# Structural Determination of a Cobalt(III) Complex with a Co to Tertiary Carbon Bond: How Long can a Co–C Bond be?

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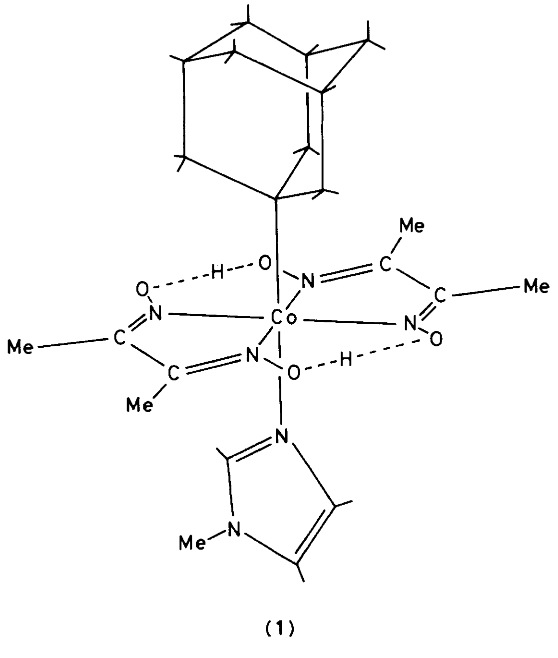
The compound *trans*-adamantylbis(dimethylglyoximato)(1-methylimidazole)cobalt(III), which has the longest accurately determined Co–C bond of 2.154(5) Å, is the first structurally characterized organocobalt $B_{12}$ model compound with a Co to tertiary carbon bond.

During many $B_{12}$-dependent enzymic processes evidence exists that, in the holoenzyme, the Co–C$^1$ bond in coenzyme $B_{12}$ (5′-deoxyadenosylcobalamin) is cleaved homolytically.[2] The initial 5′-deoxyadenosyl radical and subsequent substrate-derived radicals are obligatory intermediates in the catalytic cycle.[2] The role of the Co$^{II}$ species formed upon homolysis is uncertain but it could form a bond from Co to the substrate radical. This possibility might be considered unlikely in some processes, such as the dehydration of butane-2,3-diol by diol-dehydrase, as the intermediate would have a Co atom bound to a pseudo tertiary carbon atom.[3] Although a few $B_{12}$ model compounds reasonably suspected of containing Co to tertiary carbon bonds have been isolated,[4] hitherto none have been structurally characterized. Structural parameters for the evaluation of possible intermediates have, therefore, not been available.

A long Co–C bond [2.22(2) Å] was found in the sterically constrained compound, *trans*-isopropylbis(dimethylglyoximato)(triphenylphosphine)cobalt(III), [$PPh_3Co(DH)_2Pr^i$].[5]† However the disorder of the Pr$^i$ group limited the accuracy of this distance.



(1)

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† Abbreviations: 1-Nmeim = 1-methylimidazole, DH = dimethylglyoximato, py = pyridine.

