## The Co-C Bond in the Gas Phase

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The Co-C bond in adenosylcobalamin (AdoCbl) is considered to be a weak bond. The homolytic bond cleavage is measured to be at most 16 kcal/mol in an enzymatic environment and 34 kcal/mol in aqueous media.<sup>[1]</sup> Threshold collision-induced dissociation (T-CID) is a method used to measure reactive cross-sections in the gas phase. From the reactive cross-sections, bond dissociation energies (BDEs) are deconvoluted using ligand collision-induced dissociation (L-CID)<sup>[2]</sup>, a program written in-house. Our group previously measured the Co-C bond of the structurally similar adenosylcobinamid (AdoCbi) with T-CID/L-CID and obtained a BDE value of 41 kcal/mol.<sup>[3]</sup> When changing the adenosyl to a phenyl, *i.e.* changing a  $sp^3$ -hybridized carbon to a  $sp^2$  one, we would expect the bond strength to increase. However, T-CID measurements of PhCbi reveal a decrease of the bond strength – from 41 kcal/mol to 38 kcal/mol.<sup>[4]</sup> To rationalize this observation, we hypothesize that the bond strength is modulated significantly through London dispersion by the presence of the sidechains on Cbl/Cbi. To test this hypothesis, Costa<sup>[5]</sup> complexes, which feature a similar chemical environment around cobalt but no such sidechains, are employed to obtain the unmodulated Co-C bond-strengths in the gas phase using T-CID/L-CID. The measurements reveal the BDE of sp<sup>3</sup>-hybridized carbons to be 38 kcal/mol and 35 kcal/mol for methyl- and ethyl-Costa complexes, respectively, compared to 45 kcal/mol for the phenyl complex, which is in line with the expectation that the sp<sup>3</sup>-hybridized carbons should be bound weaker to cobalt than the sp<sup>2</sup> ones. However, the trend appeared, at first, to be broken when we reach sp-hybridized carbons, as they go through a different dissociation and thus end up having similar BDEs to sp<sup>3</sup>-hybridized ones. The BDEs for sp<sup>3</sup> and sp<sup>2</sup>-hybridized carbons bound to cobalt compare favorably to calculations at the DFT level, while the gas phase structure of the sp Costa complexes remains unclear.

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