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trans-(4-Amino-2,2,6,6-tetramethylpiperidine-N^4)bis(pentane-2,4-dionato-*O*,*O*′)(triphenylphosphine-*P*)cobalt(III) hexafluorophosphate dichloromethane solvate

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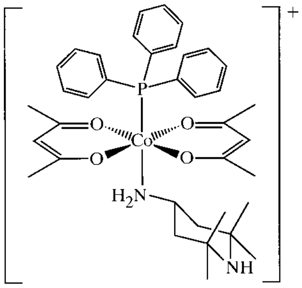
The complex cation in the title compound, $[Co(C_5H_7O_2)_2(C_9H_{20}N_2)(C_{18}H_{15}P)]PF_6\cdot CH_2Cl_2$, is the first example of a Co^{III} complex in which a *trans* configuration for the coordinated monodentate phosphine and amine ligands has been confirmed by X-ray analysis. Owing to the large steric bulkiness of the axial PPh_3 ligands influencing the interaction with the equatorial acetylacetonate ligands, the acetylacetonate planes bend away considerably from the PPh_3 ligands.

Comment

In previous studies, we have reported that *trans*-$[Co(acac)_2(PPh_3)_2]^+$ (Hacac is acetylacetone) is highly reactive toward substitution of the coordinated PPh_3. For example, the reactions with strong Lewis bases such as PMe_3 and CN^- stereoselectively gave *trans*-$[Co(acac)_2(PMe_3)_2]^+$ and *trans*-$[Co(acac)_2(CN)_2]^-$, respectively (Suzuki *et al.*, 1998). Furthermore, the reaction with an equimolar amount of substituted pyridine or amine derivatives (N-ligands) in CH_2Cl_2 afforded *trans*-$[Co(acac)_2(PPh_3)(N\text{-ligand})]^+$ in an almost quantitative yield (Suzuki *et al.*, 1996; Ogita *et al.*, 2000). These complexes are novel examples of Co^{III} complexes in which monodentate phosphine and amine ligands are located in *trans* positions (Katoh *et al.*, 1984), and there has been no reported X-ray analysis of such complexes. We report here the single-crystal structure determination of the title complex, (I), which is the product of the reaction of *trans*-$[Co(acac)_2(PPh_3)_2]PF_6$ with 4-amino-2,2,6,6-tetramethylpiperidine (atmp).

The X-ray analysis confirmed the *trans* configuration for the phosphine and amine ligands in the cation of (I) (Fig. 1), as suggested by NMR spectroscopy in a $CDCl_3$ solution. The most remarkable structural feature of the cation in (I) is the bending of the equatorial acac ligand planes away from the axial PPh_3 ligand. The bending angles of the acac plane 1 (defined by O1, O2, C2, C3 and C4) and acac plane 2 (defined by O3, O4, C7, C8 and C9) from the equatorial four-oxygen coordination plane (defined by O1, O2, O3 and O4) are 9.8 (3) and 11.5 (3)°, respectively. The dihedral angle between the two acac planes is 21.2 (3)°. Such a bending structure was also found in *trans*-$[Co(acac)_2(PPh_3)(H_2O)]PF_6$ (Suzuki *et al.*, 2000) and *trans*-$[Co(acac)_2(PPh_3)(NIT4py\ \text{or}\ IM4py)]PF_6$ [Ogita *et al.*, 2000; NIT4py is 2-(4-pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxy 3-oxide and IM4py is 2-(4-pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxy], and resulted from the large steric bulkiness of the axial PPh_3 ligand influencing the interaction with the equatorial acac ligands. The three phenyl rings [phenyl(1) C11–C16, phenyl(2) C17–C22 and phenyl(3) C23–C28] of PPh_3 have dihedral angles of 17.1 (3), 44.3 (2) and 75.6 (3)°, respectively, with the equatorial four-oxygen coordination plane. The other structural parameters concerning the Co^{III}–acac moiety are normal; the Co—O bond lengths are in the range 1.872 (4)–1.897 (4) Å and the acac bite angles (O—Co—O) are 95.0 (2) and 94.6 (2)°. These lengths and angles are similar to those in *trans*-$[Co(acac)_2(CN)_2]^-$, *trans*-$[Co(acac)_2(PPh_3)_2]^+$ (Suzuki *et al.*, 2000) and $[Co(acac)_3]$ (Kruger & Reynhardt, 1974).



(I)

In the cation of (I), the atmp ligand is coordinated to Co^{III} through the primary amine (N1) and the Co—N1 bond length is 2.014 (5) Å. This is, to our best knowledge, the first X-ray structural analysis of a metal complex containing atmp, while for its oxidized nitroxide radical, 4-amino-2,2,6,6-tetramethylpiperidinyl-1-oxide (amino-TEMPO), the crystal structure of the Ni^{II} complex, *trans*-$[Ni(hfac)_2(amino\text{-}TEMPO)(CH_3OH)]$ (hfac is 1,1,1,5,5,5-hexafluoropentane-2,4-dionate), has already been reported (Cervantes-Lee & Porter, 1991). In (I), the six-membered piperidine ring of atmp adopts an ideal chair conformation and the coordinated amino group is in an equatorial position. The piperidyl group is oriented toward the void between two acac ligands, the torsion angle of the bisector of O1—Co—O4 and the N1—C29 with respect to the Co—N1 bond, *i.e.* *X*—Co—N1—C29, where *X* is the midpoint of O1···O4, being only 4.7°. This orientation would effectively minimize the steric interaction between the piperidyl group and the bent acac planes.

