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Synthesis and characterization of diphenylglyoximato cobalt(III) complexes. The molecular structures of *trans*-bis(diphenylglyoximato)(alkyl)(pyridine)cobalt(III), with alkyl = CH_2SiMe_3, CH_2CMe_3 and CF_3

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Abstract

A series of Co(III) diphenylglyoximato (dpgh) complexes, $pyCo(dpgh)_2R$, with R = Cl (**2a**), CH_3 (**3a**), CH_2Me (**4a**), $(CH_2)_2Me$ (**5a**), $(CH_2)_3Me$ (**6a**), $CHMe_2$ (**7a**), CH_2SiMe_3 (**8a**), CH_2CMe_3 (**9a**), $CH_2CH{=}CH_2$ (**10a**), CH_2Ph (**11a**), and CF_3 (**12a**) were prepared, using $Co(dpgh)(dpgh_2)Cl_2$ (**1a**) as an entry to this system. The compounds were thoroughly characterized by ^1H and ^{13}C NMR spectroscopy, the spectra of which were compared to the corresponding Co(III) dimethylglyoximato (DH) complexes, $pyCo(DH)_2R$ (**2b**–**12b**). The NMR results suggest that the dpgh ligand is less electron-donating than DH. X-ray diffraction studies of complexes **8a**, **9a** and **12a** demonstrate that subtle, but detectable structural changes occur upon substitution of dpgh for DH, due to increased interactions of the axial alkyl ligand with the equatorial ligand set.

Keywords: Cobalt(III) complexes; Cobaloximes; Diphenylglyoximato ligands; Dimethylglyoximato ligands; NMR spectroscopy; Crystal structures

1. Introduction

Recently, there has been a resurgence of interest in the preparation and the NMR spectroscopic characterization of derivatives in the *trans*-bis(diphenylglyoximato)cobalt(III) system, $LCo(dpgh)_2X$, where dpgh is the monoanion of diphenylglyoxime and L and X are neutral and monoanionic ligands, respectively [1–9]. In addition, a few X-ray structural characterizations have been determined, including $LCo(dpgh)_2Cl$ (L = pyridine (py) [2], *p*-toluidine [2], or PBu_3 [10]), $pyCo(dpgh)_2CH_3$ [3], 4-$MepyCo(dpgh)_2CH_2Cl$ [4], $P(OMe)_3Co(dpgh)_2CH_2Me$ [4], and $[MeCH_2Co(dpgh)_2]_2$(μ-pyrazine) [7]. These reports have allowed for some beginning structural comparisons to the more extensively studied *trans*-bis(dimethylglyoximato)cobalt(III) system, $LCo(DH)_2X$, where DH is the monoanion of dimethylglyoxime [11,12]. We note that Gupta and coworkers have also studied cobaloxime derivatives containing mixed equatorial ligand sets, that include one dpgh ligand and either a DH or 1,2-cyclohexanedione dioximato ligand [13–15].

We have previously reported on investigations involving the effect of peripheral substitutions in the equatorial dioximato ligand set [16,17], as well as the effect of perfluorination of the axial alkyl ligand [18–22], on the chemistry and structural properties of organocobaloximes. In order to test whether a steric *cis*-influence might

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be observable for $pyCo(dpgh)_2R$, we felt that the R group would either have to be large in size or have a very short Co–C bond due to electron deficiency. Herein, we report on observations on improving the yields for the preparation of $pyCo(dpgh)_2R$ complexes, including examples where the steric and electronic properties of the alkyl ligand R are varied more greatly than in the previous studies. The complexes were thoroughly characterized by ^1H and ^{13}C NMR spectroscopy for comparison to their DH analogs. In addition, we have determined the solid-state structures of complexes where R is either the bulky CH_2SiMe_3 or CH_2CMe_3 ligands or the highly electron deficient CF_3 ligand.

2. Experimental

2.1. Materials and physical methods

^1H, ^{13}C and ^{19}F NMR spectra were obtained with a Varian XL-300 spectrometer at 299.9, 75.4, and 282.2 MHz, respectively. Spectra obtained in $CDCl_3$ solution were referenced to internal Me_4Si (^1H and ^{13}C) or internal $CFCl_3$ (^{19}F). We have used the designations *ipso*-C dpgh (carbon atom of the phenyl substituent that is bonded to the oxime carbon atom of the dpgh ligand), *o*-C dpgh (ortho), *m*-C dpgh (meta), and *p*-C dpgh (para) for the four types of carbon atoms in the dpgh phenyl groups in the assignments for the ^{13}C NMR spectra.

Diphenylglyoxime (Aldrich Chemicals), anhydrous cobalt(II) chloride (Aldrich Chemicals), methanol and *n*-butanol were used as received without further purification. Elemental analysis of the crystals of **12a**·$0.125C_6H_6$ was determined by Atlantic Microlabs (Norcross, GA).

2.2. Preparation of $Co(dpgh)(dpgh_2)Cl_2$ (**1a**)

A modification of the literature method [23] was employed. Diphenylglyoxime (9.62 g, 40.1 mmol) was placed in *n*-butanol (400 ml). Anhydrous cobalt(II) chloride (2.64 g, 20.3 mmol) was added and the mixture was heated and stirred overnight in the presence of air. The resulting dark brown solution was concentrated on a rotary evaporator. The dark residue was thoroughly washed with water and ethanol and air dried to give brown product (10.7 g, 88%).

2.3. Preparation of $pyCo(dpgh)_2Cl$ (**2a**)

Complex **1a** (9.00 g, 14.8 mmol) was heated and stirred in 80% methanol/water (240 ml:60 ml). When dissolution was complete, pyridine (2.40 g, 30.4 mmol) was added. The mixture was heated and stirred for 1 h, then cooled. The precipitated product was collected on a filter and washed with water and diethyl ether to give golden brown product (8.61 g, 89%). ^1H NMR ($CDCl_3$): δ 8.60 (d, 2H, α-H py), 7.83 (t, 1H, γ-H py), 7.36 (t, 2H, β-H py), 7.25 (m, 20H, dpgh phenyl). ^{13}C NMR ($CDCl_3$): δ 153.57 (C=N), 151.11 (α-C py), 139.33 (γ-C py), 129.81 (*o*-C dpgh), 129.65 (*p*-C dpgh), 129.58 (*ipso*-C dpgh), 127.93 (*m*-C dpgh), 126.04 (β-C py). The ^1H and ^{13}C NMR spectra of this compound were in good agreement with literature values [2,3].

2.4. Preparation of $pyCo(dpgh)_2R$ ($R = CH_3$, CH_2Me, $(CH_2)_2Me$, $(CH_2)_3Me$, $CHMe_2$, CH_2SiMe_3, CH_2CMe_3, $CH_2CH{=}CH_2$, CH_2Ph; **3a**–**11a**)

Complex **2a** (1.00 g, 1.53 mmol) was suspended in methanol (50 ml) and NaOH (0.104 g, 2.60 mmol) dissolved in water (3 ml) was added. Nitrogen was bubbled through the resulting dark brown solution for 20 min. Then $NaBH_4$ (0.983 g, 2.60 mmol) dissolved in water (3 ml) was added by syringe; the solution turned dark blue. An excess of alkylating agent (5.00 mmol; the corresponding alkyl iodide was employed for $R = CH_3$, CH_2SiMe_3, and CH_2CMe_3, while the corresponding alkyl bromide was used for $R = CH_2Me$, $(CH_2)_2Me$, $(CH_2)_3Me$, $CHMe_2$, $CH_2CH{=}CH_2$ and CH_2Ph) was added by syringe and the solution turned light orange–brown. After stirring for approximately 10–30 min, depending upon the identity of R, the reaction mixture was exposed to air, and acetone (5 ml) and water (10 ml) were added. Reactions times were shorter (ca. 10–15 min) for the more reactive alkyl halides ($R = CH_3$, $CH_2CH{=}CH_2$, and CH_2Ph), in an intermediate range (ca. 15–20 min) for less reactive cases ($R = CH_2Me$, $(CH_2)_2Me$ and $(CH_2)_3Me$), and longest (ca. 25–30 min) for the bulkier alkyl groups (CH_2Me, CH_2SiMe_3 and CH_2CMe_3). Concentration of the reaction mixture on a rotary evaporator provided the orange or brown–orange product. Yields and NMR spectroscopic data for the complexes follow.

