ELSEVIER

www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 602 (2000) 1–4

Journal of Organometallic Chemistry

Organocobaloximes with mixed-dioxime equatorial ligands: a one-pot synthesis☆

B.D. Gupta [a,*], V. Singh [a], K. Qanungo [a], V. Vijaikanth [a], R. Yamuna [a], T. Barclay [b], W. Cordes [b]

[a] *Department of Chemistry, I.I.T. Kanpur, Kanpur 208016, India*
[b] *Department of Chemistry and Biochemistry, University of Arkansas, Fayetteville, AR, USA*

Received 22 November 1999; received in revised form 2 February 2000

Abstract

BenzylCo(dmgH)(dpgH)Py has been synthesized by the reaction of benzyl chloride with a mixture of $Co^{I}(dmgH)_2Py$ and $Co^{I}(dpgH)_2Py$, generated in situ, by the $NaBH_4$ reduction of $ClCo(dmgH)_2Py$ and $ClCo(dpgH)_2Py$. A mixture of three products is formed. The first crystal structure of an organocobaloxime with a mixed-dioxime ligand is reported. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Cobalt; Cobaloxime; Dioxime

1. Introduction

Organocobaloximes[1], originally proposed as models of vitamin B_{12} nearly three decades ago, have been studied extensively [1–4]. This was prompted by the need to understand the factors behind the cleavage of the Co–C bond in B_{12} dependent enzymatic reactions [5]. Although a lot of insight has been gained on the Co–C bond homolysis process in vitamin B_{12} in general, and organocobaloximes in particular, the exact mechanism remains inconclusive. The use of organocobaloximes has been exploited in free radical chemistry [6,7] and these find numerous applications in organic reactions [8–13]. It is also observed that a slight variation in the equatorial ligand brings out profound changes in the Co–C bond reactivity, for example in the Diels Alder reaction [11], the alkyl–alkenyl cross coupling reaction [14] and in the oxygen insertion reaction into the Co–C bond [15]. The key feature of these reactions is the fragility of the Co–C bond [16–18] and hence a fine-tuning of its strength has been a continuing challenge. Approaches to this problem have mainly been via changes in the steric and electronic properties of axial ligands [3]. Our recent studies on organocobaloximes have shown that variation in the equatorial dioxime ligand field has a pronounced *cis* influence on the axial ligands [16]. Therefore, there has been a sustained interest in the synthesis of new organocobaloximes with new or modified equatorial ligands [11,17–23].

Keeping the above in mind, we report here a simple and general route to the synthesis of organocobaloximes of the type $RCo^{III}(L)(L')B$ with mixed-equatorial dioxime ligands. The synthesis is confirmed by the crystal structure of BnCo(dmgH)-

☆ This work is supported by the DST, New Delhi, India.

* Corresponding author. Fax: +91-512-597 436.
E-mail address: bdg@iitk.ac.in (B.D. Gupta)

[1] General formula $RCo(L)_2B$ where: R, an organic group σ-bonded to cobalt; B, axial base *trans* to the organic group; L, dioxime ligand, e.g. gH, glyoxime; dmgH, dimethylglyoxime; chgH, 1,2 cyclohexanedione dioxime; dpgH, diphenylglyoxime.

PII: S0022-328X(00)00105-4

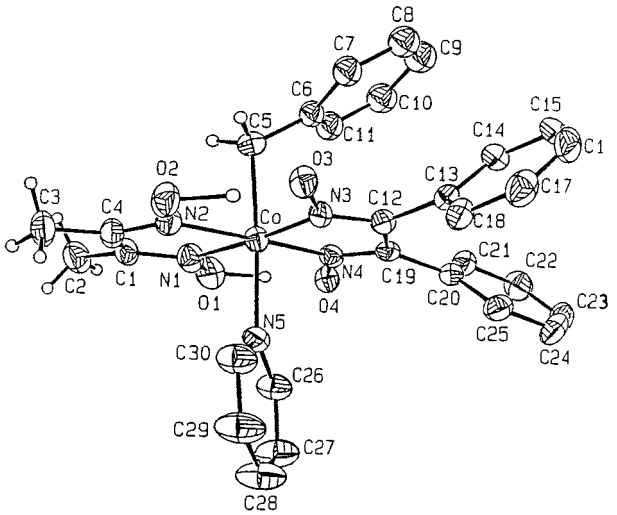


Fig. 1. Crystal structure of benzylCo(dmgH)(dpgH)Py (**2**).