The Co—P bond length in (I) is 2.292 (2) Å, which is shorter by *ca* 0.1 Å than that (2.3887 Å) in *trans*-$[Co(acac)_2(PPh_3)_2]PF_6$ (Suzuki *et al.*, 2000). Since in *trans*-$[Co(acac)_2(PPh_3)_2]PF_6$ the steric interaction between two PPh_3 and acac ligands occurs at both sides of the equatorial four-oxygen coordination plane, the substitution of one of the PPh_3 ligands by atmp may give rise to a reduction in this steric interaction on one side. As a result, shortening of the remaining Co—PPh_3 bond is induced, which causes the bending of the acac planes. Although many cobaloxime derivatives containing a tertiary phosphine have been analyzed (Bresciani-Pahor *et al.*, 1985), most of them have an anionic ligand or an organic group at the *trans* position to the phosphine, and no complexes with neutral N-ligands such as pyridines or amines have been reported so far. The Co—P bond lengths in the cobaloxime derivatives vary from 2.286 to 2.460 Å, depending on the type of *trans*-positioned ligand. As an example, the Co—P bond length in the structurally related 3,5-di-*tert*-butylcatecholate monoanion (3,5-DBcatH) complex, *trans*-[Co(Hdmg)$_2$-(PPh$_3$)(3,5-DBcatH)] (Hdmg is the dimethylglyoximate monoanion), is 2.316 (1) Å (Simándi *et al.*, 1995).

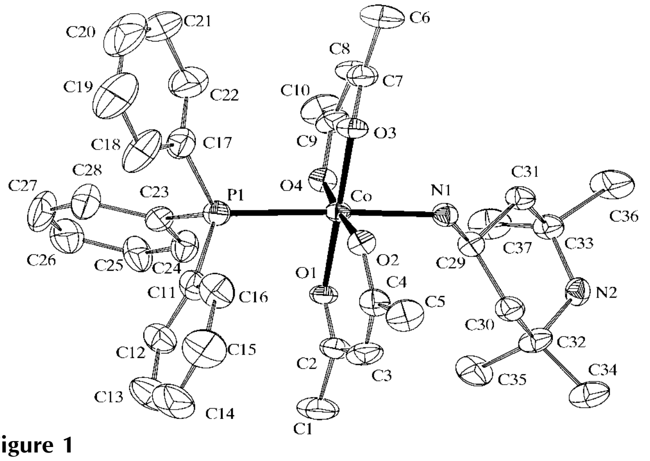


Figure 1
A perspective view of the complex cation in (I). H atoms have been omitted for clarity and displacement ellipsoids are drawn at the 40% probability level.

Experimental

Compound (I) was prepared by a reaction of *trans*-[Co(acac)$_2$-(PPh$_3$)$_2$]PF$_6$ and atmp (molar ratio 1:1) in CH_2Cl_2 at room temperature, precipitated by adding Et_2O and recrystallized from CH_2Cl_2/Et_2O (yield 77%).

Crystal data

[Co($C_5H_7O_2$)$_2$($C_9H_{20}N_2$)-($C_{18}H_{15}P$)]$PF_6\cdot CH_2Cl_2$
$M_r = 905.61$
Orthorhombic, $P2_12_12_1$
$a = 15.169$ (10) Å
$b = 25.197$ (8) Å
$c = 11.638$ (6) Å
$V = 4448$ (3) Å^3
$Z = 4$
$D_x = 1.352$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 11.1$–12.4°
$\mu = 0.641$ mm^{-1}
$T = 296.2$ K
Plate, dark red
0.32 × 0.28 × 0.13 mm

Data collection

Rigaku AFC-5*R* diffractometer
$\omega/2\theta$ scans
Absorption correction: by integration (Coppens *et al.*, 1965)
$T_{\min} = 0.843$, $T_{\max} = 0.922$
9217 measured reflections
7133 independent reflections (plus 389 Friedel-related reflections)
3148 reflections with $F > 4\sigma(F)$
$R_{\rm int} = 0.022$
$\theta_{\max} = 30°$
$h = -9 \rightarrow 21$
$k = 0 \rightarrow 35$
$l = -7 \rightarrow 16$
3 standard reflections every 150 reflections
intensity decay: 1.97%

Refinement

Refinement on F^2
$R(F) = 0.051$
$wR(F^2) = 0.193$
$S = 0.969$
7522 reflections
518 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.031$
$\Delta\rho_{\max} = 0.45$ e Å^{-3}
$\Delta\rho_{\min} = -0.52$ e Å^{-3}
Absolute structure: Flack (1983)
Flack parameter = −0.01 (3)

Table 1
Selected geometric parameters (Å, °).

Co—P1	2.292 (2)	Co—O3	1.897 (4)
Co—O1	1.872 (4)	Co—O4	1.880 (4)
Co—O2	1.875 (5)	Co—N1	2.014 (5)
P1—Co—N1	177.2 (2)	O3—Co—O4	94.6 (2)
O1—Co—O2	95.0 (2)		

The F atoms were positionally disordered and were assumed to be three sets of arrangements with occupancies of 0.5, 0.25 and 0.25, and were refined isotropically. H-atom coordinates were refined with a fixed bond length, except for methyl H atoms which were assumed as idealized tetrahedral arrangements.

Data collection and cell refinement: *Rigaku/AFC Diffractometer Control Software* (Rigaku Corporation, 1985); data reduction: *TEXSAN* (Molecular Structure Corporation and Rigaku Corporation, 1999); program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *ORTEP* (Johnson, 1970); software used to prepare material for publication: *TEXSAN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1277). Services for accessing these data are described at the back of the journal.

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