METAL-ORGANIC COMPOUNDS

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Derivatives of Bis(diphenylphosphino)difluoromethane: the Disulfide $Ph_2P(=S)CF_2P(=S)Ph_2$ and the Bis[chlorogold(I)] Complex $Ph_2P(AuCl)CF_2P(AuCl)Ph_2$

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Abstract

The title compound difluoromethylenebis(diphenylphosphine) disulfide, $C_{25}H_{20}F_2P_2S_2$, displays an S1—P1···P2—S2 torsion angle of −90.76 (5)°. The P—CF_2 bond lengths of 1.893 (2) and 1.893 (3) Å are appreciably lengthened in comparison with systems involving the non-fluorinated analogue diphenylphosphinomethane. In the title complex μ-[difluoromethylenebis(diphenylphosphine)-*P*,*P'*]-bis[chlorogold(I)], [$Au_2Cl_2(C_{25}H_{20}F_2P_2)$], the Au—P···P—Au torsion angle is 31.2 (1)° and a short intramolecular Au···Au contact of 3.1432 (8) Å is observed.

Comment

Bis(diphenylphosphino)methane (dppm), $Ph_2PCH_2PPh_2$, is a routinely used bidentate phosphine ligand. Its difluoromethane analogue bis(diphenylphosphino)difluoromethane, $Ph_2PCF_2PPh_2$, has however, to the best of our knowledge, not been used as a ligand. We present here the structures of two derivatives of bis(diphenylphosphino)difluoromethane, namely, the disulfide $Ph_2P(=S)CF_2P(=S)Ph_2$, (1), and the bis[chlorogold(I)] complex $Ph_2P(AuCl)CF_2P(AuCl)Ph_2$, (2).

(1)

(2)

The conformation of compound (1) about the P···P vector is described by the torsion angle S1—P1···P2—S2 of −90.76 (5)°; the substituents of the P1—C1 and P2—C1 bonds are staggered (Fig. 1). The structure of dppm disulfide has not been determined; dppm diselenide displays a similar conformation to that of (1) [torsion angle 95.4 (1)°; Carroll & Titus, 1977], although the two compounds are not isostructural, whereas dppm dioxide shows a fundamentally different conformation, with O—P···P—O torsion angles of 178 and −170° in two independent molecules (Antipin, Struchkov, Pisareva, Medved & Kabachnik, 1980).

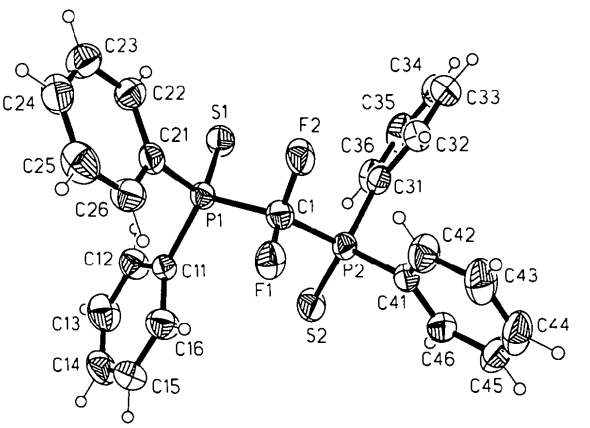

Fig. 1. A view of the molecule of compound (1) with ellipsoids corresponding to 50% probability levels. H-atom radii are arbitrary.

The P=S bond lengths in compound (1) of 1.9352 (13) and 1.9319 (11) Å are, as in $Ph_2P(=S)CF_2Br$ [1.9348 (11) Å; Jones, 1996], slightly shorter than the 'standard' value of 1.954 Å (Allen *et al.*, 1987). The P—CF_2 bond lengths of 1.893 (2) and 1.893 (3) Å are lengthened with respect to those of the non-halogenated systems; dppm [1.848 (5) and 1.868 (5) Å; Schmidbaur, Reber, Schier, Wagner & Müller, 1988], dppm dioxide [1.814 (8), 1.814 (7), 1.833 (7) and 1.816 (7) Å; Antipin *et al.*, 1980] and dppm diselenide [1.833 (10) and 1.853 (11) Å; Carroll & Titus, 1977]. The lengthened P—CF_2 bond [1.884 (3) Å] in $Ph_2P(=S)CF_2Br$ (Jones, 1996) implies that this effect may be general for P—C(halide) systems.