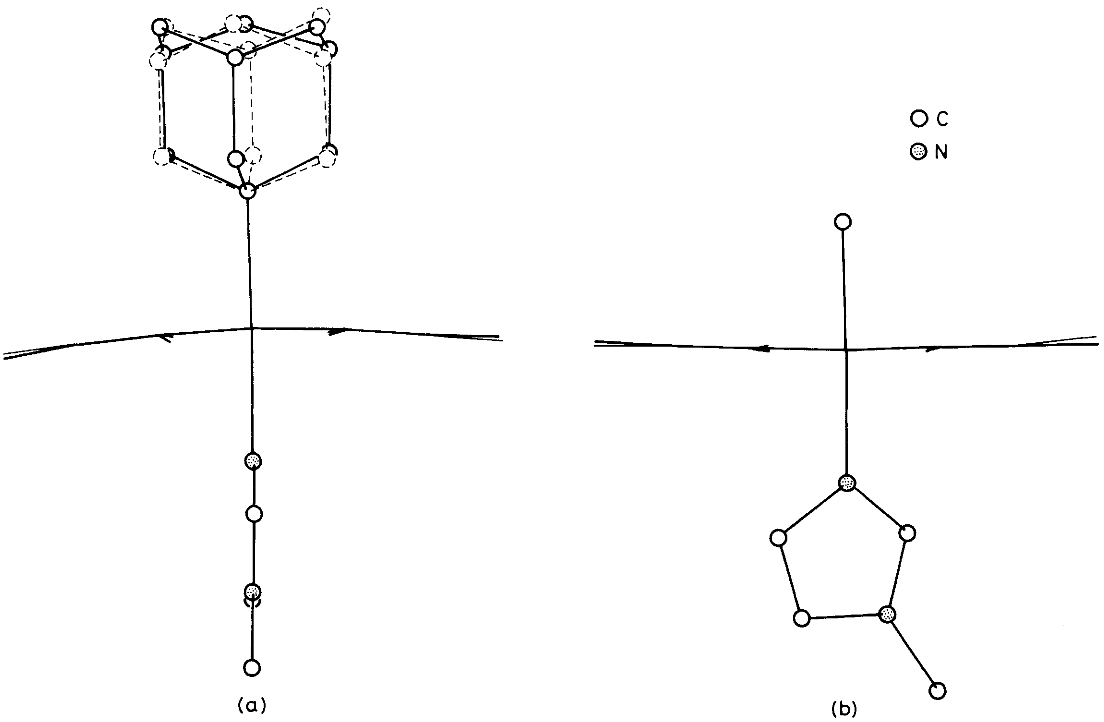

**Figure 1.** (a) A side view of the molecule of (**1**) showing the two orientations of the adamantyl group and (b) a side view of the methyl analogue

We have prepared *trans*-adamantylbis(dimethylglyoximato)(1-methylimidazole)cobalt(III) (**1**) by the standard method.[4]

The *X*-ray crystal structure of (**1**) has been determined and a side view is shown in Figure 1(a).‡ Two different orientations of the adamantyl group with respect to the equatorial ligand, which differ by a rotation of *ca.* 60° around the Co–C bond, were found to have occupancy factors of 0.9 (full line) and 0.1 (broken line) respectively.

The structure of (**1**) [Figure 1(a)] confirms that the Co is directly bonded to the tertiary $C_\alpha$ and that no rearrangement of the adamantyl cage has occurred. Despite the stability of (**1**) for long periods under ambient conditions, the structure reveals an interesting, very long Co–C bond of 2.154(5) Å, which is the longest Co–C bond reported at this level of accuracy. By comparison, the analogous methyl derivative has a Co–C bond length of 2.009(7) Å.[6] Although the adamantyl group was expected to exert a large *trans*-influence, the Co–N(1-Nmeim)† bond lengths are very similar in the adamantyl [2.065(4) Å] and methyl [Figure 1(b)] [2.058(5) Å] analogues, respectively. Some structural features are different, however. In (**1**) the displacement, *d*, of the cobalt atom out of the plane of the four equatorial N atoms is 0.057 Å and the bending angle, α, between the planes passing through the two DH† units is −10.0°. In the methyl analogue, the corresponding values are −0.054 Å and +4.5° respectively. A positive sign for *d* and α indicates displacement and bending towards the alkyl group, a negative sign towards 1-Nmeim.

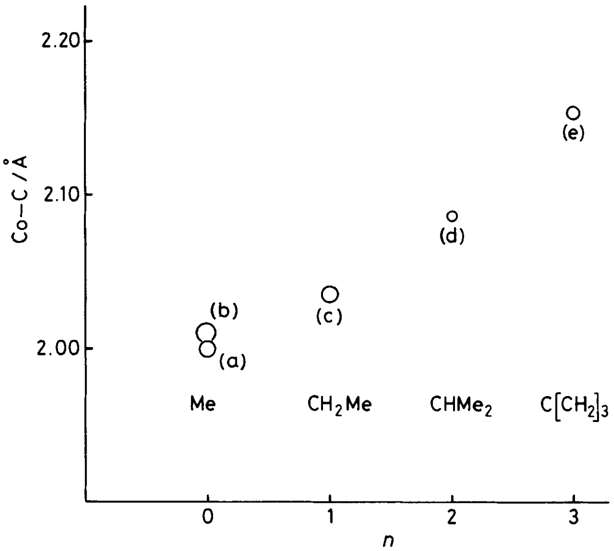

**Figure 2.** Variation of the Co–C bond lengths (Å) with the number of substituents *n* at carbon for (a) $[Co(DH)_2(py)(Me)]$,† (b) $[Co(DH)_2(1\text{-}Nmeim)(Me)]$, (c) $[Co(DH)_2\{(4\text{-}MeOC{=}NH)C_5H_4N\}(CH_2Me)]$, (d) $[Co(DH)_2(py)(CHMe_2)]$, and (e) $[Co(DH)_2(1\text{-}Nmeim)(adamantyl)]$. The radius of the open circles is the value of the estimated standard deviation for each distance.

