of the CO_2 product in Table I is obtained when the calculated model assumes a carbonyl oxygen having natural abundance ^{18}O. The slightly higher observed values of doubly labeled CO_2 indicate that exchange of the $C^{16}O^{18}O$ product with labeled water may occur to a maximum extent of 3% which is consistent with the control experiment using HCO_3^- described above.

Thus the present study affirms the oxygen transfer role of water in the $[RhCl_2(CO)_2]^-$ catalyzed reduction of NO by CO and shows that the intermediate hydroxycarbonyl species is unstable to exchange and back reaction relative to CO_2 formation.

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A Novel Diterpene from *Dollabella californica*

Sir:

The sea hare *Dollabella californica* Sterns,[1] a large soft-bodied opistobranch mollusk, was collected at Isla Partida, Gulf of California. The digestive gland of *Dollabella,* like that of *Aplysia californica,*[2] contained a number of terpenoid compounds which are probably of dietary origin. The major components of the digestive gland extracts are a series of diterpenes which appear to be closely related. We wish to report the structural determination by single-crystal x-ray diffraction analysis of a diterpene **1** having a novel 5,11-bicyclic carbon skeleton.

1 R = Ac
2 R = H

3
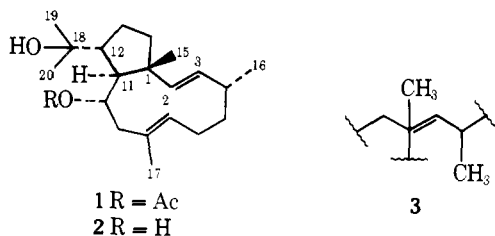
Florisil chromatography of the acetone extracts of homogenized digestive glands of *Dollabella* resulted in the isolation of six diterpenes, one of which crystallized from hexane, mp 78°, $[\alpha]^{22}D$ −101° (*c* 1.3). The crystalline material **1** (3% of extract) was shown to have the molecular formula $C_{22}H_{36}O_3$, which, together with bands at 3650 and 1740 cm^{-1} (CCl$_4$) in the infrared spectrum, suggested that the compound was a monoacetate of a diterpene diol. We were unable to measure the exact mass of the parent ion because of rapid loss of $C_2H_4O_2$; P − 60 gave *m/e* 288.244 while *m/e* 288.245 for $C_{20}H_{32}O$. This was also confirmed by treatment of the acetate
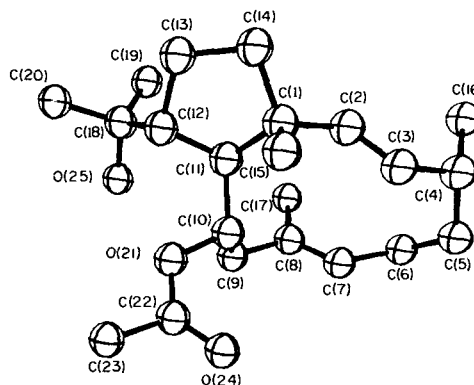
Figure 1. A computer generated perspective drawing of **1.** Hydrogens are not shown, and no absolute stereochemistry is implied.

1 with lithium aluminum hydride in anhydrous ether to obtain the corresponding diol **2,** mp 152–153°. The NMR spectrum of **1** contained six methyl signals: a singlet at δ 2.05 due to the acetate, a singlet at 1.62 due to a vinyl methyl, two singlets at 1.25 and 1.18 due to methyl groups on carbon-bearing oxygen, a doublet at 0.94, and a singlet at 0.82 ppm. The low-field region of the NMR spectrum contained an apparent doublet of triplets at δ 4.81 (J = 9, 1, 1 Hz) due to the α-acetoxy proton, a broad triplet at 5.10 (J = 7 Hz) due to the proton on the trisubstituted olefinic bond, and two signals at 5.07 (d, J = 16 Hz) and 5.22 ppm (dd, J = 16, 9 Hz) due to a trans olefin. Irradiation at δ 2.32 caused the double doublet at 5.22 to collapse to a doublet and the doublet at 0.94 to become a sharp singlet, suggesting the partial structure **3.** The ^{13}C NMR spectrum confirmed the presence of two olefinic bonds (δ 135.1, 130.9, 127.8, and 126.84 ppm) and an acetate carboxyl (168.5 ppm) but indicated only two other fully substituted carbon atoms: one at 72.7 ppm bearing hydroxy and two methyl groups, the other at 20.8 ppm bearing a methyl group at a ring junction. The acetate **1** was therefore bicyclic and contained a trans disubstituted olefin, either in a non-isoprenoid sidechain or in a medium-sized ring. Since these constraints could not be accommodated by any known diterpene skeleton,[3] the acetate **1** was subjected to single-crystal x-ray diffraction analysis.