The bond angles at phosphorus show the expected trends; those involving sulfur are larger [maximum 115.23 (10)° for C31—P2—S2] because of the extra interelectronic repulsion from the P=S double bond, whereas the smallest angles involving sulfur are those involving the more electronegative CF_2 group.

The P—C—P angle is widened to 116.89 (13) from 106.2 (3)° in dppm (Schmidbaur *et al.*, 1988), compared with values of 119.5 (4) and 121.3 (4)° in dppm dioxide (Antipin *et al.*, 1980), and 117.9 (6)° in dppm diselenide (Carroll & Titus, 1977).

The structure of the gold complex μ-[difluoromethylenebis(diphenylphosphine)-*P*,*P'*]-bis[chlorogold(I)], (2) is shown in Fig. 2. Its most striking feature is the short intramolecular Au···Au contact of 3.1432 (8) Å. Such contacts are common in gold(I) chemistry and represent

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weak attractive interactions between the formally non-bonding d^{10} metal atoms (see *e.g.* Jones, 1986); the tendency of gold(I) centres to aggregate has been termed 'aurophilicity' by Schmidbaur (1990).

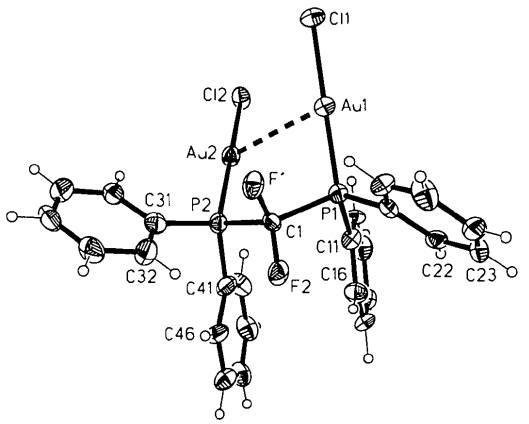

Fig. 2. A view of the molecule of compound (2) with ellipsoids corresponding to 50% probability levels. H-atom radii are arbitrary.

The Au···Au contact distance of 3.351 (2) Å in the corresponding non-fluorinated complex $(dppm)(AuCl)_2$ (Schmidbaur, Wohlleben, Wagner, Orama & Huttner, 1977), which crystallizes with twofold symmetry, is appreciably longer than that in (2). Consistent with this observation, the Au—P···P—Au torsion angle in (2) is smaller: 31.2 (1) *cf.* 67.5° in $(dppm)(AuCl)_2$. In $(dppm)(AuC_6F_5)_2$ (Jones & Thöne, 1992), an essentially *cis* conformation is observed (Au—P···P—Au 0.8°), with an Au···Au distance of 3.163 (1) Å, but a relaxation of the Au—P—C angles to 113.8 and 115.1 (4)° [*cf.* 107.3 and 109.5 (3) in (2)] prevents the Au···Au contact from becoming shorter still.

The Au—P and Au—Cl bond lengths in (2) are normal and the deviation from linearity at gold is *ca* 5° (Table 4). The P—CF_2 bonds are long [1.893 and 1.900 (10) Å], consistent with the observations noted above; the P—C—P angle is 113.2 (5)° [*cf.* 1.78 (2) Å and 116 (1)° in $(dppm)(AuCl)_2$].

Neither compound displays any unusually short intermolecular contacts.

Experimental

Compound (1) was obtained from $Ph_2PCF_2PPh_2$ and $P(=S)Cl_3$, while compound (2) was obtained from $Ph_2PCF_2PPh_2$ and (tht)AuCl (tht is tetrahydrothiophene). Both were recrystallized from dichloromethane/diethyl ether (Ruhnau, 1992).