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‡ Single crystals, obtained from acetone by slow evaporation, were checked by Weissenberg photographs; all other measurements were done on a Nonius CAD4 diffractometer. All the calculations were done using the SDP package on a PDP11/44 computer. *Crystal data:* $C_{22}H_{35}N_6O_4Co$, monoclinic space group $P2_1/c$, $a = 9.456(1)$, $b = 30.021(5)$, $c = 9.029(1)$ Å, $\beta = 109.94(1)°$, $U = 2409.5$ Å$^3$, $D_c = 1.40$ g cm$^{-3}$, $M = 506.6$, $Z = 4$, $\mu(\text{Mo-}K_\alpha) = 7.8$ cm$^{-1}$, $F(000) = 1296$, $R = 0.055$, $R_w = 0.067$ for 2 717 reflections with $I > 3\sigma(I)$ and $3° \leqslant \theta \leqslant 28°$ (crystal size 0.02 × 0.03 × 0.04 cm$^3$). Refinement was by full-matrix techniques with hydrogen atoms and adamantyl carbon atoms in the lower occupancy orientation in calculated positions. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

The plane of the 1-Nmeim ligand almost bisects the two five-membered chelate rings of the DH ligands in the methyl derivative, but bisects the oxime bridges in the adamantyl complex. These differences, shown in Figure 1, where the side views of the two complexes are compared, are clearly consistent with the different bulk of the axial alkyl group.[5] In the adamantyl derivative, the symmetry of $C_\alpha$ and the rigidity of the cage prevent significant variation of the adamantyl bond angles as observed for other more flexible alkyl groups. Therefore most of the steric strain is alleviated by the lengthening of the Co–C bond. In fact, the N(eq)–Co–C angles range from 91.3(2) to 92.0(2)° and the Co–C–C angles at the adamantyl $C_\alpha$ atom range from 108.1(4) to 111.4(4)°. The structure of a relevant cyclopentyl complex,[7] where the Co–C bond is 2.049(9) Å, but the Co–CH–C angles are 115.6(6) and 117.9(6)° respectively, is consistent with this suggestion.

Different N-ligands *trans* to the alkyl group do not influence the Co–C distance in related compounds.[8] Therefore, we can confidently analyse the variation of the Co–C bond length in the $LCo(DH)_2R$ series, where L=N-ligand and R is an alkyl group with a different number of substituents at the $C_\alpha$ atom. The previously observed relationship between the Co–C bond length and the number of side groups on C is now shown to hold for a tertiary carbon atom (Figure 2). The Co–C values in Figure 2 are typical for Me, $CH_2Me$, $CHMe_2$, and $C[CH_2]_3$ residues. Longer or shorter Co–C distances would be expected for substitution with groups bonded at $C_\alpha$ of different bulk.

The typical orientation of the $\alpha$ bending of the $Co(DH)_2$ group is that found in the Me analogue. The inversion of the bending in the adamantyl complex, which is obviously caused by the bulk of this alkyl group, prevents the 1-Nmeim ligand from adopting the orientation it has in the methyl analogue.

If the conformational change in the holoenzyme which accompanies substrate binding[2] results in a related change in orientation of the benzimidazole ligand and corrin 'pucker', enhanced non-bonded repulsive interactions between the corrin and 5′-deoxyadenosine could contribute to Co–C bond cleavage. The effect of corrin ring pucker on Co–C bond homolysis has been the subject of much speculation.[2] These and related structural results[5,8] and the estimates of low Co–C bond energies in both the coenzyme and model compounds,[9,10] taken together, are consistent with a broad shallow potential energy curve for this bond.

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## References

1 P. G. Lenhert and D. C. Hodgkin, *Nature (London)*, 1962, **192**, 937.
2 For a recent review see, '$B_{12}$,' ed. D. Dolphin, Vol. 1 and 2, Wiley New York, 1982.
3 B. M. Babior and J. S. Krouwer, *CRC Crit. Rev. Biochem.*, 1979, **6**, 35; also see ref. 2, p. 263; R. G. Fincke, D. A. Schiraldi, and B. J. Mayer, *Coord. Chem. Rev.*, 1984, **54**, 1, provides arguments against Co to substrate C bond.
4 H. Eckert, D. Lenoir, and I. Ugi, *J. Organometal. Chem.*, 1977, **141**, C23.
5 L. Randaccio, N. Bresciani Pahor, P. J. Toscano, and L. G. Marzilli, *J. Am. Chem. Soc.*, 1980, **102**, 7372.
6 A. Bigotto, E. Zangrando, and L. Randaccio, *J. Chem. Soc., Dalton Trans.*, 1976, 96.
7 E. D. MacKenzie, *Inorg. Chim. Acta*, 1978, **29**, 107.
8 M. F. Summers, P. J. Toscano, N. Bresciani-Pahor, G. Nardin, L. Randaccio, and L. G. Marzilli, *J. Am. Chem. Soc.*, 1983, **105**, 6259.
9 T. T. Tsou, M. Loots, and J. Halpern, *J. Am. Chem. Soc.*, 1982, **104**, 633.
10 R. G. Finke, D. A. Schiraldi, and B. J. Mayer, *Coord. Chem. Rev.*, 1984, **54**, 1.