Electronic Supplementary Material (ESI) for Dalton Transactions

Supporting Information

A Synthetic Strategy for a New Series of Oxo-centered Tricobalt Complexes with Mixed Bridging Ligands of Acetate and Pyrazolate Ions

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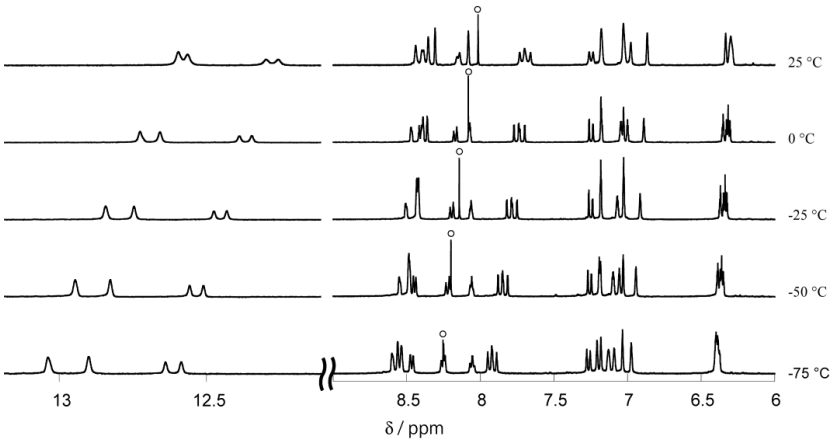

Fig. S1 ^{1}H VT-NMR spectra of **tris-1** measured in acetone-d_6. The peak marked with circle correspond the chloroform included in the recrystallized sample.

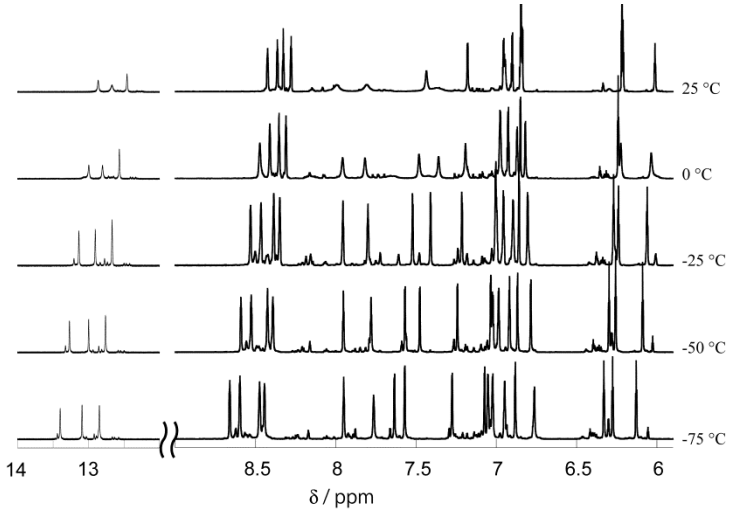

Fig. S2 ^{1}H VT-NMR spectra of **tris-3** measured in acetone-d_6.

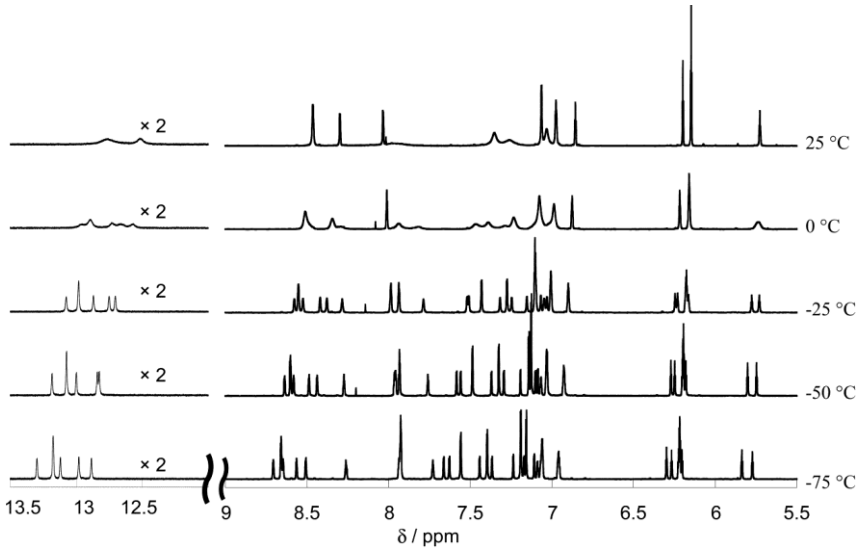

Fig. S3 ^{1}H VT-NMR spectra of **tetra-1** measured in acetone-d_6.

