An Alkylcobalt(I) Intermediate in the Formation of *trans*-Dialkylcobalt(III) Complexes of Two Tetradentate Macrocyclic Ligands

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Summary The vitamin B_{12} model compounds *trans*-[RCo(tim)X]Y and *trans*-[RCo(cr)X]Y can be reduced to neutral alkylcobalt(I) complexes of a new type, which are readily oxidatively alkylated at the cobalt atom to yield *trans*-dialkylcobalt(III) derivatives.

AMONG the major requirements for the existence of the known stable σ-bonds between alkyl groups and transition metals are[1] the non-lability and high π-bonding propensity of the other ligands, and a low oxidation state of the central metal ion. Thus, carbon was not expected to be found bound to a metal ion in higher oxidation states until the discovery of the C–Co^{III} bond in a coenzyme of vitamin B_{12}[2] and the subsequent isolation of B_{12} model compounds[3] of the type $[RCo(lig)X]^{n+}$ and $[RCo(lig)]^{n+}$ where (lig) represents an unsaturated chelating ligand(s) co-ordinated in planar fashion about cobalt.

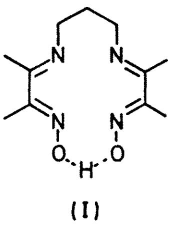
In view of the recent communication of the isolation of the first *trans*-dialkylcobalt(III) complexes of the pseudo-macrocyclic chelate[4] (I), we report that the unsaturated quadridentate macrocycles cr and tim (II and III) form *trans*-dialkylcobalt(III) complexes $[R_2Co(CR)]^+$ and $[R_2Co(tim)]^+$. In addition, we report that their formation involves prior formation, from monoalkyl complexes, of isolable neutral monoalkylcobalt(I) species as intermediates.

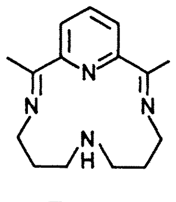
The B_{12} model compounds [RCo(tim)X]Y[5] and [RCo(cr)X]Y[3] (R = Me, $PhCH_2$; X = halide; Y = BPh_4 or PF_6) have been described in detail elsewhere. Reduction of these by $NaBH_4$ in methanol or, better, by sodium amalgam in acetonitrile gives solutions of alkylcobalt(I) complexes—one of which we have characterized as follows. After removal of solvent following the reduction of $[CH_3Co(tim)I]BPh_4$ by sodium amalgam, the green product was extracted into diethyl ether. Partial evaporation of solvent yielded crystals of $CH_3Co(tim)$ which are red by reflected light but green by transmitted light. This complex is soluble in hydrocarbons, benzene, ether, alcohols *etc.*, and is stable under an inert atmosphere.

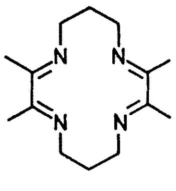
Elemental analyses (satisfactory for C, H, and N, and the absence of halogen) and spectroscopic data characterize this complex as MeCo(tim). Its i.r. and n.m.r. spectra verify that the ligand remains intact and show no indication of the BPh_4 anion. In addition, the proton resonance arising from the methyl group co-ordinated to cobalt is observed at a much higher-field position than in the cobalt(III) alkyls (see Table), as would be expected in light of the known shielding effects of low-valence-state metal ions.

These alkylcobalt(I) derivatives are significantly more stable, thermally, than any reported in the earlier literature. For example, $CH_3Co(tim)$ does not decompose below its m.p. (109—111°) in a sealed capillary. This, we feel, is a direct consequence of the immunity to substitution in the planar positions bestowed upon the metal by the rigid macrocyclic ligands, coupled with the high π-bonding power expected of conjugated imine moieties. As all the other compounds obtained by reduction of $[RCo(tim)X]^+$ and $[RCo(cr)X]^+$ (R = Me, $PhCH_2$) have equivalent properties to $CH_3Co(tim)$, they almost certainly have corresponding compositions and thermal stability.

Since two electrons are expected to occupy the highly directed d_{z^2} orbital, these complexes were expected to display the nucleophilic nature observed for other low-spin cobalt(I) complexes containing planar ligands.[6] Thus, addition of the appropriate alkyl halide results in rapid, quantitative, oxidative alkylation of the cobalt ion, the products being of the type $[R^1R^2Co(tim)]^+$ and $[R^1R^2Co(cr)]^+$ (R^1R^2 = Me or $PhCH_2$).


(I)


(II)(cr)


(III)(tim)

These *trans*-dialkylcobalt(III) complexes, obtained as bright red or orange-brown crystals on the addition of BPh_4^- or PF_6^- anions are air-stable, but sensitive to light, especially in solution. Their n.m.r. spectra confirm that the planar macrocycles are still unchanged, and that there are two alkyl groups attached to cobalt. The alkyl groups are observed at a somewhat higher field when another alkyl group is in the *trans*-position than when the sixth ligand is a halide ion (see Table). These data reflect their relative σ-donor propensities, and illustrate again[7] that in complexes of this type, there is a build-up of charge density on one axial ligand as the σ-donor power of the other axial ligand increases.

N.m.r. data for methylcobalt complexes

Complex	Solvent	τ (Co–CH_3)[a]
$[MeCo(tim)Br]BPh_4$	$(CD_3)_2SO$	8·86 (1)
$[Me_2Co(tim)]BPh_4$	"	9·64 (2)
$[MeCo(cr)Br]PF_6$	"	9·47 (1)
$[Me_2Co(cr)]BPh_4$	"	9·82 (2)
MeCo(tim)	$(CD_3)_2CO$	11·56 (1)

[a] ( ) refers to the number of equivalent methyl ligands on cobalt.

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