Preparation of 1-Methyl-2,2-diphenylcyclopropylcobaloxime and Theoretical Considerations for Its Mode of Formation

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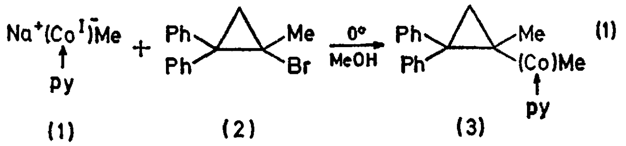
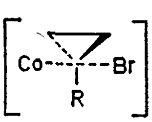
Summary The title compound, which contains a stable tertiary alkylcobalt σ-bond, is readily obtained from the reaction of pyridine[bis(dimethylglyoximato)]cobalt(I) and 1-methyl-2,2-diphenylcyclopropyl bromide; five mechanisms for the reactions of low-valent metal ions and alkyl halides are discussed.

Reaction of cobaloxime(I)[1,2] (**1**) with (**2**)[3] gives 1-methyl-2,2-diphenylcyclopropylcobaloxime (**3**) (60%) [equation (1)].† Cleavage of (**3**) by sodium in liquid ammonia, or gaseous HBr in methylene chloride gives 1-methyl-2,2-diphenylcyclopropane in yields of 65 and 52% respectively.



From optically active (**3**),[3] reaction (1) followed by acid cleavage, leads to (±)-1-phenyl-2,2-dimethylcyclopropane. However, it was not possible to decide at which point the activity was lost. Solutions of (**3**) are too highly coloured[2,4] to allow meaningful measurement of rotations.‡ The bromo-demetallation of (**3**)[4] was unsuccessful owing to com-



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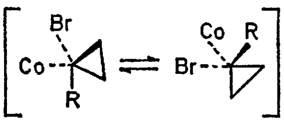

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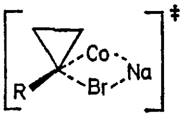

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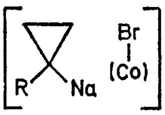

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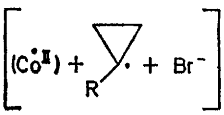

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† The elemental analysis and the n.m.r. spectrum were consistent with structure (**3**).

‡ Similarly, it was not possible to measure a rotation for optically active s-butylcobaloxime.

peting destruction of the bis-dimethylglyoxime ligand by bromine.

Compound (**3**) is of interest for its unusual structural features, *i.e.*, it contains both a tertiary and a cyclopropyl centre σ-bonded to a transition metal. Derivatives of (**2**) with main-group elements are common[5] and a few tertiary alkyl derivatives of transition metals have been reported.[6] It is interesting and perhaps significant that the only other σ-bonded cyclopropyl-transition metal compounds known[7] are derivatives of h^5-$(C_5H_5)Fe(CO)_2$ which like (**1**) forms a low-valent nucleophilic ion.

Reaction (**1**) is of considerable theoretical interest and at least five mechanisms must be considered: (i) S_N2 with inversion at carbon, transition state (**4**).[2] This mechanism has never been demonstrated at a tertiary centre. (ii) S_N2 with retention at carbon, intermediates (**5**).[8] Transition state (**4**) is of such high energy that S_N2 reactions probably proceed through intermediates (**5**) which are interconverted by turnstile or Berry pseudo-rotations. Depending upon the number of interconversions, the stereochemistry may be either retention or inversion. (iii) Metal-halide exchange, transition state (**6**). This is analogous to a proposed mechanism for the reaction of (**2**) with lithium triphenyltin which proceeds with retention of configuration.[9] (iv) Transmetallation, intermediate (**7**). This mechanism requires that the intermediates collapse in the cage to form product faster than the sodium derivative reacts with methanol (solvent). (v) Electron transfer to give free-radicals, intermediates (**8**).

At present no definitive choice can be made among the proposed mechanisms, however any mechanism must be consistent with the following observations: Optically active bromide (**2**), recovered from reaction mixtures [equation (**1**)] in up to 20% yield, retained all of its initial activity. In addition, (**2**) stirred with cobaloxime(II), a d^7 radical-like species, anaerobically for several hours at room temperature was recovered in 96% yield with no loss in optical activity. Mixtures of (**1**) with 1-bromoadamantane or 1-bromonorbornane under standard conditions[3] gave no alkyl-cobalt compounds, and upon work-up, gave unchanged alkyl bromides in high yield.

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[1] G. N. Schrauzer and E. Deutsch, *J. Amer. Chem. Soc.*, 1969, **91**, 3341.

[2] F. R. Jensen, V. Madan, and D. H. Buchanan, *J. Amer. Chem. Soc.*, 1970, **92**, 1414.

[3] H. M. Walborsky and F. J. Impastato, *J. Amer. Chem. Soc.*, 1959, **81**, 5835.

[4] F. R. Jensen, V. Madan, and D. H. Buchanan, *J. Amer. Chem. Soc.*, 1971, **93**, 5283.

[5] J. L. Webb, C. K. Mann, and H. M. Walborsky, *J. Amer. Chem. Soc.*, 1970, **92**, 2042, and references therein.

[6] D. F. Gili and B. L. Shaw, *J.C.S. Chem. Comm.*, 1972, **65**; B. K. Bowers and H. G. Tennant, *J. Amer. Chem. Soc.*, 1972, **94**, 2512; and references therein.

[7] A. Cutler, R. W. Fish, W. P. Giering, and M. Rosenblum, *J. Amer. Chem. Soc.*, 1972, **94**, 4354.

[8] P. Gillespie, P. Hoffman, H. Klusacek, D. Marquarding, S. Pfohl, F. Ramirez, E. A. Tsolis, and I. Ugi, *J. Amer. Chem. Soc.*, 1971, **10**, 687.

[9] K. Sisido, S. Kozima, and K. Takizawa, *Tetrahedron Letters*, 1967, 33.