Crystals of **1** belonged to the common, chiral space group $P2_12_12_1$ with a = 8.778 (1), b = 9.470 (1), and c = 25.785 (2) Å. The density indicated one molecule of $C_{22}H_{36}O_3$ per asymmetric unit. All unique data with $2\theta \leq 114°$ were recorded on a computer controlled four-circle diffractometer using graphite monochromated Cu Kα radiation (1.5418 Å). Periodically monitored check reflections showed no significant crystal deterioration. A total of 1703 reflections were measured and 1540 (90.4%) were judged observed after correction for Lorentz, polarization, and background effects ($F_o^2 \geq 3\sigma(F_o^2)$).

The structure was solved using a multiple solution weighted tangent formula approach.[4] The largest 150 normalized structure factors were phased and a three-dimensional E-synthesis of the best set revealed 19 of the 25 nonhydrogen atoms. Subsequent elaboration of the structure and refinement was uneventful.[5] Full matrix least squares refinements with anisotropic temperature factors for the non-hydrogen atoms and isotropic temperature factors for the hydrogens converged to a final crystallographic residual of 0.033 for the observed reflections. Tables of fractional coordinates, bond distances, bond angles, and observed and calculated structure factors can be found in the supplemental material.

Figure 1 shows a computer generated perspective drawing of **1.** As anticipated from the spectral data the double bond at C(2) is trans. The double bond at C(7) also has the E configuration. The 5- and 11-membered rings are joined in a trans fashion. The work described here does not define the absolute

configuration of **1**. The bridgehead methyl at C(1) has the β configuration, all other substituents are α. In general bond distances and angles agree with generally accepted values and there are no abnormally short intermolecular contacts.

Work in progress indicates that we have isolated several compounds having the same new carbon skeleton, which we wish to name the dollabellane skeleton **4**. Thus the acetate **1** is (1*S**, 2*E*, 4R*, 7E, 10*S**, 11R*, 12R*)-10-acetoxy-18-hydroxy-2,7-dollabelladiene.[7] The dollabellane skeleton could be formed by cyclization of geranylgeraniol pyrophosphate as shown.

4   **1**
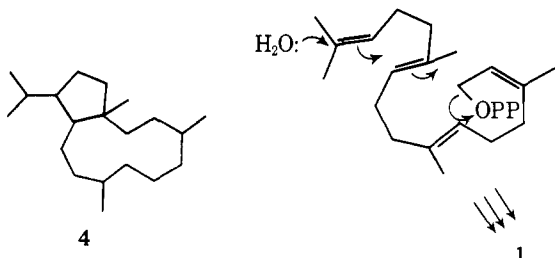
The compounds isolated from the digestive glands of mollusks have invariably been traced to a dietary source. This has not been possible in the present study, since *Dollabella* is a nocturnal feeder and there are no reports of its dietary preferences.

Supplementary Material Available: Fractional coordinates (Table I), important bond distances (Table II), important bond angles (Table III), and observed and calculated structure factors (Table IV) (11 pages). Ordering information is given on any current masthead page.

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### Reductive Elimination Reactions

Sir:

Within the set of important class reactions in coordination and catalytic chemistry[1] is the symmetric pair of "oxidative addition" and "reductive elimination". Mechanistic complexity within this pair of reactions has been clearly indicated by recent studies.[2-4] Through reactions of $HCo[P(OCH_3)_3]_4$[5] and $CH_3Co[P(OCH_3)_3]_4$[5] with H^+ and CH_3^+, we have obtained a series of $Y_2Co[P(OCH_3)_3]_4^+$ complexes which provide further information on intimate mechanism in reductive elimination. A valuable and general synthetic procedure has been developed from the elimination reactions.