$R = CH_3$ (**3a**); yield 0.822 g (84.9%); ^1H NMR ($CDCl_3$): δ 8.92 (d, 2H, α-H py), 7.83 (t, 1H, γ-H py), 7.44 (t, 2H, β-H py), 7.22 and 7.11 (m, 20H, dpgh phenyl), 1.44 (s, 3H, Co–CH_3). ^{13}C NMR ($CDCl_3$): δ 150.78 (C=N), 149.99 (α-C py), 137.99 (γ-C py), 129.94 (*ipso*-C dpgh), 129.60 (*o*-C dpgh), 128.94 (*p*-C dpgh), 127.83 (*m*-C dpgh), 125.58 (β-C py).

$R = CH_2Me$ (**4a**); yield 0.692 g (69.9%); ^1H NMR ($CDCl_3$): δ 8.92 (d, 2H, α-H py), 7.83 (t, 1H, γ-H py), 7.44 (t, 2H, β-H py), 7.22 and 7.10 (m, 20H, dpgh phenyl), 2.34 (q, 2H, Co–CH_2CH_3), 0.82 (t, 3H, Co–CH_2CH_3). ^{13}C NMR ($CDCl_3$): δ 150.80 (C=N), 150.10 (α-C py), 137.86 (γ-C py), 130.09 (*ipso*-C dpgh), 129.62 (*o*-C dpgh), 128.91 (*p*-C dpgh), 127.83 (*m*-C dpgh), 125.51 (β-C py), 16.16 (CH_2CH_3).

R = $(CH_2)_2Me$ (**5a**); yield 0.767 g (75.8%); ^1H NMR ($CDCl_3$): δ 8.92 (d, 2H, α-H py), 7.84 (t, 1H, γ-H py), 7.44 (t, 2H, β-H py), 7.22 and 7.09 (m, 20H, dpgh phenyl), 2.22 (m, 2H, Co–CH_2), 1.46 (m, 2H, Co–$CH_2CH_2CH_3$), 0.99 (t, 3H, Co–$CH_2CH_2CH_3$). ^{13}C NMR ($CDCl_3$): δ 150.85 (C=N), 150.04 (α-C py), 137.85 (γ-C py), 130.08 (*ipso*-C dpgh), 129.62 (*o*-C dpgh), 128.91 (*p*-C dpgh), 127.83 (*m*-C dpgh), 125.49 (β-C py), 24.07 (Co–$CH_2CH_2CH_3$), 15.20 (Co–$CH_2CH_2CH_3$).

R = $(CH_2)_3Me$ (**6a**); yield 0.809 g (78.3%); ^1H NMR ($CDCl_3$): δ 8.92 (d, 2H, α-H py), 7.84 (t, 1H, γ-H py), 7.44 (t, 2H, β-H py), 7.22 and 7.09 (m, 20H, dpgh phenyl), 2.23 (m, 2H, Co–CH_2), 1.41 (br m, 4H, Co–$CH_2CH_2CH_2CH_3$), 0.93 (t, 3H, Co–$CH_2CH_2CH_2CH_3$). ^{13}C NMR ($CDCl_3$): δ 150.84 (C=N), 150.06 (α-C py), 137.86 (γ-C py), 130.11 (*ipso*-C dpgh), 129.60 (*o*-C dpgh), 128.90 (*p*-C dpgh), 127.85 (*m*-C dpgh), 125.50 (β-C py), 33.25 (Co–$CH_2CH_2CH_2CH_3$), 23.80 (Co–$CH_2CH_2CH_2CH_3$), 14.10 (Co–$CH_2CH_2CH_2CH_3$).

R = $CHMe_2$ (**7a**); yield 0.716 g (72.4%); ^1H NMR ($CDCl_3$): δ 8.91 (d, 2H, α-H py), 7.79 (t, 1H, γ-H py), 7.40 (t, 2H, β-H py), 7.21 and 7.09 (m, 20H, dpgh phenyl), 2.63 (septet, 1H, Co–CH), 0.89 (d, 6H, Co–$CHMe_2$). ^{13}C NMR ($CDCl_3$): δ 151.08 (C=N), 149.91 (α-C py), 137.78 (γ-C py), 130.14 (*ipso*-C dpgh), 129.50 (*o*-C dpgh), 128.86 (*p*-C dpgh), 127.84 (*m*-C dpgh), 125.42 (*β*-C py), 26.42 (Co–$CHMe_2$).

R = CH_2SiMe_3 (**8a**); yield 0.744 g (68.9%); ^1H NMR ($CDCl_3$): δ 8.86 (d, 2H, α-H py), 7.81 (t, 1H, γ-H py), 7.41 (t, 2H, β-H py), 7.22 and 7.09 (m, 20H, dpgh phenyl), 1.07 (s, 2H, Co–CH_2), 0.11 (s, 9H, Co–CH_2SiMe_3). ^{13}C NMR ($CDCl_3$): δ 151.35 (C=N), 149.55 (α-C py), 137.99 (γ-C py), 129.97 (*ipso*-C dpgh), 129.68 (*o*-C dpgh), 128.94 (*p*-C dpgh), 127.81 (*m*-C dpgh), 125.47 (β-C py), 1.22 (Co–CH_2SiMe_3).

R = CH_2CMe_3 (**9a**); yield 0.753 g (71.4%); ^1H NMR ($CDCl_3$): δ 8.89 (d, 2H, α-H py), 7.81 (t, 1H, γ-H py), 7.41 (t, 2H, β-H py), 7.20 and 7.06 (m, 20H, dpgh phenyl), 2.34 (s, 2H, Co–CH_2), 1.10 (s, 9H, Co–CH_2CMe_3). ^{13}C NMR ($CDCl_3$): δ 151.68 (C=N), 149.51 (α-C py), 137.84 (γ-C py), 130.15 (*ipso*-C dpgh), 129.53 (*o*-C dpgh), 128.90 (*p*-C dpgh), 127.83 (*m*-C dpgh), 125.38 (β-C py), 38.05 (Co-CH_2CMe_3), 31.08 ($CoCH_2CMe_3$).

R = $CH_2CH{=}CH_2$ (**10a**); yield 0.850 g (84.3%); ^1H NMR ($CDCl_3$): δ 8.88 (d, 2H, α-H py), 7.82 (t, 1H, γ-H py), 7.43 (t, 2H, β-H py), 7.23 and 7.11 (m, 20H, dpgh phenyl), 6.07 (m, 1H, $CH{=}CH_2$), 5.30 (complex, 2H, $CH{=}CH_2$), 2.91 (d, 2H, Co–CH_2). ^{13}C NMR ($CDCl_3$): δ151.15 (C=N), 150.18 (α-C py), 144.35 ($CH{=}CH_2$), 137.95 (γ-C py), 130.17 (*ipso*-C dpgh), 129.65 (*o*-C dpgh), 128.94 (*p*-C dpgh), 127.79 (*m*-C dpgh), 125.55 (β-C py), 112.08 ($CH{=}CH_2$).

R = CH_2Ph (**11a**); yield 0.551 g (50.8%); ^1H NMR ($CDCl_3$): δ 8.86 (d, 2H, α-H py), 7.81 (t, 1H, γ-H py), 7.41 (t, 2H, β-H py), 6.90–7.35 (complex, 25H, dpgh phenyl and CH_2Ph), 3.44 (s, 2H, Co–CH_2). ^{13}C NMR ($CDCl_3$): δ 151.01 (C=N), 150.16 (α-C py), 147.33 (*ipso*-C benzyl), 137.93 (γ-C py), 129.93 (*ipso*-C dpgh), 129.66 (*o*-C dpgh), 129.13 (*o*-C benzyl), 128.89 (*p*-C dpgh), 128.29 (*m*-C benzyl), 127.65 (*m*-C dpgh), 125.52 (β-C py), 124.71 (*p*-C benzyl).