(dpgH)Py[2] (Fig. 1). This becomes the first structure of an organocobaloxime with two different dioximes in the same complex. There is only one report that mentions the formation of similar complexes in solution but such species have never been isolated before [25].

2. Results and discussion

We have used oxidative alkylation of cobaloxime(I), generated from chlorocobaloxime, for the synthesis of mixed-ligand complexes. A mixture of three products (**1**–**3**) is formed.

$$\underset{[1:1]}{ClCo(dmgH)_2Py} + ClCo(dpgH)_2Py \xrightarrow[\substack{\text{(ii) BnCl (3 eq)}\\ \text{NaOH (trace)}}]{NaBH_4} \text{Products } \mathbf{1}\text{–}\mathbf{3}$$

1, $BnCo(dpgH)_2Py$; **2**, BnCo(dmgH)(dpgH)Py; **3**, $BnCo(dmgH)_2Py$.

A detailed examination of the product distribution (Table 1) indicates that the formation of the mixed-ligand complex **2** is a function of time. The yield reaches a maximum (entry 5) and then declines (entry 6).

The yield of **2** is low at the initial stages of the reaction (entries 1–3) and is practically independent of the residence time of cobalt(I) (entries 1–3). This indicates that the following reaction is either very slow or does not occur in the reaction time scale, otherwise, we would have seen the formation of **2** in the beginning of the reaction itself (entries 1–3).

Table 1
Product distribution [a]

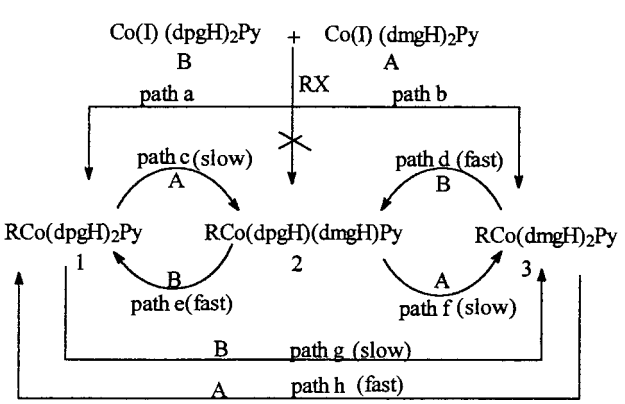
$ClCo(dmgH)_2Py$, $ClCo(dpgH)_2Py$ (one equivalent each)	BnCl (three equivalents)	Residence time of Co^I (min)	Reaction time (min) [b]	% Molar distribution (after column) (1, 2, 3) [c]
Entry 1 do	do	30	15	73, 3, 23
Entry 2 do	do	5	15	63, 0.4, 36
Entry 3 do	do	5	30	63, 0.8, 36
Entry 4 do	do	5	60	61, 17, 21
Entry 5 do	do	10	180	35, 42, 23
Entry 6 do	do	10	400	63, 0.8, 36

[a] **1**, BnCo $(dpgH)_2Py$; **2**, BnCo(dmgH)(dpgH)Py; **3**, $BnCo(dmgH)_2Py$.

[b] Reaction time: time between the addition of benzyl chloride and work up. The Julabo refrigerated circulator was turned off after the addition of the halide.

[c] Refers to the time before the addition of benzyl chloride to Co(I).

