A Benzyl–Carbon Bond Dissociation Energy of One-third the Normal Value: A Quantitative Study of Benzyl–Carbon Bond Homolysis in [$Co^{III}(L^2–CH_2Ph)I$], a Cobalt-to-Carbon Benzyl Migration Product Derived from the Coenzyme B_{12} Model Complex [$Co^{III}(L^1)(CH_2Ph)I$]†

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Benzyl–carbon bond thermal homolysis studies using the TEMPO radical-trapping method reveals a low benzyl–carbon bond dissociation energy (BDE) in [$Co^{III}(L^2–CH_2Ph)I$] of 25 ± 3 kcal mol^{-1}, a value one-third the normal BDE of *ca.* 76 kcal mol^{-1} and approximately equal to the *cobalt*–carbon homolytic BDE in the parent complex [$Co^{III}(L^1)(CH_2Ph)I$]; such little-documented low BDEs relate back to Gomberg's classic example of $Ph_3C–C_6H_5CPh_2$ and its *ca.* 11 kcal mol^{-1} carbon–(*p*-phenyl)carbon BDE (1 cal = 4.184 J).

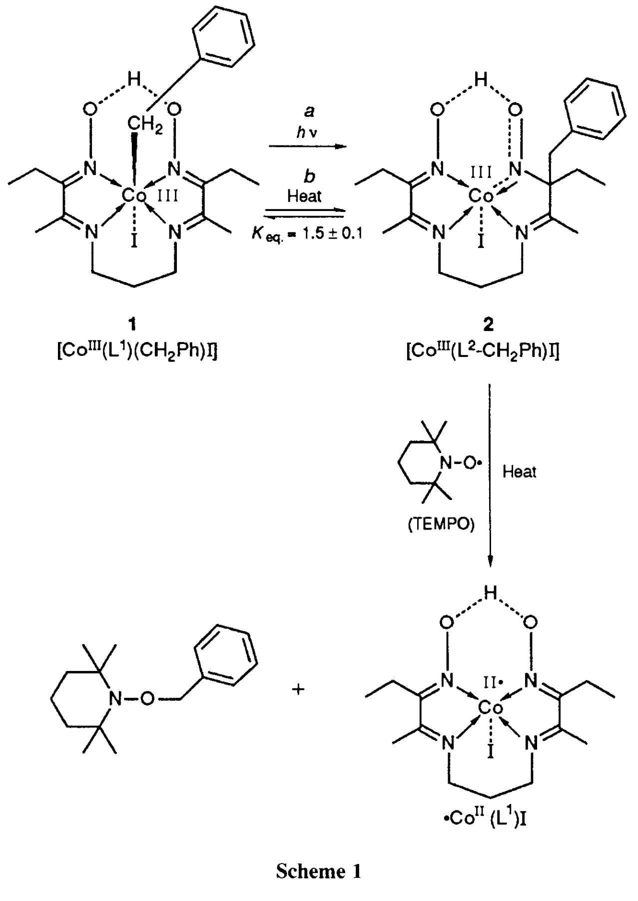
Recently we reported[1] that the anaerobic solution photolysis of the Coenzyme B_{12} model complex [$Co^{III}(L^1)(CH_2Ph)I$] **1** quantitatively yields the unprecedented rearrangement product **2** (Scheme 1, step *a*). The synthetic details and full characterization of **2** (by ^1H NMR, ^{13}C NMR, visible spectroscopy, mass spectroscopy, elemental analysis and X-ray crystallography) have been published elsewhere.[1a] The crystallographic results are the basis for the shorter distances and thus increased bonding between cobalt, nitrogen and oxygen represented by the dashed lines between those atoms within **2** in Scheme 1.[1a] Interestingly, the anaerobic solution *thermolysis* of **1** or **2** yields a near temperature-independent equilibrium mixture of **1** and **2** (Scheme 1, step *b*); details of the K_{eq} = 1.5 ± 0.1 and ΔH = *ca.* 0 measurements are also reported elsewhere.[1b]

The finding that ΔH = *ca.* 0 requires the presence of a relatively weak benzyl–carbon bond in **2**. This in turn prompted a quantitative investigation, reported herein, of the thermal homolysis and solution bond dissociation energy (BDE) in **2** using the nitroxide radical-trapping technique,[3] a method that we have successfully employed in several systems including **1**,[3a] 5′-deoxyadenosyl-B_{12},[4a–c] 5′-deoxyadenosylcobinamide,[4d] methyl-B_{12},[5] and neopentyl-B_{12}.[6]