2.5. Preparation of $pyCo(dpgh)_2CF_3$ (*12a*)

To a solution of **2a** (2.00 g, 3.07 mmol) and NaOH (0.40 g, 10.0 mmol) in degassed methanol (100 ml) under nitrogen was added $NaBH_4$ (0.370 g, 9.74 mmol) dissolved in water (3 ml). The solution was stirred for 10 min, followed by the addition of degassed acetone (5 ml). After 5 min, CF_3Br was briefly bubbled through the solution three times. The solution turned from dark blue to brown and was stirred for 20 min after the last CF_3Br addition. The reaction mixture was then opened to air and acetone (15 ml) and water (10 ml) were added. The solution volume was concentrated on a rotary evaporator and the product was collected. The crude material was dissolved in acetone (40 ml) to which was added pyridine (5 drops) and water (15 ml). Slow evaporation in air gave the purified product (1.10 g, 52%). ^1H NMR ($CDCl_3$): δ 8.86 (d, 2H, α-H py), 7.91 (t, 1H, γ-H py), 7.49 (t, 2H, β-H py), 7.25 and 7.11 (m, 20H, dpgh phenyl). ^{13}C NMR ($CDCl_3$): δ 152.60 (C=N), 149.96 (α-C py), 138.90 (γ-C py), 129.53 (*o*-C dpgh), 129.49 (*p*-C dpgh), 129.41 (*ipso*-C dpgh), 127.96 (*m*-C dpgh), 125.90 (β-C py). ^{19}F NMR ($CDCl_3$): δ −31.82 (s, CF_3).

2.6. Preparation of $pyCo(DH)_2R$ ($R = Cl$, CH_3, CH_2Me, $(CH_2)_2Me$, $(CH_2)_3Me$, $CHMe_2$, CH_2SiMe_3, CH_2CMe_3, $CH_2CH{=}CH_2$, CH_2Ph, CF_3; ***3a–12a***)

These organocobalt complexes were prepared by standard literature procedures [19,24,25]. Full NMR spectroscopic data follow.

R = Cl (**2b**); ^1H NMR ($CDCl_3$): δ 8.27 (d, 2H, α-H py), 7.72 (t, 1H, γ-H py), 7.24 (t, 2H, β-H py), 2.40 (s, 12H, DH–CH_3). ^{13}C NMR ($CDCl_3$): δ 152.58 (C=N), 151.04 (α-C py), 138.97 (γ-C py), 125.67 (β-C py), 13.09 (DH–CH_3).

R = CH_3 (**3b**); ^1H NMR ($CDCl_3$): δ 8.61 (d, 2H, α-H py), 7.73 (t, 1H, γ-H py), 7.33 (t, 2H, β-H py), 2.13 (s, 12H, DH–CH_3), 0.81 (s, 3H, Co–CH_3). ^{13}C NMR ($CDCl_3$): δ 150.06 (α-C py), 148.98 (C=N), 137.48 (γ-C py), 125.21 (β-C py), 11.98 (DH–CH_3).

R = CH_2Me (**4b**); ^1H NMR ($CDCl_3$): δ 8.60 (d, 2H, α-H py), 7.71 (t, 1H, γ-H py), 7.32 (t, 2H, β-H py), 2.13 (s, 12H, DH–CH_3), 1.74 (q, 2H, Co–CH_2CH_3), 0.36 (t, 3H, Co–CH_2CH_3). ^{13}C NMR ($CDCl_3$): δ 150.10 (α-C py), 149.01 (C=N), 137.34 (γ-C py), 125.16 (β-C py), 15.91 (CH_2CH_3), 11.95 (DH–CH_3).

R = $(CH_2)_2Me$ (**5b**); ^1H NMR ($CDCl_3$): δ 8.60 (d, 2H, α-H py), 7.71 (t, 1H, γ-H py), 7.31 (t, 2H, β-H py), 2.12 (s, 12H, DH–CH_3), 1.62 (m, 2H, Co–CH_2), 0.98 (m, 2H, Co–$CH_2CH_2CH_3$), 0.79 (t, 3H, Co–$CH_2CH_2CH_3$). ^{13}C NMR ($CDCl_3$): δ 149.96 (α-C py), 149.10 (C=N), 137.35 (γ-C py), 125.13 (β-C py), 23.88 (Co–$CH_2CH_2CH_3$), 14.82 (Co–$CH_2CH_2CH_3$), 12.02 (DH–CH_3).

R = $(CH_2)_3Me$ (**6b**); ^1H NMR ($CDCl_3$): δ 8.59 (d, 2H, α-H py), 7.72 (t, 1H, γ-H py), 7.32 (t, 2H, β-H py), 2.13 (s, 12H, DH–CH_3), 1.64 (m, 2H, Co–CH_2), 1.19 (m, 2H, Co–$CH_2CH_2CH_2CH_3$), 0.89 (m, 2H, Co–$CH_2CH_2CH_2CH_3$), 0.80 (t, 3H, Co–$CH_2CH_2CH_2CH_3$). ^{13}C *NMR* ($CDCl_3$): δ 149.96 (α-C py), 149.12 (C=N), 137.39 (γ-C py), 125.16 (β-C py), 33.01 (Co–$CH_2CH_2CH_2CH_3$), 23.69 (Co–$CH_2CH_2CH_2CH_3$), 13.97 (Co–$CH_2CH_2CH_2CH_3$), 12.02 (DH–CH_3).

R = $CHMe_2$ (**7b**); ^1H NMR ($CDCl_3$): δ 8.59 (d, 2H, α-H py), 7.69 (t, 1H, γ-H py), 7.29 (t, 2H, β-H py), 2.13 (s, 12H, DH–CH_3), 1.94 (septet, 1H, Co–CH), 0.47 (d, 6H, Co–$CHMe_2$). ^{13}C NMR ($CDCl_3$): δ 150.01 (α-C py), 149.30 (C=N), 137.21 (γ-C py), 125.04 (β-C py), 26.33 (Co–$CHMe_2$), 12.00 (DH–CH_3).

R = CH_2SiMe_3 (**8b**); ^1H NMR ($CDCl_3$): δ 8.55 (d, 2H, α-H py), 7.69 (t, 1H, γ-H py), 7.29 (t, 2H, β-H py), 2.12 (s, 12H, DH–CH_3), 0.45 (s, 2H, Co–CH_2), −0.15 (s, 9H, Co–CH_2SiMe_3). ^{13}C NMR ($CDCl_3$): δ 149.68 (α-C py), 149.59 (C=N), 137.42 (γ-C py), 125.14 (β-C py), 12.10 (DH–CH_3), 0.54 (Co–CH_2SiMe_3).

R = CH_2CMe_3 (**9b**); ^1H NMR ($CDCl_3$): δ 8.56 (d, 2H, α-H py), 7.69 (t, 1H, γ-H py), 7.28 (t, 2H, β-H py), 2.11 (s, 12H, DH–CH_3), 1.73 (s, 2H, Co–CH_2), 0.78 (s, 9H, Co–CH2CMe_3). ^{13}C NMR ($CDCl_3$): δ 149.54 (α-C py), 149.94 (C=N), 137.84 (γ-C py), 125.05 (β-C py), 36.84 (Co–CH_2CMe_3), 30.64 (Co–CH_2CMe_3), 12.04 (DH–CH_3).

R = $CH_2CH{=}CH_2$ (**10b**); ^1H NMR ($CDCl_3$): δ 8.56 (d, 2H, α-H py), 7.71 (t, 1H, γ-H py), 7.30 (t, 2H, β-H py), 5.67 (m, 1H, $CH{=}CH_2$), 4.92 (complex, 2H, $CH{=}CH_2$), 2.30 (d, 2H, Co–CH_2), 2.15 (s, 12H, DH–CH_3). ^{13}C NMR ($CDCl_3$): δ 150.17 (α-C py), 149.41 (C=N), 145.17 ($CH{=}CH_2$), 137.45 (γ-C py), 125.22 (β-C py), 110.54 ($CH{=}CH_2$), 12.41 (DH–CH_3).

R = CH_2Ph (**11b**); ^1H NMR ($CDCl_3$): δ 8.55 (d, 2H, α-H py), 7.69 (t, 1H, γ-H py), 7.28 (t, 2H, β-H py), 6.95–7.15 (complex, 5H, CH_2Ph), 2.85 (s, 2H, Co–CH_2), 1.95 (s, 12H, DH–CH_3). ^{13}C NMR ($CDCl_3$): δ 150.27 (α-C py), 149.33 (C=N), 147.41 (*ipso*-C benzyl), 137.40 (γ-C py), 128.71 (*o*-C benzyl), 127.42 (*m*-C benzyl), 125.17 (β-C py), 124.09 (*p*-C benzyl), 11.91 (DH–CH_3).

