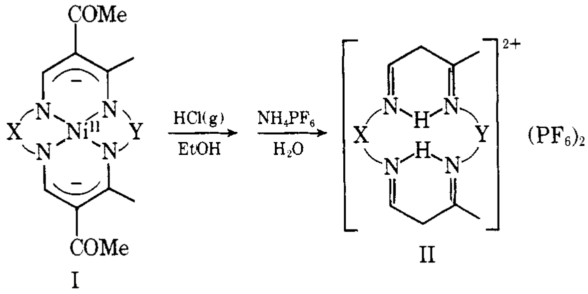
Synthesis and Structures of New Sexadentate Complexes Produced by Electrophilic Reactions of Macrocyclic Ligands in Their Transition Metal Complexes

Sir:

Increasing attention is turning toward the generation of ligand structures, based on macrocyclic frameworks, that facilitate the total control of the chemical environment in the vicinity of the metal ion. In natural systems the extra-macrocyclic role is often played by the protein. Earlier studies in this laboratory produced the first synthetic example of a ligand having a fifth donor atom held in a favorable position for coordination at one of the axial sites remaining after planar tetradentate chelation by the parent macrocycle.[1] Others have appended an imidazole ligand to a porphyrin ring[2] and built a picket fence structure to limit the closeness of approach of iron porphyrin units,[3] as well as added a hydrocarbon moiety to a tetradentate macrocyclic structure in such a way as to shield the region directly above the metal ion site.[4,5] Cytochrome *c* exemplifies the case where the two coordination sites not filled by a tetradentate macrocyclic ligand are occupied by donor groups propitiously arrayed by the protein portion of a natural product. We report here the fortuitous synthesis, characterization, and structural determination of a simple example of a structure that is analogous to the latter case.

A series of 14-, 15-, and 16-membered tetraaza, tetraene, macrocyclic ligands devoid of functional substituents has been prepared. Their syntheses utilize complexes of structure I.[6,7] This preparative route is based on the facile deacylation[8] and subsequent demetalation of the complexes of structure I with acid (dry HCl gas) in ethanol solvent. The macrocyclic ligands having structure II are isolated as their dihydrohexafluorophosphate salts after the evaporation of the ethanol and redisolution in water, followed by the addition of NH_4PF_6 (eq 1). Deprotonation of the ligand salts with 2 equiv of base (NEt_3 or OR^-) in the presence of solvated ferrous ion in acetonitrile results in rapid formation of the red-orange complexes, which can be isolated as orange-red crystals (75% yield) by reducing the solution volume, followed by the addition of hot absolute ethanol. All reactions were carried out in an inert atmosphere.



(1)

a, X = Y = $(CH_2)_2$
b, X = $(CH_2)_2$; Y = $(CH_2)_3$
c, X = Y = $(CH_2)_3$

Although all of the complexes conform to the stoichiometry $Fe(MAC)(PF_6)_2 \cdot 2CH_3CN$, only the 14-membered ring derivative has the obvious structure wherein the macrocycle is coordinated in a planar fashion about the Fe^{2+} ion with the acetonitrile molecules occupying axial sites. During preliminary characterization of the 15- and 16-membered ring derivatives the weak-C≡N stretch was found to be absent from their infrared spectra and an N–H vibration at 3310 cm^{-1} was observed. The NMR spectrum showed related complexities. The compounds were also found to be remarkably inert toward bases, and this observation was particularly difficult to rationalize. At this stage an X-ray crystallographic study was performed on one of the compounds (Ic), thereby revealing an unusual structure and a most interesting and novel ligand reaction as well.

The reaction and structure of the final products are given in Scheme I. *cis*-[3,11-Bis(1-iminoethyl)-2,12-dimethyl-1,5,9,13-tetraazacyclohexadeca-1,4,8,12-tetraeneiron(II)] hexafluorophosphate was isolated as orange crystals from an acetonitrile–methanol solution. Both analytical data and the results of physical measurements are readily reconciled with the solid state structure, indicating the integrity of that structure in solution. Anal. Calcd: C, 31.96; H, 4.42; N, 12.43. Found: C, 32.06; H, 4.47; N, 12.47. The compound