Anaerobic solutions (*ca.* 10^{-4} mol dm^{-3}) of **2** in benzene were thermolysed in the presence of ⩾10 equiv. of the TEMPO free-radical trap over a 30 °C temperature range (60–90 °C).‡ This reaction quantitatively yields $\cdot Co^{II}(L^1)I$ and benzyl-TEMPO (Scheme 1, step *b*).[1b] An Eyring plot of $\ln(k_{TEMPO})$ *vs.* $1/T$ for these thermolysis reactions gave a linear plot§ with $\Delta H^{\ddagger}_{obs} = 26 \pm 2$ kcal mol^{-1} and $\Delta S^{\ddagger}_{obs} = -6 \pm 7$ cal mol^{-1} K^{-1}; these values combine to give $\Delta G^{\ddagger}_{obs} = 27 \pm 3$ kcal mol^{-1} at 25 °C (1 cal = 4.184 J).

From this $\Delta H^{\ddagger}_{obs}$ measurement a close estimate for the homolytic bond dissociation energy in solution of the benzyl–carbon bond in **2** can be determined. The proper equation for estimating the bond dissociation energy from solution thermolysis measurements is BDE = *ca.* $\Delta H^{\ddagger}_{obs} - F_c\Delta H^{\ddagger}_{\eta}$,[7] where F_c is the cage efficiency factor and $\Delta H^{\ddagger}_{\eta}$ is the activation enthalpy for viscous flow (and solvation effects are assumed to be negligible).[7] Given our finding[1b] of an inefficient cage ($F_c \leqslant 0.5$) and computing $\Delta H^{\ddagger}_{\eta}$ = *ca.* 2 kcal mol^{-1} for benzene,[7] this equation reduces to BDE = *ca.* $\Delta H^{\ddagger}_{obs} - 1$ (± *ca.* 2) kcal mol^{-1}. The resultant benzyl–carbon BDE *estimate* for **2** is BDE = *ca.* 26 (±2) − 1 (±2) or 25 ± 3 kcal mol^{-1}.

This is a very interesting result for two reasons. First, the average homolysis BDE for a benzyl–carbon bond is of the order of 76 kcal mol^{-1}.[8] Clearly, the BDE of the benzyl–carbon bond in **2** is much less, roughly one third this value, indicating that *the benzyl-carbon bond in* **2** *is highly activated.*[9,10] Second, the *cobalt*–carbon homolysis BDE of **1** was previously determined to be *ca.* 26 ± 1 kcal mol^{-1}.[3a] Thus, not only is the benzyl–carbon bond in **2** roughly one-third the average benzyl–carbon bond dissociation



Scheme 1

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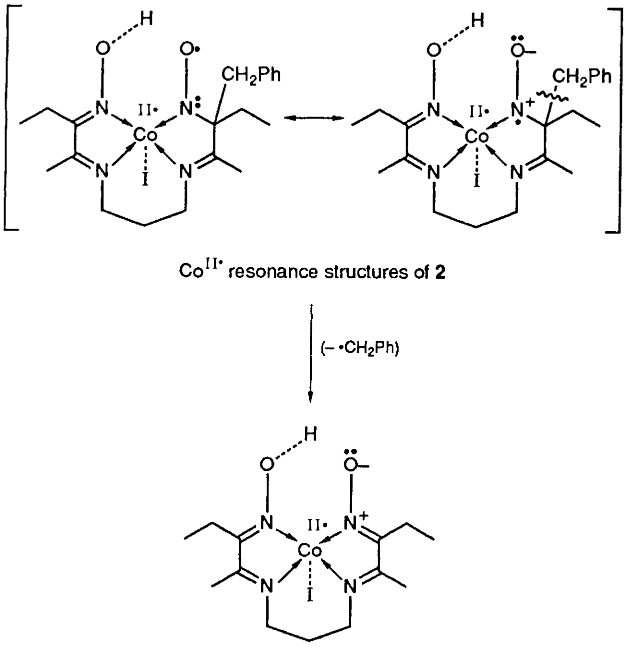
† The ligands L^1 and L^2–CH_2Ph are shown in Scheme 1; L^1 = 4,10-dimethyl- 5,9-diazatrideca-4,9-diene-3,11-dione dioximato(1−), and is referred to in the literature[1–3] as the [$C_2(DO)(DOH)_{pn}$] or equivalently the [EMO(EMOH)] 'modified-Costa'[2a] B_{12} model ligand; L^2–CH_2Ph = 11-benzyl-11-hydroxyamino-4,10-dimethyl-5,9-diazatrideca-4,9-dien-3-one oximato(2−) and the rearrangement product **2** may be named on the basis of *Chemical Abstracts* systems as (*SP*-5-15)-[2-[[3-[[2-(hydroxyamino-1-methyl-2-(phenylmethyl)butylidene]amino]propyl]imino]pentan-3-one oximato(2−)-*N*,*N*′, *N*″, *N*‴]-iodocobalt. TEMPO = 2,2,4,4-tetramethylpiperidin-1-oxyl.

