
A Cobaloxime Substituted Terminal Alkene Which Rapidly Isomerizes to a Cobaloxime Substituted Internal Alkene Complex

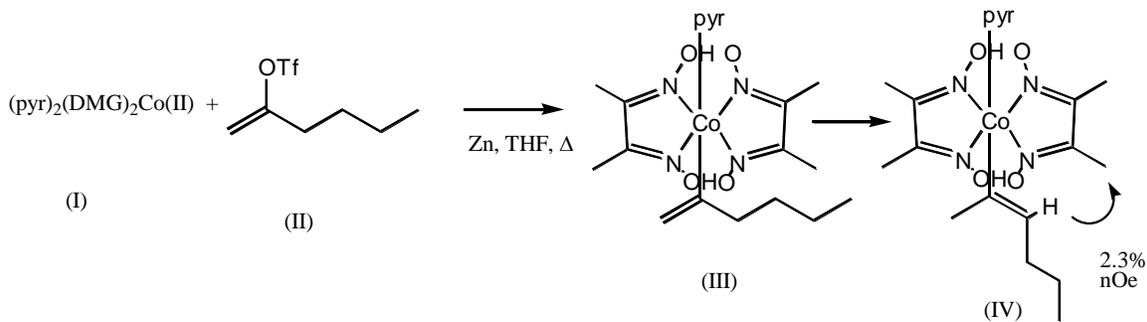
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An unusual cobaloxime substituted terminal alkene has been isolated and characterized by X-ray crystallography. The double bond in the alkene readily isomerizes but the title compound could be isolated and structurally characterized at low temperature.

Comment

We have been interested in the preparation of cobaloxime complexes (cobaloxime = (pyridine)(dimethylglyoxime)₂cobalt) which contain cobalt-*sp*² carbon bonds and the use of these complexes in cycloaddition chemistry (Welker, 2001). In 2000, we reported a new method for the preparation of cobalt-*sp*² carbon bonds which involved a zinc mediated coupling of alkenyl halides and triflates (II) to (pyr)₂(dmg)₂Co (Pickin and Welker, 2000). One of the coupling products prepared, a 2-cobaloxime substituted 1-hexene (III) isomerized readily to (E)-2-cobaloxime-2-hexene (IV). The 2-cobaloxime 1-hexenyl complex (III) has now been crystallized at low temperature and its structure is reported here.



The molecular structure of compound (III) is depicted in Figure 1 and selected geometric parameters are given in Table 1. The cobalt in III is coordinated in a slightly distorted octahedral geometry. The equatorial plane cobalt-nitrogen bond distances are Co-N1 = 1.871(5) Å, Co-N2 = 1.877(5) Å, Co-N3 = 1.881(5) Å, and Co-N4 = 1.903(5) Å. The cobalt-N5 (pyridine ligand nitrogen) bond length is 2.089(4) Å and the Co-C10 distance is 1.994(5) Å. The cobalt resides in the N1-N2-N3-N4 plane, ie its deviation from that plane is insignificant (0.019 Å). The C9-C10-C11 plane and the N5-C15-C16-C17-C18-C19 (pyridine ligand) plane are almost coincident and these planes bisect the N4-Co-N1 and N2-Co-N3 angles. The cobalt- sp^2 carbon bond (Co-C10 1.994(5) Å) falls in the range of other cobalt- sp^2 carbon bond lengths that we have reported previously for cobaloxime dienyl complexes (1.954(15) Å to 2.019(6) Å) (Stokes *et al.*, 1995; Wright, *et al.*, 1994). This bond length is significantly longer than those reported previously for cobaloxime ethenyl complexes (1.945(5) Å to 1.953(3) Å) (McCauley *et al.*, 2002) but comparable to cobalt- sp^2 carbon bond lengths in cobaloxime complexes containing longer carbon chains in the alkenyl fragment (1.971(13) Å, 1.972(7) Å, and 1.976(4) Å) (Stolter *et al.*, 1975; Adams *et al.*, 1998; Adams *et al.*, 1997). Previously reported cobalt- sp^3 carbon bond lengths in cobaloxime complexes range from 1.998(5) Å for the cobaloxime methyl complex to 2.085(3) Å for the isopropyl complex (Brescani-Pahor *et al.*, 1985). The carbon-carbon double bond in the hexenyl ligand (C9-C10, 1.324(7) Å) is largely unaffected by the presence of the cobaloxime and this observation has also been true of the other cobaloxime substituted alkenyl complexes referenced above. The Co-C10-C9 and Co-C10-C11 bond angles are 119.3(4)° and 117.5(4)° respectively. Most cobalt-C α sp^2 -C β sp^2 bond angles reported previously have been >120° but we have

reported two other examples of cobaloxime alkenyl and dienyl complexes where these angles were less than 120° ; $118.3(3)^\circ$ and $116.7(5)^\circ$ (Adams *et al.*, 1997; Stokes *et al.*, 1995).