R = CF_3 (**12b**) [19]; ^1H NMR ($CDCl_3$): δ 8.54 (d, 2H, α-H py), 7.78 (t, 1H, γ-H py), 7.35 (t, 2H, β-H py), 2.20 (s, 12H, DH–CH_3). ^{13}C NMR ($CDCl_3$): δ 151.38 (C=N), 149.82 (α-C py), 138.44 (γ-C py), 125.54 (β-C py), 12.24 (DH–CH_3). ^{19}F NMR ($CDCl_3$): δ −32.34 (s, CF_3).

2.7. X-ray crystallography

Orange octahedral prisms of compounds **8a** and **9a** were obtained by slow evaporation of saturated acetone+water solutions at 0–5 °C. Under the same conditions, compound **12a** invariably produced twinned crystals. In one crystallization attempt, a small amount of benzene was serendipitously added to an acetone+water solution of **12a**. The crystals of **12a** obtained at 0–5 °C were a benzene solvate. Subsequent X-ray crystal studies (vide infra) and elemental analyses established that approximately 1/8 (one-eighth) of a benzene molecule was present for each molecule of **12a** in the crystals. *Anal.* Calc. for $C_{34}H_{27}CoF_3N_5O_4Co\cdot 0.125C_6H_6$: C, 60.03; H, 4.02; N, 10.07. Found: C, 60.28; H, 4.21; N, 10.10%.

X-ray intensity data for **8a** and **9a** were measured at 173(2) K (Bruker KRYO–FLEX) on a Bruker SMART APEX CCD-based X-ray diffractometer system equipped with a Mo-target X-ray tube ($\lambda = 0.71073$ Å) operated at 1800 W power. The detector was placed at a distance of 6.14 cm from the crystals.

A total of 1850 frames were collected for each crystal with a scan width of 0.3° in ω and an exposure time of 20 s/frame. The frames were integrated with the Bruker SAINT software package using a narrow-frame integration algorithm. The final unit cell constants are based upon the refinement of the XYZ-centroids of 9966 and 6950 reflections above $20\sigma(I)$ for **8a** and **9a**, respectively. The unit cells of **8a** and **9a** were found to be isomorphous. Analysis of the data showed negligible decay during data collection for both compounds. Data were corrected for absorption effects using the empirical multiscan method (SADABS). The structures of **8a** and **9b** were solved by Patterson methods and refined by full matrix least-squares procedures on $|F^2|$ with SHELXTL-97, version 6.12 [26]. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located and refined. Crystal data and further data collection parameters are summarized in Table 1.

X-ray intensity data for **12a**·$0.125C_6H_6$ were measured on a Bruker R3m diffractometer in the ω–2θ mode with variable scan speed (3–20° min^{-1}) and graphite monochromated Mo Kα radiation (λ = 0.71073 Å). Data were corrected for background, attenuators, Lorentz and polarization effects in the usual fashion, but not for absorption [27]; atomic scattering factors were taken from the literature [28]. Structure solution via Patterson methods and full-matrix least-squares refinements on $|F|$ were accomplished with the SHELXTL PLUS package of programs. The space group was determined to be *C*2/*c* rather than *Cc* via successful solution in the former. The asymmetric unit for **12a**·$0.125C_6H_6$ contains two crystallographically independent molecules of py$Co(dpgh)_2CF_3$. In addition, a benzene molecule is situated at a center of

Table 1
Crystallographic data and parameters for **8a**, **9a** and **12a**·0.125C_6H_6

	8a	**9a**	**12a**·0.125C_6H_6
Formula	$C_{37}H_{38}CoN_5O_4Si$	$C_{38}H_{38}CoN_5O_4$	$C_{34}H_{27}CoF_3N_5O_4\cdot 0.125C_6H_6$
Formula weight	703.7	687.7	1390.6
Crystal color	orange	orange	orange
Habit	octahedral prism	octahedral prism	plate
Crystal dimensions (mm^3)	0.16 × 0.19 × 0.20	0.20 × 0.50 × 0.70	0.20 × 0.25 × 0.60
Temperature (K)	173(2)	173(2)	293(2)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$C2/c$ (No. 15)
Unit cell dimensions			
a (Å)	11.4436(5)	11.4843(6)	51.27(2)
b (Å)	20.2746(9)	19.9348(11)	11.246(2)
c (Å)	14.6975(6)	14.6643(8)	26.763(7)
α (°)	90	90	90
β (°)	99.1580(10)	99.0310(10)	120.54(2)
γ (°)	90	90	90
V ($Å^3$)	3366.6(3)	3315.6(3)	13290(7)
Z	4	4	16
D_{calc} (g cm^{-3})	1.388	1.378	1.390
μ (Mo Kα) (mm^{-1})	0.594	0.567	0.574
$F(000)$	1472	1440	438
θ_{max} (°)	28.28	28.28	25.0
Reflections collected	29175	28666	12891
Independent reflections	7928 (R_{int} = 2.08%)	7804 (R_{int} = 3.18%)	11205 (R_{int} = 0.96%)
Observed reflections	7059 ($I > 2.0\sigma(I)$)	6295 ($I > 2.0\sigma(I)$)	5463 ($F > 6.0\sigma(F)$)
T_{min}/T_{max}	0.891/0.911	0.915/0.967	n/a
Number of parameters	585	585	523
R_1 [a], wR_2 [b] ($I > 2.0\sigma(I)$)	0.0337, 0.0931	0.0424, 0.1029	n/a
R_1 [a], wR_2 [b] (all data)	0.0379, 0.0958	0.0565, 0.1099	n/a
R [c]	n/a	n/a	0.0756
wR [d]	n/a	n/a	0.0939
GOF	1.057 [e]	1.035 [e]	2.50 [f]

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$.
[b] $wR_2 = [\Sigma\, w(F_o^2-F_c^2)^2/\Sigma\, w(F_o^2)^2]^{1/2}$; $w = 1/[\sigma^2(F_o^2)+(aP)^2+bP]$.
[c] $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$.
[d] $wR = [\Sigma\, w(|F_o|-|F_c|)^2/\Sigma\, w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(F_o)+g(F_o)^2$.
[e] GOF = $[\Sigma\, w(F_o^2-F_c^2)^2/(N_{obs}-N_{params})]^{1/2}$, based on F^2 for all data.
[f] GOF = $[\Sigma\, w(|F_o|-|F_c|)^2/(N_{obs}-N_{params})]^{1/2}$, based on F for all data.

symmetry (the benzene ring centroid is at (1/2, 0, 0)). The three crystallographically independent carbon atoms of the benzene molecule at this site were modelled at only one half occupancy, in accord with the empirical formula derived from elemental analysis of the crystals of **12a** (vide supra). Thus, the unit cell of these crystals contains sixteen cobalt complexes of **12a** and two benzene solvates (that is, four benzene molecules at half occupancy each). Thus, we arrive at the empirical formula, py$Co(dpgh)_2CF_3\cdot 0.125C_6H_6$. All non-hydrogen atoms in the dpgh chelate rings, the pyridine ligand and the CF_3 ligand, as well as the cobalt atom, for both crystallographically independent molecules of **12a**·$0.125C_6H_6$ were refined anisotropically. Carbon atoms in the phenyl substituents of the dpgh ligands were refined as rigid groups. Hydrogen atom positions for **12a**·$0.125C_6H_6$ were calculated geometrically, fixed at a C–H distance of 0.96 Å, and not refined, except that the hydrogen atom positions for the disordered benzene solvate and for the oxime groups were neither located nor calculated. Crystal data and further data collection parameters are summarized in Table 1.