Compound (1)

Crystal data

$C_{25}H_{20}F_2P_2S_2$
M_r = 484.47
Triclinic
$P\bar{1}$
a = 9.519 (3) Å
b = 11.446 (4) Å
c = 11.650 (4) Å
α = 108.67 (3)°
β = 104.86 (3)°
γ = 94.68 (3)°
V = 1143.6 (7) Å^3
Z = 2
D_x = 1.407 Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 50 reflections
θ = 10–11.5°
μ = 0.400 mm^{-1}
T = 178 (2) K
Prism
0.88 × 0.60 × 0.50 mm
Colourless

Data collection

Siemens $R3$ diffractometer
ω scans
Absorption correction: none
5225 measured reflections
4041 independent reflections
3093 observed reflections [$I > 2\sigma(I)$]
R_{int} = 0.0209
θ_{max} = 25.05°
$h = -11 \rightarrow 11$
$k = -13 \rightarrow 13$
$l = -13 \rightarrow 13$
3 standard reflections monitored every 147 reflections
intensity decay: 3.5%

Refinement

Refinement on F^2
$R(F)$ = 0.0383
$wR(F^2)$ = 0.1050
S = 1.021
4038 reflections
281 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0532P)^2 + 0.4407P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.282 e Å^{-3}
$\Delta\rho_{min}$ = −0.284 e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0047 (15)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (1)*

$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
P1	0.72888 (7)	0.20127 (6)	0.43075 (6)	0.03212 (17)
P2	0.62214 (7)	0.32679 (6)	0.21890 (6)	0.03414 (18)
S1	0.55388 (7)	0.07266 (6)	0.34478 (7)	0.0456 (2)
S2	0.73387 (9)	0.22322 (7)	0.12384 (7)	0.0522 (2)
F1	0.81697 (17)	0.43775 (12)	0.44772 (14)	0.0475 (4)
F2	0.59118 (17)	0.39359 (14)	0.45317 (13)	0.0470 (4)
C1	0.6917 (3)	0.3468 (2)	0.3928 (2)	0.0362 (5)
C11	0.8952 (3)	0.1581 (2)	0.3938 (2)	0.0332 (5)
C12	0.8974 (3)	0.0310 (2)	0.3506 (3)	0.0473 (7)
C13	1.0212 (4)	−0.0122 (3)	0.3235 (3)	0.0605 (8)
C14	1.1414 (3)	0.0700 (3)	0.3391 (3)	0.0572 (8)
C15	1.1417 (3)	0.1964 (3)	0.3832 (3)	0.0565 (8)
C16	1.0196 (3)	0.2422 (3)	0.4111 (3)	0.0497 (7)
C21	0.7765 (3)	0.2589 (2)	0.6033 (2)	0.0358 (5)
C22	0.6902 (3)	0.2048 (2)	0.6579 (3)	0.0446 (6)
C23	0.7282 (3)	0.2380 (3)	0.7890 (3)	0.0533 (7)
C24	0.8511 (3)	0.3254 (3)	0.8644 (3)	0.0537 (8)
C25	0.9382 (3)	0.3818 (3)	0.8115 (3)	0.0568 (8)
C26	0.9023 (3)	0.3481 (3)	0.6807 (3)	0.0482 (7)
C31	0.4246 (3)	0.2697 (2)	0.1655 (2)	0.0366 (6)
C32	0.3263 (3)	0.3451 (3)	0.2056 (3)	0.0443 (6)
C33	0.1753 (3)	0.3018 (3)	0.1536 (3)	0.0561 (8)
C34	0.1225 (3)	0.1853 (3)	0.0610 (3)	0.0595 (8)
C35	0.2176 (4)	0.1107 (3)	0.0204 (3)	0.0588 (8)