This cobaloxime alkenyl complex (III) containing a terminal alkene underwent facile double bond isomerization upon attempted silica chromatography or simply upon standing in CDCl_3 . The rate constant for isomerization was determined by analysis of the appearance of the alkenyl methyl signal and this analysis was carried out for several half lives. A rate constant of $3.9 \times 10^{-2} \text{ min}^{-1}$ ($R = 0.9707$) with a half-life of 18 minutes was calculated. The alkenyl complex which III isomerized to was demonstrated to contain the E alkene geometry shown in structure IV based on the observation of a strong nOe from the alkenyl proton to the dimethylglyoxime ligand methyls and the absence of a nOe from those same ligand methyl groups to the methyl or methylene protons α to the alkene in the hexenyl ligand.

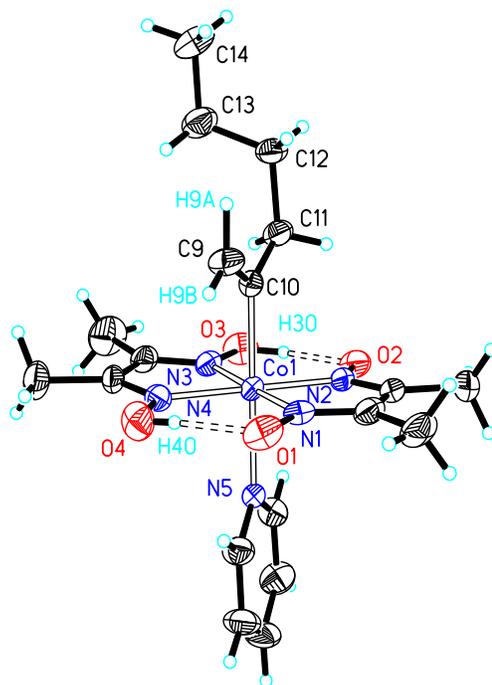


Figure 1

The molecular structure of (III). All nonhydrogen atoms are represented by thermal vibration ellipsoids drawn to encompass 50% of their electron density. Hydrogen atoms are represented by arbitrarily-small spheres, which are in no way representative of their true thermal motion. Hydrogen-bonding interactions are represented with dashed open bonds.

Table 1

Selected geometric parameters (Å, °).

Co ₁ -N ₁	1.871(5)	Co ₁ -N ₃	1.881(5)
Co ₁ -N ₂	1.877(5)	Co ₁ -N ₄	1.903(5)
Co ₁ -C ₁₀	1.994(5)	Co ₁ -N ₅	2.089(4)
O ₁ -N ₁	1.360(6)	O ₃ -N ₃	1.349(6)
O ₂ -N ₂	1.342(6)	O ₄ -N ₄	1.330(6)
O ₃ -H ₃₀	0.91(9)	O ₄ -H ₄₀	0.77(5)
N ₁ -C ₁	1.303(8)	N ₃ -C ₃	1.297(7)
N ₂ -C ₂	1.292(7)	N ₄ -C ₄	1.303(8)
N ₅ -C ₁₅	1.338(6)	N ₅ -C ₁₉	1.342(6)
C ₁ -C ₂	1.458(8)	C ₃ -C ₄	1.448(10)
C ₁ -C ₅	1.485(8)	C ₃ -C ₇	1.503(8)

C ₂ -C ₆	1.488(8)	C ₄ -C ₈	1.499(9)
C ₉ -C ₁₀	1.324(7)	C ₁₀ -C ₁₁	1.482(7)
N ₃ -C _{O1} -N ₄	81.3(2)	N ₂ -C _{O1} -N ₅	89.4(2)
N ₂ -C _{O1} -N ₃	98.3(2)	N ₃ -C _{O1} -N ₅	91.7(2)
N ₁ -C _{O1} -N ₄	98.7(2)	N ₄ -C _{O1} -N ₅	90.5(2)
N ₁ -C _{O1} -C ₁₀	89.7(2)	N ₁ -C _{O1} -N ₃	178.4(2)
N ₂ -C _{O1} -C ₁₀	90.6(2)	N ₂ -C _{O1} -N ₄	179.6(2)
N ₃ -C _{O1} -C ₁₀	88.8(2)	C ₁₀ -C _{O1} -N ₅	179.5(2)
N ₄ -C _{O1} -C ₁₀	89.5(2)	C ₉ -C ₁₀ -C ₁₁	123.2(5)
C ₁₀ -C ₁₁ -C ₁₂	117.5(4)	C ₉ -C ₁₀ -C _{O1}	119.3(4)
C ₁₃ -C ₁₂ -C ₁₁	113.6(5)	C ₁₁ -C ₁₀ -C _{O1}	117.5(4)
C ₁₄ -C ₁₃ -C ₁₂	111.3(5)		

Experimental

Complex (III) (1-hexen-2-ylpyridinebis(dimethylglyoximate)-cobalt(II)) was prepared as described previously (Pickin and Welker, 2000). Crystals of III were grown by slow diffusion of pentane into a 1,2-dichloroethane solution of III at 253°K. The isomerization kinetics experiment was carried out in CDCl₃ and the rate constant was determined by analysis of the appearance of the alkenyl methyl signal and this analysis was carried out for several half lives. An array of ¹H spectra (acquisition time of 1.0 min) were acquired every 10.0 minutes for 170 minutes (9 half lives). All spectra were process and phased with the same parameters. The appearance of the alkenyl methyl was integrated relative to the *ortho* pyridine signal. SigmaPlot 2000 (SPSS Science Inc. Chicago, IL) was used to determine the rate constant for an integration versus time plot. The equation for an exponentially rising peak going to a maximum, $I = I_o(1 - e^{-kt})$, was used to curve fit the data. A rate constant of $3.9 \times 10^{-2} \text{ min}^{-1}$ (R = 0.9707) with a half-life of 18 minutes was calculated.