3. Results and discussion

3.1. Synthesis

We chose $Co(dpgh)(dpgh_2)Cl_2$ (**1a**) as our entry into the bis(diphenylglyoximato)cobalt(III) series by analogy to the successful application of $Co(DH)(DH_2)Cl_2$ (**1b**) as a convenient starting material for bis(dimethylglyoximato)cobalt(III) complexes [24]. We prepared **1a** by a modification of the literature method [23]. Complex **1a** was converted to py$Co(dpgh)_2Cl$ (**2a**) by a procedure that was straightforwardly derived from the correspond-

ing dimethylglyoximato chemistry [24]. We note that **2a** has previously been prepared by direct air oxidation of $CoCl_2$ in the presence of diphenylglyoxime and pyridine in *n*-butanol [23], as well as by addition of pyridine to $(H_2O)Co(dpgh)_2Cl$ [2].

The syntheses of $pyCo(dpgh)_2R$, where $R = CH_3$ (**3a**), CH_2Me (**4a**), $(CH_2)_2Me$ (**5a**), $(CH_2)_3Me$ (**6a**), $CHMe_2$ (**7a**), CH_2SiMe_3 (**8a**), CH_2CMe_3 (**9a**), $CH_2CH{=}CH_2$ (**10a**), and CH_2Ph (**11a**), involved reduction of **2a** with excess $NaBH_4$ to form the $[pyCo(dpgh)_2]^-$ anion, followed by the addition of the corresponding alkyl bromide or iodide and differed only in minor respects to the previously reported method for the preparation of $pyCo(dpgh)_2R$ ($R = CH_3$, CH_2Me) [3]. However, our isolated yields were reproducibly in the good to excellent range (70–85%), with the exception of $R = CH_2Ph$ (51%), and were significantly higher in most cases than those previously reported in preparations of $pyCo(dpgh)_2R$ ($R = CH_3$, CH_2Me, $(CH_2)_2Me$, $(CH_2)_3Me$, $CHMe_2$; range: 19–67% [3,6]; $R = CH_2Ph$: 70% [29]). We found that prolonged reaction times in the presence of the excess $NaBH_4$ led to the undesired reduction of the organometallic product to reform the $[pyCo(dpgh)_2]^-$ anion, as evinced by the reappearance of the blue color of the reduced cobalt intermediate. The desired organometallic compounds could be reobtained by the addition of more alkylating agent; however, the need for such action was avoided by judiciously quenching the reaction with acetone after shorter reaction times in order to avoid the undesired reduction.

Attempts to prepare $pyCo(dpgh)_2CF_3$ (**12a**) by methods analogous to those that worked well for $pyCo(DH)_2CF_3$ [19], viz. reduction of **2a** with less than stoichiometric amounts of $NaBH_4$ in order to prevent replacement of fluorine by hydrogen in the coordinated alkyl ligand of the organometallic product, were unsuccessful. The product so obtained under these conditions was contaminated by considerable amounts of paramagnetic impurities as judged by extremely broad ^1H NMR resonances for the product. Instead, we chose to reduce **2a** with an excess of $NaBH_4$ and quench the unreacted $NaBH_4$ with acetone after the formation of the blue, reduced cobalt intermediate. Subsequent addition of CF_3Br, followed by recrystallization of the crude product, gave pure **12a** in respectable yield (52%).

3.2. NMR spectroscopic comparisons

Full ^1H and ^{13}C NMR spectral data can be found in the Experimental Section for the diphenylglyoximato cobalt(III) complexes **2a**–**12a**, as well as for the analogous dimethylglyoximato series **2b**–**12b**. Spectra were remeasured if complete data were not available in the literature. In general, good agreement with previously reported spectral values was observed [1–3,6,11,14]. We will discuss first the trends in chemical shifts within the equatorial ligand sets, then proceed to consider chemical shifts for the axial pyridine and alkyl ligands.

3.2.1. Equatorial ligands

For the DH series of compounds, $pyCo(DH)_2R$, it has been noted previously that the ^1H NMR chemical shift of the $DH{-}CH_3$ group moves to lower field as the electron-donating ability of the axial anionic ligand decreases [11]. This trend is evident here for compounds **2b** ($R = Cl$), **10b** ($R = CH_2CH{=}CH_2$) and **12b** ($R = CF_3$). There is little change in the chemical shift of this resonance for DH complexes having axial hydrocarbyl ligands, with the exception of compound **11b**, where $R = CH_2Ph$. Here, an anomalously high field ^1H NMR resonance for the $DH{-}CH_3$ groups is observed, due to ring-current effects originating from the coordinated benzyl ligand.

The ^1H NMR spectra of the organometallic diphenylglyoximato cobalt(III) complexes **3a**–**12a**, $pyCo(dpgh)_2R$, generally have a pair of complex multiplets in the region of δ 7.05–7.25 that are assignable to the dpgh phenyl protons [2,3,6,14]. The only exception was nonorganometallic complex **2a** ($R = Cl$), for which both dpgh phenyl multiplets overlap each other at about δ 7.25. This suggests that the upfield multiplet for **2a** is shifted approximately 0.16 ppm downfield from the average value for the same resonance in the organometallic dpgh derivatives, **3a**–**12a**. Previously, the multiplet at higher field was assigned to the *ortho* protons (*o*-H) of the dpgh phenyl groups [2,3]. The observed downfield shift of this resonance for **2a** lends credence to this notion, since the displacement is in the same direction as the somewhat larger downfield change (ca. 0.27 ppm) that is observed for the ^1H NMR chemical shift for the $DH{-}CH_3$ resonance of compound **2b** versus compounds **3b**–**9b** (vida supra). Within the series of compounds **3a**–**12a**, however, there was very little variation in the chemical shifts of either dpgh multiplet as a function of the axial alkyl ligand (R), surprisingly even for $R = CH_2CH{=}CH_2$ (**10a**) or CF_3 (**12a**). Presumably, no variation was observed here for the putative dpgh *o*-H multiplet due to the relative remoteness of the dpgh *o*-H atoms from the axial alkyl ligand.

Assignments for the ^{13}C NMR resonances for the dpgh phenyl groups were based upon previous determinations for diphenylglyoximato cobalt(III) complexes [3], as well as a close examination of the ^{13}C chemical shifts for substituted benzene molecules [30]. The ^{13}C chemical shift for the dpgh *ipso*-C fell in the range δ 130.05 ± 0.12 for all the diphenylglyoximato complexes, except **2a** ($R = Cl$) and **12a** ($R = CF_3$), where this resonance appeared at higher field. In the DH series, the $DH{-}^{13}CH_3$ resonance occurs at δ 12.00 ± 0.10 for most of the organometallic complexes, with the excep-

tion of those for **10b** ($R = CH_2CH{=}CH_2$) and **11b** ($R = CH_2Ph$), probably due to ring-current and anisotropy effects. For the chloro derivative (**2b**) and other complexes with poor electron-donating alkyl groups, such as CF_3 (**12b**), the DH–$^{13}CH_3$ resonance is observed at lower fields [11]. At this time, we have no explanation for the reversal of the trends for the *cis*-influence of R on dpgh *ipso*-^{13}C versus equatorial DH–$^{13}CH_3$ chemical shifts.

We also observed rather little variation in the ^{13}C chemical shifts for the dpgh *o*-C (δ 129.59 ± 0.09), dpgh *m*-C (δ 127.82 ± 0.04), and dpgh *p*-C atoms (δ 128.90 ± 0.03) as a function of R for the majority of the $pyCo(dpgh)_2R$ complexes. Notable values outside of these ranges include: (a) **2a** (R = Cl) where the dpgh *o*-^{13}C, dpgh *m*-^{13}C, and dpgh *p*-^{13}C resonances were approximately 0.20, 0.10 and 0.75 ppm downfield from the above ranges, respectively, (b) **11a** ($R = CH_2Ph$) where the dpgh *m*-^{13}C resonance is approximately 1.0 ppm downfield and the dpgh *p*-^{13}C resonance is at slightly lower field, and (c) **12a** ($R = CF_3$) where the dpgh *m*-^{13}C and dpgh *p*-^{13}C chemical shifts are approximately 0.14 and 0.60 ppm downfield. It appears that both electronic and through-space ring current effects are responsible for these results.