C36	0.3697 (3)	0.1517 (2)	0.0723 (3)	0.0470 (7)
C41	0.6422 (3)	0.4865 (2)	0.2200 (2)	0.0378 (6)
C42	0.6272 (3)	0.5898 (2)	0.3160 (3)	0.0523 (7)
C43	0.6364 (4)	0.7068 (3)	0.3029 (3)	0.0614 (8)
C44	0.6578 (3)	0.7202 (3)	0.1956 (3)	0.0611 (9)
C45	0.6732 (3)	0.6196 (3)	0.1017 (3)	0.0553 (8)
C46	0.6663 (3)	0.5027 (3)	0.1133 (3)	0.0451 (6)

Table 2. *Selected geometric parameters (Å, °) for (1)*

P1—C11	1.811 (2)	P2—C41	1.818 (3)
P1—C21	1.821 (3)	P2—C1	1.893 (3)
P1—C1	1.893 (2)	P2—S2	1.9319 (11)
P1—S1	1.9352 (13)	F1—C1	1.376 (3)
P2—C31	1.814 (3)	F2—C1	1.373 (3)
C11—P1—C21	105.78 (11)	C31—P2—S2	115.23 (10)
C11—P1—C1	109.12 (11)	C41—P2—S2	113.76 (9)
C21—P1—C1	102.35 (11)	C1—P2—S2	110.50 (8)
C11—P1—S1	115.25 (9)	F2—C1—F1	105.5 (2)
C21—P1—S1	114.52 (9)	F2—C1—P2	109.8 (2)
C1—P1—S1	108.96 (9)	F1—C1—P2	107.8 (2)
C31—P2—C41	105.25 (11)	F2—C1—P1	106.1 (2)
C31—P2—C1	107.51 (11)	F1—C1—P1	110.1 (2)
C41—P2—C1	103.75 (11)	P2—C1—P1	116.89 (13)

Compound (2)

Crystal data

$[Au_2Cl_2(C_{25}H_{20}F_2P_2)]$
M_r = 885.18
Orthorhombic
$P2_12_12_1$
a = 12.998 (4) Å
b = 13.719 (3) Å
c = 13.873 (3) Å
V = 2473.8 (11) Å^3
Z = 4
D_x = 2.377 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 50 reflections
θ = 10–11.4°
μ = 12.221 mm^{-1}
T = 178 (2) K
Prism
0.36 × 0.24 × 0.18 mm
Colourless

Data collection

Siemens $R3$ diffractometer
ω scans
Absorption correction:
ψ scans (*XEMP*; Nicolet, 1987)
T_{min} = 0.610, T_{max} = 0.988
6151 measured reflections
5693 independent reflections
4560 observed reflections
$[I > 2\sigma(I)]$

R_{int} = 0.0338
θ_{max} = 27.56°
$h = -16 \rightarrow 0$
$k = -17 \rightarrow 17$
$l = 0 \rightarrow 18$
3 standard reflections monitored every 147 reflections
intensity decay: 4%

Refinement

Refinement on F^2
$R(F)$ = 0.0405
$wR(F^2)$ = 0.0945
S = 0.974
5693 reflections
298 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0492P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.001$

$\Delta\rho_{max}$ = 2.003 e Å^{-3} (adjacent to Au atoms)
$\Delta\rho_{min}$ = −1.647 e Å^{-3} (adjacent to Au atoms)
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute structure: Flack (1983)
Flack parameter = −0.006 (12)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (2)*