‡ These thermolysis reactions were followed by visible spectroscopy; an isosbestic point at 488 nm is maintained throughout the reaction. Plots of $\ln(A_t - A_\infty)$ *vs.* time were linear over > three half-lives indicating that the reaction is first-order overall, and thus zero-order in TEMPO. Confirming that the reaction is zero-order in TEMPO, the 69 °C thermolysis of **2** with six different concentrations of TEMPO (1×10^{-4} to 3×10^{-3} mol dm^{-3}; 1 to 30 equiv. *vs.* [**2**]) all yielded the same rate constant.

§ Plots of the data were supplied to the referees.



•Co^{II}(L^1)I

Fig. 1 Co$^{II•}$ resonance structures of 2 that can rationalize a C–CH$_2$Ph β-scission in 2, resulting in the homolysis of the benzyl–carbon bond

energy, it is essentially the same strength (weakness!) as the cobalt–carbon bond in **1**. Independent confirmation of this result (derived from the equilibrium thermolysis studies of **2** without TEMPO)[1b] is the finding that the **1** $\rightleftharpoons$ **2** equilibrium exhibits a ΔH = *ca.* 0; hence, the benzyl–cobalt bond (in **1**) and the benzyl–carbon bond (in **2**) must have essentially the same solution[7,11] bond dissociation energies.

Why is the benzyl–carbon bond in **2** so weak? Focusing on the Co$^{II•}$ resonance form of **2**,¶ it can be drawn to put unpaired spin-density β to the benzyl–carbon bond as shown in Fig. 1. β-Scission, a well-established, general type of radical reaction (in the present case, β-scission of the benzyl–carbon bond, as shown), yields a delocalized (stabilized) benzyl radical; concomitant regeneration of the C=N double bond and especially the formation of the delocalized, *persistent* d^7 •Co^{II}(L^1)I stable radical helps minimize the endothermicity of the C–CH$_2$Ph β-scission step. Hence, one key to the weak benzyl–carbon bond in **2** seems to be the formation of highly delocalized homolysis products.|| However, molecular orbital calculations that might shed additional insight into the origins of the low benzyl–carbon BDE in **2** would be welcome.

Are there other examples of such weak carbon–carbon bonds? One is Gomberg's classic studies[9] of a carbon–(*p*-phenyl)carbon bond dissociation energy[9b,c] of *ca.* 11 kcal mol^{-1} for Ph$_3$C–C$_6$H$_5$CPh$_2$ dissociation to 2Ph$_3$C•. Another, somewhat related example is the 18 kcal mol^{-1} carbon–(*p*-phenyl)carbon bond in (Bu$^t_3$SiO)$_3$-TiOCPh$_2$C$_6$H$_5$CPhOTi(OSiBu$^t_3$).[10] Note that both these, as well as the present example, form delocalized homolysis products (*i.e.* Ph$_3$C•, PhCH$_2$•).

What are the significance and possible broader implications of the low alkyl–carbon BDE found in **2**? Similar rearrangement products have been reported in cobaloxime, Schiff's base, and other B$_{12}$ model systems[12,13] (as well as other metal macrocycle systems, notably metalloporphyrins[1]). However, no quantitative or BDE determinations are available for those systems; indeed, even their product structures are not unequivocally determined.[1,12,13] Similar low alkyl–carbon BDEs may in fact exist in these systems as well. Hence, the quantitative thermolysis and BDE study reported herein should prove of specific interest to such metal macrocycle systems, and of broader interest to the general understanding of carbon-carbon bond energies.

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¶ Co^{III} and Co^{I} as well as Co$^{II•}$ contributing resonance structures for **2** can be drawn.[1b]

|| A referee has suggested that steric crowding in **2** might be important as opposed to the largely electronic rationalization provided in the text. Two facts argue against this view: The lack of steric crowding in the structure[1a] of **2**, and the fact that the entropy is the *opposite* ($\Delta S^{\ddagger}$ = -6 ± 7 cal. mol^{-1} k^{-1}) of the positive entropy expected for significant relief of steric strain in the transition state for benzyl–carbon bond homolysis.