Within both series of cobalt complexes, the ^{13}C chemical shift for the oxime (C=N) carbon of the equatorial ligand set appears to be affected by both electronic and steric effects [11]. For all axial anionic ligands except R = Cl and CF_3, the ^{13}C resonance for the C=N moiety in the dpgh ligand set occurs 1.74 ± 0.06 ppm downfield from the position observed in the corresponding DH series. The reasons for the anomalous chemical shifts for R = Cl and CF_3 are not known, but the behavior is not surprising in view of the behavior of other ^{13}C NMR resonances in the equatorial ligand set for these two axial anionic ligands (vide supra).

3.2.2. Axial ligands

We now consider NMR chemical shifts for the axial pyridine ligand. In both the dpgh and DH series of complexes, little variation in chemical shift is observed within each series for the ^{1}H NMR resonances of the α-H(py), β-H(py) and γ-H(py) of the coordinated pyridine ligand. For the diphenylglyoximato complexes **3a**–**11a**, the shifts for these protons occur at δ 8.89 ± 0.03, 7.42 ± 0.02 and 7.81 ± 0.03, respectively, while for the DH series, compounds **3b**–**11b**, they occur at δ 8.58 ± 0.04, 7.30 ± 0.03 and 7.71 ± 0.02, respectively. The only compounds that do not conform to these chemical shift ranges are once again the chloro derivatives (**2a** and **2b**) and the CF_3 derivatives (**12a** and **12b**). In the chloro complexes, the chemical shifts for the α-H(py) and the β-H(py) are approximately 0.30 and 0.06 ppm upfield, respectively, from the ranges for the other compounds in the two series. The CF_3 complexes have ^{1}H NMR shifts that are slightly different than the other organometallic complexes with the β-H(py) and γ-H(py) shifts approximately 0.06 and 0.10 ppm to lower field from the typical ranges, respectively.

Interestingly, however, the changes in ^{1}H chemical shift for the α-H(py), β-H(py) and γ-H(py) of the pyridine ligand for each pair of corresponding complexes in the dpgh and DH series are virtually constant as a function of R. More specifically, the replacement of the DH equatorial ligand set with the dpgh ligand set produces downfield shifts for the α-H(py), β-H(py) and γ-H(py) resonances of 0.32 ± 0.01, 0.12 ± 0.02 and 0.11 ± 0.02 ppm, respectively, no matter the identity of R. The downfield shifts, particularly those for the remote γ-H atom of the pyridine ligand where ring-current effects from the phenyl substituents of the dpgh ligands should be minimal, can be taken as tentative evidence for less electron donation by the dpgh ligand set versus the DH ligand set.

The ^{13}C chemical shift for the α-C(py) was virtually unchanged upon substitution of dpgh for DH. However, the ^{13}C resonances for the β-C(py) and particularly the γ-C(py), which has been employed as an indicator for electron-donating ability of the *trans* ligand [10], appeared respectively at 0.35 ± 0.03 and 0.52 ± 0.06 ppm to lower field for the dpgh derivatives (with the exception of R = Cl in the case of the γ-C(py)). These observations are similar to those involving the ^{1}H chemical shifts for the pyridine ligand in these two series and again suggest poorer electron donation by the dpgh ligand set. Further, we can likely exclude ring current effects, at the very least for the γ-^{13}C resonance of the pyridine ligand, since we would expect these carbon atoms to be well-distanced from the dpgh phenyl substituents.

Finally, we consider NMR chemical shifts for the axial alkyl ligand in the organometallic complexes. It has previously been observed for a smaller number of complexes that a substitution of dpgh for DH caused 0.59 ± 0.05 and 0.46 ± 0.02 ppm downfield shifts for the ^{1}H resonances of hydrogen atoms attached to the α-C and β-C atoms of the alkyl chain, respectively [3]. We have found that these ranges generally hold true for alkyl ligands having vastly different substituents, with some small exceptions. We also observe that the shift to lower field for the dpgh derivatives decreases as the hydrogen atom in question is more remotely located along the alkyl chain; for the hydrogen atoms on the γ-C atoms of the chain, the dpgh derivatives resonate only approximately 0.26 ± 0.06 ppm further downfield than their DH analogs, excluding $CH_2CH{=}CH_2$ which is slightly out of this range. In the one case where there are protons on a δ-C ($R = (CH_2)_3Me$), the methyl resonance for the dpgh compound is 0.13 ppm to lower field than that for the corresponding resonance in the DH complex. Curiously, the difference in ^{19}F chemical shifts for

the complexes with R = CF_3 in the two series also nearly conforms to the range found for hydrogen atoms.

Unfortunately, the ^{13}C NMR resonance for the α-C of the axial alkyl ligand could not be observed accurately due to broadening by the ^{59}Co quadrupole. In general, the β-^{13}C, γ-^{13}C and δ-^{13}C resonances of the alkyl ligands were at lower field in the dpgh compounds as compared to the DH complexes. One notable exception was the allyl complexes (**11a** and **11b**), where the β-C resonance was 0.82 ppm to higher field for the dpgh complex, while the γ-C resonance was 1.54 ppm to lower field. The *ipso*-^{13}C resonance for the benzyl ligand in the dpgh series was also slightly upfield to that of the corresponding DH complex. Presumably, we are again observing the effect of π-electron anisotropies on the chemical shifts. Further excellent discussion and insights on variations in the chemical shifts for alkyl ligands in the dpgh series have been reported [6,14].

3.3. Structural studies

The solid-state structures of compounds **8a**, **9a**, and **12a** were studied via single crystal X-ray diffraction methods. These compounds were chosen because either the alkyl ligands have significant steric bulk (**8a** and **9a**) or because a very short Co–C bond was expected (**12a**). In either case, we hoped to maximize potential steric interactions between the equatorial dpgh ligand set and the axial alkyl ligand. Previous structural determinations on bis(diphenylglyoximato) cobalt(III) complexes have involved relatively small, anionic ligands, such as Cl, CH_3, CH_2Me and CH_2Cl [2–4,7,10].

The asymmetric units of **8a** and **9a**, which are isomorphous, contain one discrete molecule of the respective cobalt complex (Figs. 1 and 2). As such, bond lengths and angles within the coordination spheres of **8a** and **9a** correspond quite closely (Table 2). Bond lengths and angles within the equatorial dpgh ligand sets are unexceptional and within expected ranges [2–4,7,10]. As expected, the axial Co–C bonds in **8a** and **9a** are significantly longer than the Co–CH_3 bond lengths found for py$Co(dpgh)_2CH_3$ (1.997(4) Å; [3]) and 4-Mepy$Co(dpgh)_2CH_2Cl$ (2.011(6) Å; [4]). The axial Co–N(py) bond lengths for **8a** and **9a** are comparable to those observed for these same two previously studied compounds [3,4].

We now turn to structural comparisons of the diphenylglyoximato cobalt(III) complexes **8a** and **9a** to the corresponding dimethylglyoximato cobalt(III) complexes **8b** and **9b** [31]. Along the axial direction, there is relatively little difference in bond lengths or angles involving the Co atom and the axial py and alkyl ligands, with the exception of the Co–N(py) axial bond length being somewhat shorter for **8a** versus **8b** (Table 3).

However, the maintenance of these structural parameters involving the axial ligands apparently comes at a slight cost. For the dimethylglyoximato complexes **8b** and **9b**, the Co atom is essentially situated in the plane defined by the four nitrogen donor atoms of the oxime ligands, while there is a slight bending of the dimethylglyoximato chelate planes away from the bulky alkyl ligands (Table 3). The projection of the Co–C bond of the alkyl ligand for **8b** and **9b** on the equatorial ligand plane is coincident with a Co–N(oxime) bond, while the plane defined by the py ligand nearly bisects the O···O vectors of the dioximato ligands [31]. These latter observations are quite usual for py$Co(DH)_2R$ com-