$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
Au1	0.43218 (3)	0.31964 (3)	0.83491 (3)	0.02645 (10)
Au2	0.27217 (3)	0.26527 (3)	0.67377 (3)	0.02627 (10)
P1	0.5197 (2)	0.3729 (2)	0.7077 (2)	0.0239 (6)
P2	0.3946 (2)	0.2380 (2)	0.5643 (2)	0.0248 (6)
Cl1	0.3519 (2)	0.2602 (2)	0.9702 (2)	0.0328 (6)
Cl2	0.1367 (2)	0.2987 (2)	0.7749 (2)	0.0290 (6)
C1	0.5252 (8)	0.2694 (8)	0.6176 (7)	0.022 (2)
F1	0.5574 (4)	0.1876 (4)	0.6666 (5)	0.0322 (13)
F2	0.5964 (5)	0.2857 (4)	0.5491 (5)	0.0322 (15)
C11	0.4665 (7)	0.4723 (8)	0.6370 (7)	0.024 (2)
C12	0.3759 (7)	0.5141 (7)	0.6685 (8)	0.026 (2)
C13	0.3323 (9)	0.5892 (8)	0.6157 (9)	0.033 (2)
C14	0.3788 (8)	0.6219 (8)	0.5312 (8)	0.031 (2)
C15	0.4705 (9)	0.5786 (8)	0.5006 (9)	0.036 (2)
C16	0.5134 (9)	0.5030 (8)	0.5542 (8)	0.031 (2)
C21	0.6535 (9)	0.4005 (7)	0.7294 (7)	0.026 (2)
C22	0.6935 (8)	0.4943 (8)	0.7153 (7)	0.026 (2)
C23	0.7953 (8)	0.5141 (9)	0.7345 (8)	0.033 (2)
C24	0.8585 (9)	0.4404 (7)	0.7679 (8)	0.034 (2)
C25	0.8207 (9)	0.3469 (9)	0.7842 (9)	0.040 (3)
C26	0.7189 (9)	0.3286 (8)	0.7649 (8)	0.033 (2)
C31	0.4096 (8)	0.1138 (8)	0.5249 (7)	0.030 (2)
C32	0.5005 (9)	0.0783 (8)	0.4864 (8)	0.035 (3)
C33	0.5081 (10)	−0.0198 (9)	0.4591 (9)	0.040 (3)
C34	0.4248 (9)	−0.0810 (9)	0.4704 (8)	0.041 (3)
C35	0.3339 (11)	−0.0467 (8)	0.5086 (9)	0.043 (3)
C36	0.3271 (9)	0.0502 (8)	0.5347 (8)	0.032 (2)
C41	0.3814 (8)	0.3162 (8)	0.4599 (8)	0.031 (2)
C42	0.3027 (8)	0.3842 (8)	0.4582 (8)	0.032 (2)
C43	0.2941 (9)	0.4457 (8)	0.3801 (8)	0.037 (3)
C44	0.3613 (8)	0.4388 (9)	0.3050 (8)	0.035 (3)
C45	0.4370 (9)	0.3690 (8)	0.3037 (8)	0.032 (2)
C46	0.4468 (8)	0.3066 (8)	0.3813 (8)	0.031 (2)

Table 4. *Selected geometric parameters (Å, °) for (2)*

Au1—P1	2.223 (3)	P1—C1	1.893 (10)
Au1—Cl1	2.297 (3)	P2—C31	1.799 (11)
Au1—Au2	3.1432 (8)	P2—C41	1.811 (12)
Au2—P2	2.232 (3)	P2—C1	1.900 (10)
Au2—Cl2	2.298 (3)	C1—F2	1.345 (11)
P1—C21	1.805 (11)	C1—F1	1.377 (12)
P1—C11	1.817 (11)		
P1—Au1—Cl1	176.12 (11)	C31—P2—C41	109.2 (5)
P1—Au1—Au2	81.48 (8)	C31—P2—C1	103.7 (5)
Cl1—Au1—Au2	101.33 (8)	C41—P2—C1	105.2 (5)
P2—Au2—Cl2	174.65 (10)	C31—P2—Au2	116.3 (3)
P2—Au2—Au1	92.98 (8)	C41—P2—Au2	112.2 (3)
Cl2—Au2—Au1	91.46 (7)	C1—P2—Au2	109.5 (3)
C21—P1—C11	107.4 (4)	F2—C1—F1	105.9 (8)
C21—P1—C1	103.4 (5)	F2—C1—P1	111.6 (7)
C11—P1—C1	102.8 (5)	F1—C1—P1	107.2 (6)
C21—P1—Au1	115.5 (3)	F2—C1—P2	112.2 (7)
C11—P1—Au1	118.7 (3)	F1—C1—P2	106.2 (7)
C1—P1—Au1	107.3 (3)	P1—C1—P2	113.2 (5)

For both compounds, data collection: *P3* (Nicolet, 1987); cell refinement: *P3*; data reduction: *XDISK* (Siemens, 1991); program(s) used to solve structures: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993); molecular graphics: *XP* (Siemens, 1994); software used to prepare material for publication: *SHELXL93*.

