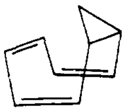
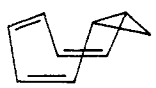
1,5-hydrogen shift mechanisms.[12,13] However, the essentially stereospecific formation of the primary product, **2**, is particularly significant in view of the fact that the stereoselectivity is *completely reversed* from that reported for the major product in all other bicyclo[6.1.0]nona-2,4,6-triene isomerizations.[1a-e,h]

This can be explained on the basis of the two most probable conformations for bicyclo[6.1.0]nona-2,4,6-trienes, *viz.*, A and B. We suggest that activated complexes leading to *cis*-8,9-dihydroindenes arise from conformation A,[14] but that this pathway would be highly sterically strained in the case of the 9,9-dimethyl derivative **1** and therefore is not competitively formed. Thus 1,1-dimethyl-8,9-dihydroindene (**2**) is probably formed *via* conformation B, either by conrotatory opening to a *cis,cis,cis,trans*-1,3,5,7-cyclononatetraene followed by disrotatory closure, or by a direct [1,3]-antarafacial sigmatropic migration of C_1 with retention of configuration.[15] Both of these latter processes are "symmetry allowed,"[16] *i.e.*, they occur *via* "aromatic"[17] activated complexes. We are currently investigating additional aspects of these rearrangements.



A



B

Acknowledgment. We are pleased to acknowledge the support of this work by the National Science Foundation and the Petroleum Research Fund, administered by the American Chemical Society. We also thank Badische Anilin- und Soda-Fabrik AG for a generous gift of cyclooctatetraene.

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[12] W. R. Roth, *Chemia*, **20**, 229 (1966).

[13] We have shown that *cis*-8,9-dihydroindene is not formed from the *trans* isomer (*e.g.*, *via* two 1,5-hydrogen migrations) to a significant extent upon heating at 98° (2% v/v in heptane) for 75 min.

[14] Inspection of Dreiding models clearly shows that only a small structural reorganization is required for this process. The importance of this factor has been demonstrated by Doering in his elegant studies of the Cope rearrangement: W. von E. Doering and W. R. Roth, *Tetrahedron*, **19**, 715 (1963).

[15] A 1,3 shift can occur with inversion of configuration: J. A. Berson and G. L. Nelson, *J. Am. Chem. Soc.*, **89**, 5503 (1967). This process has also been suggested by Israel, *et al.*, but an alternate mechanism involving an isocyanate intermediate is also possible: M. Israel, L. C. Jones, and E. J. Modest, *Tetrahedron Lett.*, 4811 (1968).

[16] We use this term advisedly since there is no element of symmetry in the activated complex.

[17] M. J. S. Dewar, *Tetrahedron Suppl.*, **8**, 75 (1967).

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The Geometry of Coordinated Molecular Nitrogen. The Structure of $Co(H)(N_2)(P(C_6H_5)_3)_3$

Sir:

We wish to report further structural details on the molecular nitrogen complex of cobalt, $Co(H)(N_2)(P(C_6H_5)_3)_3$. Our original structural study[1] was carried out on a limited set of 903 visually estimated X-ray intensities from a crystal, prepared in diethyl ether, of composition $Co(H)(N_2)(P(C_6H_5)_3)_3 \cdot (C_2H_5)_2O$. Despite many attempts we were unsuccessful in preparing further suitable samples of this material.

However, a sample was finally grown from an *n*-butyl ether solution. The method used was a significant modification of that originally reported.[2] A mixture of powdered trisacetylacetonatocobalt(III) (0.375 g) and triphenylphosphine (1.5 g) was added to *n*-butyl ether (100 ml). The suspension was stirred, flushed with dry nitrogen, and cooled in an ice bath. To the cold suspension, into which a constant stream of dry nitrogen gas was passed, triethylaluminum (0.85 ml) was added drop by drop. The resultant mixture was allowed to warm to room temperature during which time a reaction took place, the color of the mixture changing from green to reddish brown. The solution was cooled and stirred in an ice–water bath under a steady nitrogen flow for 45 min. The unreacted trisacetylacetonatocobalt(III) was filtered off under a nitrogen atmosphere, and the filtrate was left to stand in a refrigerator at 0°. After 2 days a crop of thin prismatic crystals was filtered off. A Nujol mull of these crystals showed two absorption bands at 2085 and 2105 cm^{-1}, but the crystals were not suitable for X-ray analysis. A further crop of crystals was filtered off 2 days later and similarly discarded. After 2 weeks a sample was isolated from the filtrate which contained crystals suitable for X-ray analysis, and one crystal was mounted in a thin-walled glass capillary. The crystal was a parallelepiped of dimensions $0.10 \times 0.15 \times 0.45$ mm. An infrared spectrum of the remaining sample also showed absorptions at 2085 and 2105 cm^{-1}. This sample was found to be diamagnetic by Faraday balance techniques, and the elemental composition from C, H, and N analysis was found to correspond to $Co(H)(N_2)(P(C_6H_5)_3)_3$ or to $Co(N_2)(P(C_6H_5)_3)_3$.