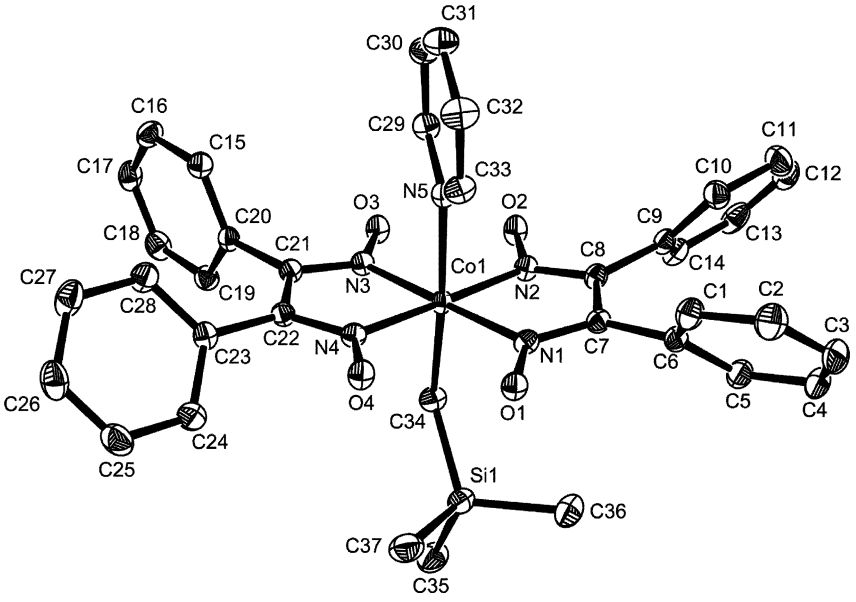

Fig. 1. Molecular structure and atom numbering scheme for **8a**. Hydrogen atoms have been omitted for clarity.

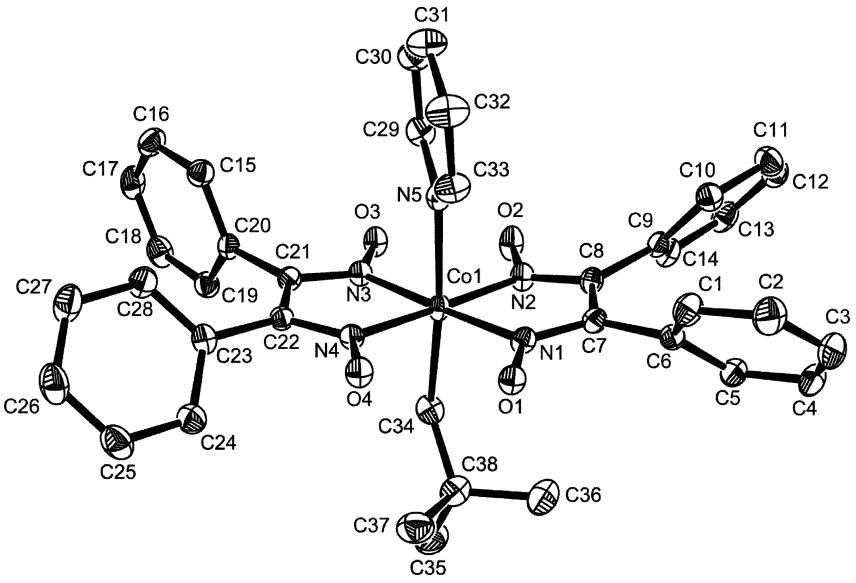

Fig. 2. Molecular structure and atom numbering scheme for **9a**. Hydrogen atoms have been omitted for clarity.

plexes containing the Co–CH_2X moiety, where X is an alkyl substituent [11,12]. Indeed, the plane of the pyridine ligand bisects the O···O vectors of the diphenylglyoximato ligands for $pyCo(dpgh)_2CH_3$ [3] and 4-$MepyCo(dpgh)_2CH_2Cl$ [4] also.

On the other hand, for the diphenylglyoximato complexes **8a** and **9a**, the py ligand is rotated approximately 17–18(1)° from the plane that bisects the O···O vectors of the dioximato ligands; further, the alkyl ligand is rotated away from the Co–N(oxime) bonds so that the projection of the Co–C bond is now coincident with the plane of the axial py ligand. The chelate ring on the side of the diphenylglyoximato complexes, under which the substituent of the alkyl ligand resides (defined by N(1), C(7), C(8), and N(2)), is bent somewhat more towards the py ligand (−4.5(1) and –4.1(1)° for **8a** and **9a**, respectively) than the other chelate ring (defined by N(3), C(21), C(22) and N(4); −2.8(1) and −2.1(1)° for **8a** and **9a**, respectively) as judged by the dihedral angles made by these planes to the equatorial plane. The cobalt atom moves slightly out of the equatorial plane towards the alkyl group and the overall bending of the dpgh chelate rings away from the alkyl ligand increases slightly (Table 3). The implication is that the large alkyl ligands sterically interact with the equatorial ligand set in the diphenylglyoximato series

Table 2
Selected bond lengths (Å) and bond angles (°) for **8a** and **9a**

	8a	**9a**
Bond lengths		
Co(1)–N(1)	1.896(1)	1.892(2)
Co(1)–N(2)	1.887(1)	1.885(2)
Co(1)–N(3)	1.877(1)	1.882(1)
Co(1)–N(4)	1.874(1)	1.871(1)
Co(1)–N(5)	2.059(1)	2.079(2)
Co(1)–C(34)	2.037(1)	2.078(2)
Bond angles		
N(1)–Co(1)–N(2)	81.40(5)	81.38(6)
N(1)–Co(1)–N(3)	179.31(5)	178.03(7)
N(1)–Co(1)–N(4)	98.76(5)	99.11(6)
N(1)–Co(1)–N(5)	89.86(5)	89.14(5)
N(1)–Co(1)–C(34)	95.17(5)	96.83(5)
N(2)–Co(1)–N(3)	98.31(5)	98.07(5)
N(2)–Co(1)–N(4)	178.78(5)	178.43(5)
N(2)–Co(1)–N(5)	89.83(5)	90.21(5)
N(2)–Co(1)–C(34)	90.65(6)	91.04(6)
N(3)–Co(1)–N(4)	81.51(5)	81.40(5)
N(3)–Co(1)–N(5)	89.51(5)	88.98(5)
N(3)–Co(1)–C(34)	85.46(5)	85.06(5)
N(4)–Co(1)–N(5)	88.96(5)	88.30(5)
N(4)–Co(1)–C(34)	90.53(6)	90.38(6)
N(5)–Co(1)–C(34)	174.96(5)	174.02(5)

Table 3
Structural comparisons between $pyCo(dpgh)_2CH_2SiMe_3$ (**8a**)/$pyCo(DH)_2CH_2SiMe_3$ (**8b**) and $pyCo(dpgh)_2CH_2CMe_3$ (**9a**)/$pyCo(DH)_2CH_2CMe_3$ (**9b**)

Parameter	**8a**	**8b** [a]	**9a**	**9b** [a]
Co–N(py), (Å)	2.059(1)	2.091(5)	2.079(2)	2.081(4)
Co–C (Å)	2.037(1)	2.031(6)	2.078(2)	2.060(6)
N(py)–Co–C (°)	174.96(5)	174.1(2)	174.02(5)	174.7(2)
Co–C–X (°)	127.38(8) [b]	127.7(7) [b]	129.8(1) [c]	130.3(4) [c]
d [d] (Å)	−0.028	0.00	−0.015	0.00
α [e] (°)	−7.3	−1.2	−6.2	−5.2

[a] Ref. [31].
[b] X = Si.
[c] X = C.
[d] Displacement of the Co atom out of the plane defined by the four equatorial oxime nitrogen atoms; positive values indicate displacement towards the py ligand.
[e] Interplanar angle between the planes defined by the dioximato chelate rings; positive values indicate bending away from the py ligand.

