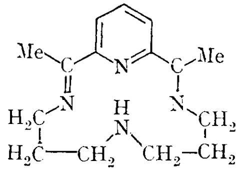
# Organic Derivatives of a Cobalt(III) Macrocylic Complex

By EI-ICHIRO OCHIAI and DARYLE H. BUSCH*

(*Department of Chemistry, The Ohio State University, Columbus, Ohio* 43210)

SEVERAL of the reported model complexes of vitamin $B_{12a}$ contain cobalt–carbon σ-bonds. One of them, alkylcobaltoxime, RCo $dmg_2L$,[1] (R = alkyl or analogous group, dmg = dimethylglyoxime, L = base, *e.g.* water or pyridine) has been studied in detail. These investigations have dealt with the synthesis, chemical characteristics, biochemical implications, and nucleophilicity of cobalt(I) in the complex.[2] Other examples include RCo baen,[3] RCo salen,[4] and RCo(porphyrin),[5] [baen = bis(acetylacetone)ethylenediamine, salen = bis(salicylaldehyde)ethylenediamine]. We report the synthesis of a new model complex of the general formula [$RCo^{III}$ cyp Br]Y {R = alkyl or analogous groups, cyp = 2,12-dimethyl-3,7,11,17-tetra-azabicyclo[11,3,1]heptadeca-1(17),2,11,13,15-pentaene (I)}.



(I)

The general method of preparation involves the reduction of $Co^{II}$ cyp $Br_2,H_2O$ with sodium borohydride in the presence of an alkyl halide, or its analogue, under nitrogen in methanol. The compound is crystallized by the addition of an aqueous solution of ammonium hexafluorophosphate. Complexes [MeCo cyp Br]$PF_6$, [EtCo cyp-Br]$PF_6,\frac{1}{2}H_2O$, and [$CH_2$:CH·CO cypBr]$PF_6,\frac{1}{2}H_2O$ gave satisfactory elemental analysis. Molar conductances, in methanol, at concentrations of *ca.* $7 \times 10^{-4}$M fall in the range 109—114 mho/cm.$^2$. This shows that these compounds are 1 : 1 electrolytes.[6] The i.r. spectra show the typical cyp skeletal bands, as observed for [$\mathrm{Co^{III}}$ cyp $\mathrm{X_2}$]Y,[7] where X and Y are halogens or analogues. The spectrum of [$\mathrm{CH_2{:}CH{\cdot}Co}$ cypBr]$^+$ shows an absorption band due to the C=C stretching mode at 1608 cm.$^{-1}$.

The electronic spectra of these complexes resemble those of approximately octahedral cobalt(III) complexes. They consist of two bands: $^1T_{1g} \rightarrow {}^1A_{1g}$, *ca.* 480 and $^1T_{2g} \leftarrow {}^1A_{1g}$, *ca.* 390 mμ. However, the intensities of these bands are fairly large, ε 600—2000, compared with the ordinary octahedral cobalt(III) complexes. This is consistent with the expectation of a considerable amount of covalency in the bond between $\mathrm{Co^{III}}$ (probably $d_{z^2}$ orbital) and the carbon atom. These spectra are similar to that of EtCo $\mathrm{dmg_2}$ py (py = pyridine) which has bands at 448 (ε 1210) and 380 mμ (ε 1760).†

These complexes are photo-labile in solution as are RCo $\mathrm{dmg_2L}$, RCo baen, and RCo salen. Simple molecular orbital considerations suggest the existence of the bonding orbital composed of the cobalt $d_{z^2}$ and the carbon σ-orbital at a relatively high level, *i.e.*, just below the *d*-orbitals. An electron in this orbital is readily excited into the vacant antibonding orbital composed mainly of $d_{z^2}$; this transition corresponds to the charge transfer $\mathrm{Co^{III}} \leftarrow \mathrm{R^-}$. This results in the decomposition of the complex into a $\mathrm{Co^{II}}$ derivative and an alkyl radical, as shown by Schrauzer[1] in the case of RCo $\mathrm{dmg_2L}$ complexes.

Evidence also exists for the compounds [$\mathrm{PhCH_2{\cdot}}$Co cypBr]$\mathrm{PF_6}$ [δ(CH) benzyl at 739 and 695 cm.$^{-1}$], [$\mathrm{NC{\cdot}CH_2{\cdot}CH_2{\cdot}Co}$ cypBr]$\mathrm{PF_6}$ [ν(C≡N) at 2240 cm.$^{-1}$] and [$\mathrm{Cl{\cdot}CH_2{\cdot}Co}$ cypBr]$\mathrm{PF_6}$. The benzyl derivative is very sensitive to light, probably because of the stability of benzyl radical. The formation reaction of the allyl derivative proceeds in close similarity to the other cases, but this substance is so reactive that no solid product has yet been isolated.

(*Received, May* 30*th*, 1968; *Com.* 703.)

---

† This complex was prepared by a method similar to that of Schrauzer *et al.*[1] and its spectrum was obtained in the present study.

[1] G. N. Schrauzer, *Accounts Chem. Res.*, 1968, **1**, 97 and references cited therein.
[2] G. N. Schrauzer, E. Deutsch, and R. J. Windgassen, *J. Amer. Chem. Soc.*, 1968, **90**, 2441.
[3] G. Costa and G. Mestroni, *J. Organometallic Chem.*, 1968, **11**, 325.
[4] G. Costa, G. Mestroni, and G. Pellizer, *J. Organometallic Chem.*, 1968, **11**, 333.
[5] D. A. Clarke, R. Grigg, and A. W. Johnson, *Chem. Comm.*, 1966, 208.
[6] E. C. Evers and A. K. Gnox, *J. Amer. Chem. Soc.*, 1951, **73**, 1739; R. E. Jervis, D. R. Muir, J. P. Butler, and A. R. Gordon, *ibid.*, 1953, **75**, 2855.
[7] K. M. Long, Ph.D. Thesis, The Ohio State University, 1967.