On the basis of Weissenberg and precession photographs we assigned the crystal to the monoclinic space group $P2_1/c$. The unit cell dimensions, as determined from a least-squares refinement of a number of high-angle reflections, are $a = 37.159\ (14)$, $b = 11.355\ (5)$, $c = 21.779\ (8)$ Å; $\beta = 101.3\ (2)°$, $V = 9011$ Å^3 (Cu Kα_1 = 1.5406 Å). In the previous structural determination[1] the volume of the molecule was approximately 1320 Å^3, and it is apparent that there are eight molecules in the present cell and hence the solution of the structure requires the huge task of locating the two independent molecules (120 nonhydrogen atoms) in the asymmetric unit.

A total of 6070 independent reflections was collected on a Picker diffractometer, in two separate runs, out to a maximum 2θ (Cu Kα) of 110°. The positions of the two cobalt and six phosphorus atoms were eventually found with difficulty by direct methods and were consistent with a sharpened, origin-removed Patterson function. The 4 nitrogen atoms and 18 phenyl rings were found from successive difference Fourier maps. An absorption correction was applied, and in the refinement the phenyl rings were treated as rigid groups. After a preliminary least-squares refinement, the cobalt and phosphorus atoms were allowed to vibrate anisotropically but the nitrogen atoms were constrained to isotropic vibration. The phenyl hydrogen atoms were then included as fixed contributions,

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[1] J. H. Enemark, B. R. Davis, J. A. McGinnety, and J. A. Ibers, *Chem. Commun.*, 96 (1968).

[2] A. Yamamoto, S. Kitazume, L. S. Pu, and S. Ikeda, *ibid.*, 79 (1967).

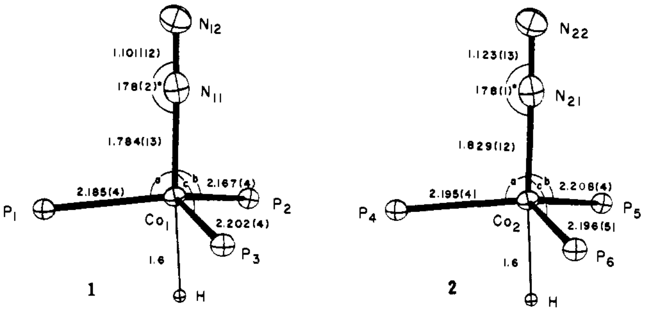

Figure 1. The inner coordination spheres of the two independent molecules of $Co(H)(N_2)(P(C_6H_5)_3)_3$. The N–Co–P angles are: molecule 1, $a = 97.5$ (5), $b = 99.6$ (4), $c = 98.4$ (4)°; molecule 2, $a = 96.3$ (4), $b = 99.3$ (4), $c = 96.9$ (4)°.

and a cycle of least-squares refinement on F_o for the 3312 independent observations with $|F_o| > 3\sigma(F_o)$ converged to values of R_1 of 0.077 and R_2 of 0.074.

At this point difference Fourier syntheses were calculated around the cobalt atoms in an attempt to locate the coordinated hydrogen atoms. These were clearly visible at an electron density of 0.46 (5) e/Å^3 on molecule 1 and 0.42 (5) e/Å^3 on molecule 2. In a final cycle of refinement these hydride ligands were included as fixed contributions, the nitrogen atoms were allowed to vibrate anisotropically, and the refinement converged to values of R_1 and R_2 of 0.065 and 0.061. A final difference Fourier map showed no peaks of height greater than 0.37 (5) e/Å^3.