The cis complex[6] $H_2Co[P(OCH_3)_3]_4^+$ was readily generated by protonation of $HCo[P(OCH_3)_3]_4$ with a nonmineral acid[5,8] and isolated in high yields as $H_2Co[P(OCH_3)_3]_4^+\cdot PF_6^-$.[9,10] In solution at 25°, the dihydride[11] slowly evolved hydrogen to form $Co[P(OCH_3)_3]_5^+$.[12] Exposure of solutions[13,14] of the dihydride cation to deuterium gave an equilibrium[13b] mixture of $D_2Co[P(OCH_3)_3]_4^+$ and H_2 in ~24 h; no HD was detected.[15] Hence a conventional equilibrium (eq 1)

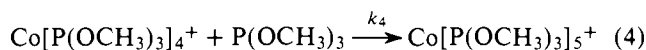$$H_2Co[P(OCH_3)_3]_4^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H_2 + Co[P(OCH_3)_3]_4^+ \quad (1)$$
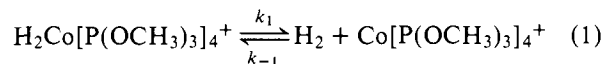
must be extant with the H_2 elimination step strictly intramolecular. An analogous exchange was observed in acetonitrile although a small amount of HD was produced due to a deprotonation step (eq 2) that occurs slowly in donor solvents.[15]

$$S + H_2Co[P(OCH_3)_3]_4^+ \overset{slow}{\rightleftharpoons} SH^+$$
$$+ HCo[P(OCH_3)_3]_4 \quad (2)$$
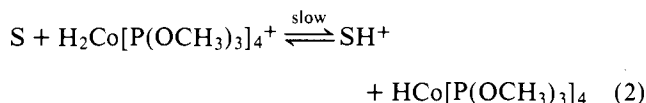
Kinetic studies of the reaction of the dihydride with trimethyl phosphite (eq 3)

$$H_2Co[P(OCH_3)_3]_4^+ + (P(OCH_3)_3 \rightarrow H_2$$
$$+ Co[P(OCH_3)_3]_5^+ \quad (3)$$
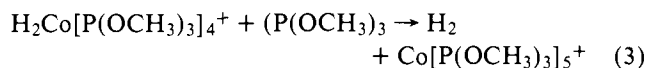
and the isolation of solid $Co[P(OCH_3)_3]_4^+PF_6^-$ and of labile adducts of $Co[P(OCH_3)_3]_4^+$ further delineate the solution chemistry of the dihydride and the clean character of this reversible reductive elimination step. Reaction rate for the phosphite reaction (eq 3) with the dihydride in dichloromethane solution was, under pseudo-first-order conditions, essentially insensitive to reactant ratio. Reaction order in phosphite was established by the initial rates method, and the data were fully consistent with a steady state condition for the intermediate complex formed in eq 1, followed by reaction 4

$$Co[P(OCH_3)_3]_4^+ + P(OCH_3)_3 \overset{k_4}{\longrightarrow} Co[P(OCH_3)_3]_5^+ \quad (4)$$

where the very stable $Co[P(OCH_3)_3]_5^+$ complex was formed with the condition of $-d\{H_2Co[P(OCH_3)_3]_4^+\}/dt = k_1k_4\{H_2Co[P(OCH_3)_3]_4^+\}[P(OCH_3)_3]/(k_{-1}[H_2] + k_4\cdot[P(OCH_3)_3])$ at 30 °C with $k_1 = 4.2 \times 10^{-5}$ s^{-1}. Reaction rate was substantially higher in coordinating solvents indicating that the further equilibrium reaction (eq 5)

$$Co[P(OCH_3)_3]_4^+ + S \rightleftharpoons SCo[P(OCH_3)_3]_4^+ \quad (5)$$
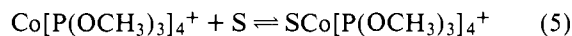
must be considered in such solvents (vide infra). The slow decomposition of the dihydride in the absence of added phosphite results from reaction 4 with free phosphite derived from the dissociative reaction (eq 6).

$$H_2Co[P(OCH_3)_3]_4^+ \rightleftharpoons H_2Co[P(OCH_3)_3]_3^+$$
$$+ P(OCH_3)_3 \quad (6)$$
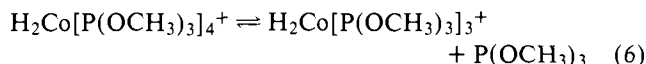
An estimate of the ligand dissociation rate, for dihydride, based on ^1H DNMR spectra[16] in the +20 to 70° range, is about 10^2 s^{-1} at 70°.

Methylation of $HCo[P(OCH_3)_3]_4$ or protonation[17] of $CH_3Co[P(OCH_3)_3]_4$ quantitatively (eq 7) yielded methane; the major cobalt products[12] identified were $Co[P(OCH_3)_3]_5^+$ and cobalt metal.