[2] Single crystals of $C_6H_5CH_2Co(dmgH)(dpgH)Py$ were grown from methanol. Formula: $C_{30}H_{30}CoN_5O_2$; fw: 583.53; crystal size: 0.20 × 0.38 × 0.46 mm; $a = 17.1950(19)$, $b = 9.5165(13)$, $c = 18.170(4)$ Å, $\beta = 107.050(14)°$; $V = 2842.6(8)$ Å^3; cell detn, reflections: 25; cell detn: 2θ range, 18–20°; $D_{calc} = 1.36$ g cm^{-3}; space group: $P2_1/c$; $Z = 4$; $F(000) = 1217.7$; radiation: Mo–K_α, graphite monochromated; $\lambda = 0.7107$ Å; temperature: 293 K; linear absorption coefficient: 0.64 mm^{-1}; diffractometer: Enraf-Nonius CAD-4; scan technique: θ–2θ; 2θ range: 4–50°; h, k, l ranges: −20–20; −11–0; −21–0; standard reflection indices: −3, −2, −6; 8, −1, −1; −2, −1, −7; drift of standards: 2.5%; absorption correction: analytical; absorption range: 0.78–0.89; reflections measured: 5179; unique reflections: 5002; R for merge: 0.016; reflections in refinement, $I > 2.0s(I)$: 2877; solution method: Patterson; parameters refined: 331; $R(F)$, $Rw(F)$: 0.054, 0.072; R for $I > 3.0\sigma(I)$: 0.047; GoF: 1.26; p: $w^{-1} = [s^2(I) + pI^2]/4F^2$ 0.04; largest $\Delta/$: 0.00; final difference map: −0.32(7), +0.64(7) e Å^{-3}; programs: NRC386 (PC version of NRCVAX) [24]; scattering factors: International Tables for Crystallography, Vol. 4; H atom treatment: idealized (C–H = 0.95 Å).



Scheme 1.

$$Co^{I}(dmgH)_2Py + Co^{I}(dpgH)_2Py \rightarrow 2Co^{I}(dmgH)dpgH)Py$$

Thus, **2** is not formed by direct alkylation of Co^{I}(dmgH)(dpgH)Py. $BnCo(dpgH)_2Py$ (**1**) or $BnCo(dmgH)_2Py$ (**3**), once formed in solution by direct alkylation of $Co^{I}(dpgH)_2Py$ or $Co^{I}(dmgH)_2Py$ (paths a and b; Scheme 1), reacts further with $Co^{I}(dmgH)_2Py$ or $Co^{I}(dpgH)_2Py$, respectively, (path c and d) to yield the mixed-dioxime complex **2**. This has been confirmed by independent experiment [26] using equimolar quantities of each reactant. It is observed that path d is more facile than path c. Nearly all of the $BnCo(dpgH)_2Py$ is recovered in the latter reaction while most of the $BnCo(dmgH)_2Py$ is consumed in the former (Scheme 1).

It is noticed that in all these reactions the yield of $BnCo(dpgH)_2Py$ (**1**) is always more as compared to $BnCo(dmgH)_2Py$ (**3**). This suggests that processes other than simple alkylation of $Co^{I}(dpgH)_2Py$ are responsible for its formation, for example the independent reactions [26] show that (a) $BnCo(dpgH)_2Py$ is formed by *trans*-alkylation reaction of $BnCo(dmgH)_2Py$ with $Co^{I}(dpgH)_2Py$ (path h) and (b) BnCo(dmgH)(dpgH)Py reacts with $Co^{I}(dpgH)_2Py$ (path e) and forms $BnCo^{III}(dpgH)_2Py$ in high yields while the reaction with $Co^{I}(dmgH)_2Py$ (path f) produces $BnCo(dmgH)_2Py$ in low yields in the same reaction. This also explains the depletion of the mixed-dioxime complex **2** in the later stages of the reaction.

Though the exact mechanism of the reaction can be deciphered by detailed kinetic experiments, the preliminary studies here show that the dioxime ligand exchange along with alkyl transfer in the presence of cobalt(I) is taking place. The independent reactions [26] have shown that **2** is formed, albeit in low yield, if $ClCo(dmgH)_2Py$ is reduced with borohydride in the presence of excess dpgH and benzyl chloride.