Crystal data

Co(NC₅H₅)(N₂C₂(CH₃)₂O₂H)₂(C₆H₁₁)

$M_r = 451.41$

Monoclinic, Pn (an alternate setting of Pc – C_s² (No.7))

$a = 8.268(3)\text{Å}$

$b = 11.757(3)\text{Å}$, $\beta = 93.72(2)^\circ$

$c = 11.025(2)\text{Å}$

$\beta = 93.72(2)^\circ$

$V = 1069.5(4)\text{Å}^3$

$Z = 2$

$D_x = 1.402\text{ g cm}^{-3}$

Mo $K\alpha$ radiation

Cell parameters from 3254 reflections

$\theta = 2.54\text{--}27.50^\circ$

$\mu = 0.837\text{ mm}^{-1}$

$T = 228(2)\text{K}$

orange needle

0.18 x 0.24 x 0.45 mm

Data Collection

Bruker-AXS P4 autodiffractometer

ω scans

Absorption correction: multi-scan

(SADABS; Bruker, 1999)

$T_{\min} = 0.1513$, $T_{\max} = 0.1869$

3254 measured reflections

2971 independent reflections

2660 reflections with $I > 4\sigma(I)$

$R_{\text{int}} = 0.034$

$\theta_{\text{max}} = 27.50^\circ$

$h = -1$ to 10

$k = -15$ to 1

$l = -14$ to 14

Refinement

Refinement on F^2

$R[F^2 > 4\sigma(F^2)] = 0.042$

$wR(F^2) = 0.101$

$S = 1.048$

2971 reflections

278 parameters

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + 0.0361P]^2 + 0.0284P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} =$

$\Delta\rho_{\text{max}} = 0.650\text{ e Å}^{-3}$

$\Delta\rho_{\text{min}} = -0.242\text{ e Å}^{-3}$

Hydrogen atoms H_{3O}, H_{4O}, H_{9A} and H_{9B} were located from a difference Fourier map and refined as independent isotropic atoms. The methyl groups (C₅, C₆, C₇, C₈, C₁₄ and their hydrogen atoms) were refined as rigid rotors with idealized sp³-hybridized geometry and a C-H bond length of 0.97Å. The remaining hydrogen atoms were included in the structure factor calculations as idealized atoms (assuming sp²- or sp³-hybridization of the

carbon atoms and C-H bond lengths of 0.94-0.98 Å) "riding" on their respective carbon atoms. The isotropic thermal parameters for H_{3O}, H_{4O}, H_{9A} and H_{9B} refined to final U_{iso} values of 0.07(3)Å², 0.02(1)Å², 0.05(2)Å², and 0.03(1)Å², respectively. The isotropic thermal parameters of the remaining hydrogen atoms were fixed at values 1.2 (non-methyl) or 1.5 (methyl) times the equivalent isotropic thermal parameters of the carbon atoms to which they are covalently bonded.

All calculations were performed using the SHELXTL-PC (Version 6.12) interactive software package (G. Sheldrick, Bruker AXS, Madison, WI).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference:). Services for accessing these data are described at the back of this journal.

References

- Adams, T.A., Welker, M.E., & Day, C.S. (1998). *J. Org. Chem.* **63**, 3683-3686.
- Adams, T.a., Welker, M.E., Liable-Sands, L.M. & Rheingold, A.L. (1997). *Organometallics* **16**, 1300-1307.
- Bresciani-Pahor, N., Forcolin, M., Marzilli, L.G., Randaccio, L., Summers, M.F. & toscano, P.J. (1985). *Coord. Chem. Rev.* **63**, 1-125.
- McCauley, K.M., Wilson, S.R. & van der Donk, W.A. (2002). *Inorg. Chem.* **41**, 393-404.
- Pickin, K.A. & Welker, M.E. (2000). *Organometallics* **19**, 3455-3458.
- Stokes, H.L., Richardson, B.M., Wright, M.W., Vaughn, S.M., Liable-Sands, L. & Rheingold, A.L. (1995). *Organometallics* **14**, 5520-5532.
- Stolter, D.A., Sheldrick, G.M. & Taylor, R. (1975). *J. Chem. Soc. Dalton Trans.* 2124-2128.
- Welker, M.E. (2001). *Curr. Org. Chem.* **5**, 785-807.
- Wright, M.W., Smalley, T.L., Welker, M.E. & Rheingold, A.L. (1994). *J. Am. Chem. Soc.* **116**, 6777-6791.