Crystals of both compounds were kindly provided by Dr C. Ruhnau and Professor M. Fild of this Institute. We thank the Fonds der Chemischen Industrie for financial support and Mr A. Weinkauf for technical assistance.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: FG1184). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). C**52**, 2399–2402

(*cis*-1,2-Dichlorovinyl)bis(dimethylglyoximato-*N*,*N*′)(pyridine-*N*)cobalt(III) Chloroform Solvate, $[Co(dmgH)_2(py)(CCl{=}CHCl)].CHCl_3$

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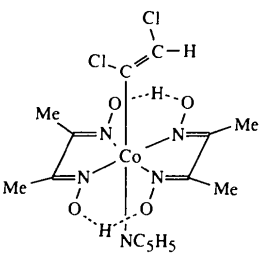
Abstract

In the title complex, $[Co(C_2HCl_2)(C_4H_7N_2O_2)_2(C_5H_5N)].CHCl_3$, the Co atom exhibits a distorted octahedral coordination with the two dimethylglyoximate (dmgH) ligands in equatorial positions [Co—N 1.891 (2)–1.897 (3) Å]. The axial positions are occupied by the pyridine (py) and *cis*-1,2-dichlorovinyl ligands [N—Co—C 179.0 (1)°], which are nearly coplanar. The Co—Cl distance is 1.958 (3) Å. The Co—N_{py} bond length of 2.028 (2) Å indicates a lower *trans* influence for the dichlorovinyl ligand compared with alkyl ligands.

Comment

Organocobaloximes, $[Co(dmgH)_2(L)R]$ ($dmgH_2$ is dimethylglyoxime, *L* is an axial base and *R* is a σ-organo ligand), are not only model complexes for vitamin B_{12} coenzymes (Schrauzer, 1976, 1977; Randaccio, Bresciani-Pahor, Zangrando & Marzilli, 1989), but have also been widely used for investigations of the reactivity of σ-Co—C bonds and the *trans* influence of σ-organo ligands (Pattenden, 1988; Sweany, 1995). We report here the molecular structure of the *cis*-1,2-dichlorovinyl (*R* = CCl=CHCl) complex, (1), with pyridine as the axial base *L*.



(1)

The crystal structure of (1) consists of discrete molecules of the complex $[Co(dmgH)_2(py)(CCl{=}CHCl)]$ and chloroform solvate molecules. The Co atom exhibits distorted octahedral coordination, with four oxime N-atom donors in equatorial positions. The two dimethylglyoximato ligands are connected by two strong intramolecular hydrogen bonds [O2···O3 2.501 (4) and O1···O4 2.490 (3) Å]. The four Co—N bond distances range from 1.891 (2) to 1.897 (3) Å. These values do not differ significantly from those of other organocobaloximes (Bresciani-Pahor *et al.*, 1985).

The four oxime N atoms are coplanar to within 0.007 Å. The Co atom is displaced by 0.010 (1) Å (*d*) from the mean plane towards the pyridine ligand. The two nearly planar dmgH ligands (r.m.s. deviations of 0.023 and 0.024 Å for the C7–C10, N3, N4, O3, O4 and C3–C6, N1, N2, O1, O2 planes, respectively) subtend an interplanar angle, α, of 1.3 (1)°. The values of *d* and α are smaller than in the vinyl complex $[Co(dmgH)_2(py)(CH{=}CH_2)]$ [(2); *d* = 0.04 Å and α = 6.3°; Bresciani-Pahor, Calligaris & Randaccio, 1980] and in many other organocobaloximes (Bresciani-Pahor *et al.*, 1985; Randaccio *et al.*, 1989).

The N5—Co—C1 unit is linear [N5—Co—C1 179.0 (1)°]. The dichlorovinyl and pyridine ligands are

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