The method is found to be applicable to various combinations of the dioximes (dpgH, gH, chgH), axial organic moiety (alkyl/benzyl) as well as neutral bases other than pyridine. The examples of organocobaloximes with glyoxime as an equatorial ligand are few due to the instability of the reduced cobaloxime(I) precursor and its poor nucleophilicity [27–29]. Our method enables glyoxime to be incorporated as one of the equatorial ligands.

Mixed-dioxime complexes would allow a better understanding of the steric and electronic factors of the equatorial ligands that control the Co–C bond reactivity. It is postulated that these complexes would have Co–C bond reactivity, often utilized in initiating free radical reactions, midway from the symmetrical dioxime complexes. Eventually this would be helpful to delineate the individual steric and electronic contributions of the two equatorial dioximes on the cobalt–carbon bond reactivity. Studies are underway in this direction.

3. Experimental

The following procedure was adopted for all reactions.

NaOH (one pellet dissolved in 1.0 ml of water) was added to a suspension of $ClCo^{III}(dmgH)_2Py$ [15] (0.201 g, 0.5 mmol) and $ClCo^{III}(dpgH)_2Py$ [30] (0.326 g, 0.5 mmol) in methanol (10.0 ml) and the reaction mixture was thoroughly purged with argon for 15 min. The temperature was brought down to 0°C by a Julabo Refrigerator circulator. The reaction mixture turned deep blue after the addition of $NaBH_4$ (0.048 g, 1.27 mmol, dissolved in 1.0 ml of water). Benzyl chloride (0.189 g, 1.5 mmol) in methanol (5.0 ml) was added dropwise. The reaction mixture was stirred for 3 h in the dark during which the reaction mixture was brought to ambient temperature and then the contents were poured into water. The orange–red solid was filtered, dried and chromatographed on a silica gel column with ethylacetate–chloroform as eluent yielding three cobaloximes (**1**, **2** and **3**). The products **1** and **3** were compared with the authentic samples from this laboratory [15]. The analytical and spectral data for **2** is as follows: Elemental Anal.: C, 61.73 (61.75); H, 5.18 (5.14); N, 12.04 (12.01). $R_f = 0.5$ (EtOAc: $CHCl_3$, 10:90). ^{1}H-NMR (400 MHz, $CDCl_3$, TMS int. std): 2.02 (6H, s, dmgH-Me), 3.16 (2H, s, Co–CH_2), 6.87–6.99 (5H, m, C_6H_5), 7.04–7.29 (10H, m, dpgH-φ), 7.37 (2H, m, Py_β), 7.75 (1H, t, Py_γ), 8.71 (2H, d, Py_α), 18.47 (2H, O–H–O). ^{13}C-NMR (100 MHz, $CDCl_3$): 12.1. 125.4, 127.6, 127.7, 127.8, 127.8, 128.6, 128.9, 129.6, 129.7, 130.2, 137.7, 149.7, 150.2.

4. Supplementary material

Crystallographic data for the structural analysis (interatomic distances and angles, torsion angle, $\mu(i, j)$ values and atomic parameters) have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 135131. Copies of the data can be obtained free of charge from The Director, CCDC, 12 Union Rd., Cambridge CB2 1EX, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.com.ac.uk or www: http://www.ccdc.cam.ac.uk).

References

[1] N. Bresciani-Pahor, M. Forcolin, L.G. Marzilli, L. Randaccio, M.F. Summers, P.J. Toscano, Coord. Chem. Rev. 63 (1985) 1 and Refs. therein.
[2] P.J. Toscano, L.G. Marzilli, Prog. Inorg. Chem. 104 (1984) 105.
[3] N. Bresciani-Pahor, E. Zangrando, L.G. Marzilli, Chem. Soc. Rev. 18 (1989) 225 and Refs. cited therein.
[4] B.D. Gupta, S. Roy, Inorg. Chim. Acta. 146 (1988) 209.