Table 4
Selected bond lengths (Å) and bond angles (°) for **12a**·0.125C_6H_6

	Molecule 1	Molecule 2
Bond lengths		
Co(1)–N(1)	1.867(7)	1.883(8)
Co(1)–N(2)	1.882(7)	1.894(8)
Co(1)–N(3)	1.891(6)	1.886(8)
Co(1)–N(4)	1.870(7)	1.904(8)
Co(1)–N(5)	2.040(9)	2.049(8)
Co(1)–C(34)	1.926(14)	1.948(13)
Bond angles		
N(1)–Co(1)–N(2)	82.3(3)	81.4(4)
N(1)–Co(1)–N(3)	179.5(4)	178.7(5)
N(1)–Co(1)–N(4)	98.6(3)	99.2(4)
N(1)–Co(1)–N(5)	87.0(3)	88.9(3)
N(1)–Co(1)–C(34)	90.5(4)	88.8(4)
N(2)–Co(1)–N(3)	97.6(3)	97.8(4)
N(2)–Co(1)–N(4)	179.1(3)	179.2(3)
N(2)–Co(1)–N(5)	90.1(4)	90.4(3)
N(2)–Co(1)–C(34)	89.6(4)	90.5(5)
N(3)–Co(1)–N(4)	81.5(3)	81.5(3)
N(3)–Co(1)–N(5)	92.5(3)	90.1(3)
N(3)–Co(1)–C(34)	90.0(4)	92.3(4)
N(4)–Co(1)–N(5)	90.1(4)	89.3(3)
N(4)–Co(1)–C(34)	90.3(4)	89.8(5)
N(5)–Co(1)–C(34)	177.5(4)	177.3(4)

somewhat more than in the dimethylglyoximato series, leading to these subtle, but detectable structural differences. While crystal packing effects on these structural parameters can not be entirely excluded [11,12], we note that the molecules appear to be well separated; for instance, there are no long range intermolecular interactions between phenyl substituents in **8a** and **9a**.

The asymmetric unit of **12a**·0.125C_6H_6 contains two crystallographically independent molecules of **12a**, that differ only slightly in the rotational configurations of the peripheral phenyl substituents (Fig. 3 depicts molecule 1 of the asymmetric unit). In addition, the asymmetric unit contains half of a benzene molecule, which was modelled at half site occupancy (see Section 2). Because of the fair quality of the crystallographic data, due in part to the presence of the benzene solvate, discussion on the **12a** molecules will be limited. Bond lengths and angles within the coordination spheres (Table 4) and within the dpgh ligand sets of both molecules are comparable and are as expected [2–4,7,10,19]. The short Co–C bond lengths are accompanied by an elongation of the tetrahedra around C(34) (independent molecule 1) and C(34′) (independent molecule 2) as evinced by the summation of the F–C–F and the summation of the Co–C–F bond angles, respectively (Table 5). These observations have been interpreted as arising from a combination of electrostatic and hybridization alterations due to the electronegative fluorine substituents [32,33]. The situation is entirely analogous to that found for **12a** [19].

Comparisons of relevant bonding parameters (Table 5) for the two independent molecules of **12a** versus **12b** [19] reveal that there are some small differences between the diphenylglyoximato and dimethylglyoximato complexes. The cobalt atom has moved from slightly towards the py ligand out of the equatorial ligand plane for **12b** to slightly on the alkyl side of this plane for the **12a** molecules; concurrently, the equatorial ligand set bends away from the alkyl ligands for both **12a** molecules, rather than away from the py ligand as for **12b**. The py ligands for both molecules of **12a** are rotated slightly (ca. 5(1)°) from the plane that bisects the O···O vectors of the dioximato ligands. Otherwise, there are no major differences and the remainder of the important bonding parameters are comparable for both **12a** and **12b**.

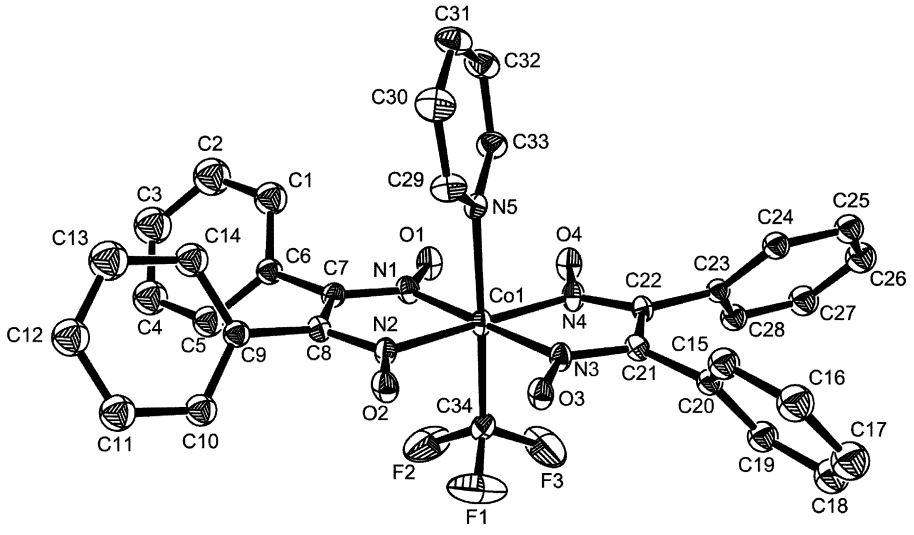

Fig. 3. Molecular structure and atom numbering scheme for crystallographically independent molecule 1 for **12a**. The numbering scheme for independent molecule 2 of **12a** is identical, except that a 'prime' is attached to the atom labels. Hydrogen atoms have been omitted for clarity.

Table 5
Structural comparisons between $pyCo(dpgh)_2CF_3$ (**12a**)/$pyCo(DH)_2CF_3$ (**12b**)

Parameter	**12a** (molecule 1)	**12a** (molecule 2)	**12b** [a]
Co–N(py) (Å)	2.040(9)	2.049(8)	2.043(3)
Co–C (Å)	1.926(14)	1.948(13)	1.949(4)
N(py)–Co–C (°)	177.5(4)	177.3(4)	177.4(2)
Σ Co–C–F (°)	350.8	344.1	346.0
Σ F–C–F (°)	302.9	311.1	308.9
d [b] (Å)	−0.004	−0.010	+0.002
α [c] (°)	−2.9	−3.6	+3.0

[a] Ref. [19].
[b] Displacement of the Co atom out of the plane defined by the four equatorial oxime nitrogen atoms; positive values indicate displacement towards the py ligand.
[c] Interplanar angle between the planes defined by the dioximato chelate rings; positive values indicate bending away from the py ligand.

4. Conclusions

In summary, we can conclude that the diphenylglyoximato cobalt(III) complexes are not optimal for the elucidation of *cis* and *trans* influences in this class of cobalt complex by NMR techniques, since there are a number of mitigating factors, such as ring current and electronic effects, that can contribute to the observed chemical shifts as discussed by Gupta and coworkers [6]. However, the NMR data suggest that no unusually large steric interactions occur between the dpgh phenyl substitutents and the axial ligands. For example, many NMR resonances for the pyridine ligand shift downfield in the dpgh series *vs*. the DH series by exactly the same amount, regardless of the steric or electronic nature of the *trans* anionic ligand. The same is true in a general sense for the chemical shift trends for the axial alkyl ligands. While ring current contributions to the chemical shifts can not be ignored, it appears overall that the dpgh ligand is not as good an electron-donating ligand as DH, as judged by the shift to lower fields for many comparable resonances in the axial and equatorial ligands in the dpgh series as compared to the DH analogs that should not be affected appreciably by ring currents.

However, even though there may not be unusually large steric interactions between the axial ligands and the dpgh ligands in $pyCo(dpgh)_2R$ complexes, the X-ray structural results suggest that there can be subtle, if not significant structural perturbations if R is large enough, such as for **8a** ($R = CH_2SiMe_3$) and **9a** ($R = CH_2CMe_3$). While bond lengths and angles of the axial ligands remain fairly constant for both the diphenylglyoximato and dimethylglyoximato cobalt(III) complexes, the former show clear indications of an interaction of the axial alkyl ligand with the equatorial dpgh ligand set as demonstrated by changes in the rotational conformation of the axial py ligands and increases in the bending of the equatorial chelate rings. Much less dramatic, but still similarly detectable structural alterations occur for **12a** ($R = CF_3$). Such steric effects involving diphenylglyoximato vis-à-vis dimethylglyoximato cobalt(III) complexes likely have some impact on the more favorable *exo*/*endo* selectivity observed in Diels–Alder reactions of bis(diphenylglyoximato)cobalt-substituted diene complexes [34], as well as on increased rates of oxygen insertion [29] and increased rates of ligand substitution for complexes of dpgh [35–37].

5. Supplementary material

Crystallographic data for the structural analysis, including atomic coordinates, bond lengths and angles and anisotropic thermal parameters have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 199118, 199119 and 199120 for compounds **8a**, **9a** and **12a**·$0.125C_6H_6$, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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