The geometry of the inner coordination spheres is shown in Figure 1, together with important bond distances and bond angles. The attachment of the nitrogen molecules is end on, the Co–N–N angles of 178 (2) and 178 (1)° representing an essentially linear arrangement. The N–N distances of 1.123 (13) and 1.101 (12) Å do not differ significantly and are comparable with the values of 1.0976 (2) Å in gaseous N_2[3] and 1.118 Å in N_2^+.[4]

The mode of attachment of the nitrogen molecules is strongly reminiscent of that of the isoelectronic molecule carbon monoxide. There is no significant lengthening of the N–N bond from that of gaseous nitrogen, just as no significant lengthening of the C–O bond is observed in coordinated carbon monoxide compared with the free molecule.

The Co–N distances of 1.829 (12) and 1.784 (13) Å do not differ significantly. The Co–N mean distance (1.806 (16) Å) is comparable with that for the Co–C bond of 1.75 (3) Å found in $(Co(CO)_3(P(n\text{-}C_4H_9)_3))_2$[5] and that of 1.797 (7) Å found for the axial Co–C bond in $Co(CO)_4(SiCl_3)$.[6] The Co–N distance is, however, significantly shorter than that of a typical Co–N bond distance of 1.96 Å found in various cobalt ammines.

This work provides unambiguous proof that the compound is a hydride of formula $Co(H)(N_2)(P(C_6H_5)_3)_3$ as suggested in our previous communication.[1] The positional parameters of the hydride ligands, as derived from interpolation of electron density peaks in the difference Fourier maps, result in Co–H distances of 1.67 and 1.64 Å. These values compare well with the distance predicted from the sums of covalent radii.

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Studies on the Mechanism of Estrogen Biosynthesis. VI. The Stereochemistry of Hydrogen Elimination at C-2 during Aromatization

Sir:

In previous publications on the mechanism of estrogen biosynthesis we reported that in the aromatization of androstenedione[1,2] (androst-4-ene-3,17-dione), 19-norandrostenedione,[2] and 19-hydroxyandrostenedione[3] by placental tissue, the 1β hydrogen is eliminated. We now wish to report on the stereochemistry of loss of hydrogen at C-2 during the aromatization of androstenedione.

Androstenedione stereoselectively deuterated at 1α or 2β or 1α, 2α was used in the study. The 2β-*d* compound was prepared by equilibrating androstenedione for 16 hr in 10% deuterium oxide–diglyme containing 2.2 mmol of deuterated sodium hydroxide.[4] The compound (0.995 atom of deuterium per molecule) had essentially the deuterium distribution previously found (2β/2α = 10) as judged by combustion analysis,[5] mass, ir, and nmr spectra, and enzymatic dehydrogenation.[4]

Androstenedione-1α,2α-*d* was prepared by α-face reduction of androsta-1,4-diene-3,17-dione with deuterium and tris(triphenylphosphine)rhodium(I) chloride.[6] The product showed deuterium absorption at 2155 and 2195 cm^{-1} and little at 2145 cm^{-1} (2β-*d*). Equilibration with base gave androstenedione-1α-*d* with absorption at 2155 cm^{-1} (1α-*d*).

The deuterated compounds and nondeuterated androstenedione, mixed with androstenedione-4-^{14}C of negligible mass, were incubated separately in duplicate as previously described[2] using 300 μg of substrate (40,000 dpm), placental microsomes equivalent to 80 g wet weight of tissue, and an NADPH generating system suspended in 12 ml of 0.05 *M* phosphate buffer, pH 7.2. After incubation for 1 hr the steroids were extracted and separated by tlc in 65% ether–hexane to give estrone and androstenedione. The products were chromatographed in the Bush B_3 and A paper systems, respectively, and were further purified on silica gel columns using ethyl acetate–benzene mixtures for elution. The yield of each material was 45–65 μg.

Product estrone and recovered androstenedione from incubation of undeuterated substrate both gave mass spectra with quantitatively similar peak ratios in the $M - 1$ to $M + 5$ area as those obtained with purified standard materials, showing that the method of purifica-

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