[5] D. Dolphin ((Ed.), B_{12}, vols. 1–2, Wiley-Interscience, Chichester, 1982.
[6] M. Tada, K. Kaneko, J. Org. Chem. 60 (1995) 6635.
[7] T.M. Brown, C.J. Cooksey, A.T. Dronsfield, A.S. Wilkinson, Appl. Organomet. Chem. 10 (1996) 415.
[8] T. Brown, A. Dronsfield, A. Jablonski, A-S. Wilkinson, Tetrahedron Lett. 37 (1996) 5413.
[9] G.B. Gill, G. Pattenden, G.A. Roan, Tetrahedron Lett. 37 (1996) 9369.
[10] J.L. Gage, B.P. Branchaud, Tetrahedron Lett. 40 (1997) 7007.
[11] (a) W.M. Wright, T.L. Smalley Jr., M.E. Welker, A.L.. Rheingold, J. Am. Chem. Soc.116 (1994) 6777. (b) M.W. Wright, M.E., Welker, J. Org. Chem. 61 (1996) 133. (c) T.L. Smalley Jr., M.W. Wright, S.A. Garmon, M.E. Welker, A.L. Rheingold, Organometallics 12 (1993) 998.
[12] B.D. Gupta, V. Singh, K. Qanungo, V. Vijaikanth, R.S. Sengar, J. Organomet. Chem. 582 (1999) 279.
[13] B.D. Gupta, V. Dixit, I. Das, J. Organomet. Chem. 572 (1999) 49.
[14] B.P. Branchaud, Y.L. Choi, Tetrahedron Lett. 29 (1988) 6037.
[15] B.D. Gupta, V. Vijaikanth, V. Singh, J. Organomet. Chem. 570 (1998) 1 and Refs. cited therein.
[16] B.D. Gupta, K. Qanungo, T. Barclay, W. Cordes, J. Organomet. Chem. 560 (1998) 155.
[17] B. Kohler, M. Knauer, W. Clegg, M.R.J. Elsegood, B.T. Golding, J. Retey, Angew. Chem. Int. Ed. Engl. 34 (1995) 2389.
[18] R. Dreos, S. Germia, G. Nardin, L. Randaccio, G. Tauzher, S. Vuano, Inorg. Chim. Acta. 272 (1998) 74.
[19] F. Asaro, R. Dreos, S. Germia, G. Nardin, G. Pellizer, L. Randaccio, G. Tauzher, S. Vuano, J. Organomet. Chem. 548 (1997) 211.
[20] C. Lopez, S. Alvarez, X. Solans, M. Font-Bardia, Polyhedron 11 (1992) 1637.
[21] A. Bakac, J.H. Espenson, Inorg. Chem. 19 (1980) 242.
[22] B. Fraser, L. Brand, W.K. Stoval, H.D. Kaesz, S.I. Khan, J. Organomet. Chem. 472 (1994) 317.
[23] V.I. Tsapkov, N.N. Samus, M.V. Gandzii, Zh. Neorg. Chim. 39 (1994) 252.
[24] E.J. Gabe, Y. Lepage, J.P. Charland, F.L. Lee, P.S. White, NRCVAX — An interactive program system for structure analysis, J. Appl. Crystallogr. 22 (1989) 383.
[25] D. Dodd, M.D. Johnson, B.L. Lockman, J. Am. Chem. Soc. 99 (1977) 3664.
[26] Supplementary material with the author, unpublished work.
[27] G.N. Schrauzer, R.J. Windgassen, J. Am. Chem. Soc. 88 (1966) 3738.
[28] P.J. Toscano, T.F. Swider, L.G. Marzilli, N. Bresciani-Pahor, L. Randaccio, Inorg. Chem. 22 (1983) 3416.
[29] N. Bresciani-Pahor, L. Randaccio, E. Zangrando, P.J. Toscano, Inorg. Chim. Acta 96 (1985) 193.
[30] C. Lopez, S. Alvarez, M. Aguilo, X. Solans, M. Font-Altaba, Inorg. Chim. Acta 127 (1987) 153.