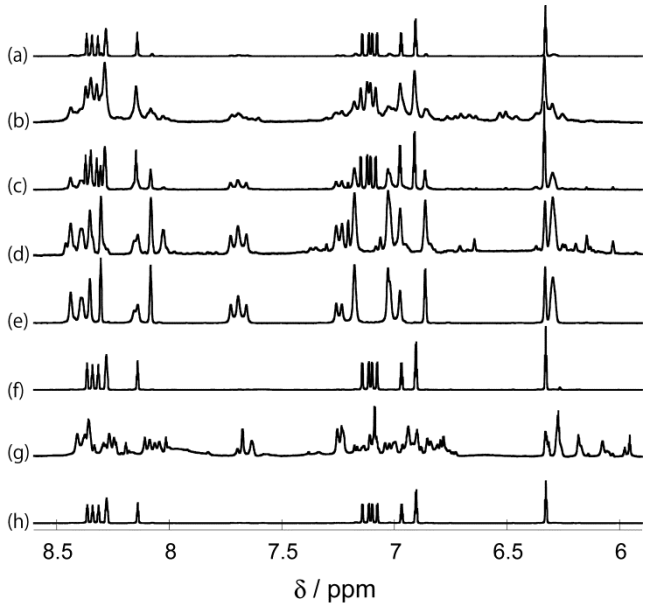

Fig. S4 ^{1}H NMR spectra of (a) **bis-1**, (b) **bis-1** after reflux in ethanol, (c) **bis-1** after reflux with Hpz (1 equiv.) in ethanol, (d) **bis-1** after reflux with Hpz (9 equiv.) in ethanol, (e) **tris-1**, (f) **bis-1** after stirring with Hpz (9 equiv.) in ethanol for 24 h at ambient temperature, (g) **bis-1** after reflux with Hpz (9 equiv.) in acetic acid, and (h) **bis-1** after reflux with Hpz (9 equiv.) in butanone. Reflux was done for 30 min unless otherwise noted. All ^{1}H NMR spectra were recorded in acetone-d_6.

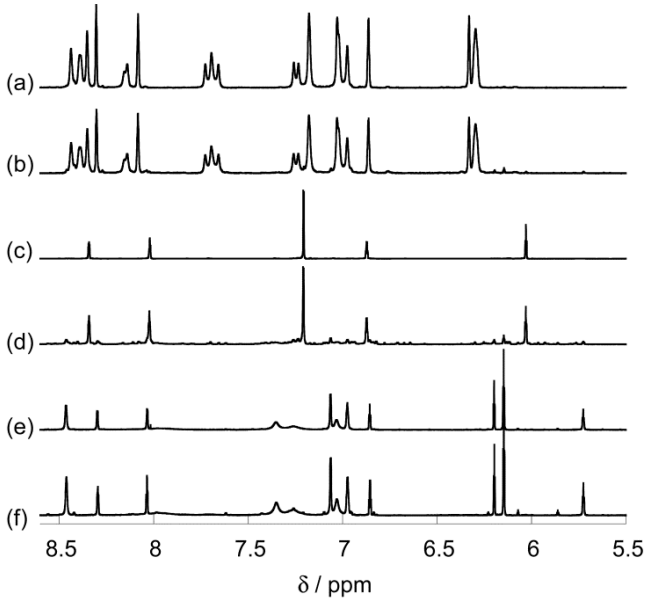

Fig. S5 ^{1}H NMR spectra of (a) **tris-1**, (b) **tris-1** after reflux with Hpz (9 equiv.) in ethanol for 30 min, (c) **tris-2**, (d) **tris-2** after reflux with Hpz (9 equiv.) in ethanol for 30 min, (e) **tetra-1**, (f) **tetra-1** after reflux with Hpz (9 equiv.) in ethanol for 30 min. All ^{1}H NMR spectra were recorded in acetone-d_6.

Table S1. Crystallographic and experimental data for **mono**, **bis-1**, **bis-2** and **tris-1**.

Compound	**mono**	**bis-1**	**bis-2**	**tris-1**
Formula	$C_{24}H_{33}Co_3F_6N_9O_{11}P$	$C_{27}H_{38}Co_3F_6N_{10}O_{11}P$	$C_{25}H_{32}Cl_6Co_3F_6N_{10}O_9P$	$C_{26}H_{38}Co_3F_6N_{12}O_9P$
Formula weight	945.35	1000.43	1151.07	984.44
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\ 2_1/c$	$P\ 2_1/n$	$P\ 2_1/c$	$C\ 2/c$
a / Å	16.8429(9)	8.7406(3)	9.9668(4)	21.584(3)
b / Å	7.9148(4)	28.1478(10)	35.7616(14)	11.7176(14)
c / Å	26.7022(14)	16.0824(6)	12.1666(5)	15.8966(19)
β°	97.033(1)	92.7707(4)	102.6166(4)	112.4080(10)
V / Å^3	3532.8(3)	3952.1(2)	4231.8(3)	3716.8(8)
Z	4	4	4	4
Dc/ Mg m^{-3}	1.777	1.681	1.807	1.759
T	120(2)	100(2)	100(2)	120(2)
Dimensions / mm	0.33×0.26×0.08	0.37×0.21×0.14	0.40×0.22×0.13	0.36×0.16×0.07
μ(Mo-Kα) / mm^{-1}	1.538	1.38	1.665	1.464
F(000)	1912	2032	2304	2000
Reflections collected / unique	38610/8089	44429/9058	47616/9627	20138/4225
Used reflections with$I > 2\sigma(I)$	6052	7526	8250	2881
Parameters	541	529	545	325
[a]GOF on F^2	1.046	1.072	1.137	1.033
[b]R [$I > 2\sigma(I)$]	0.0489	0.0325	0.0542	0.0525
[c]$wR(F^2)$ [all data]	0.1248	0.1015	0.1452	0.1145

[a] $\mathrm{GOF} = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$ (n; number of reflections, p; total number of parameters refined), [b] $R1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$, [c] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Table S2. Crystallographic and experimental data for **tris-2**, **tris-3**, and **tetra-1**.

Compound	**tris-2**	**tris-3**	**tetra-1**
Formula	$C_{32}H_{39}Co_3F_6N_{13}O_7P$	$C_{49}H_{61}Cl_3Co_6F_{12}N_{24}O_{14}P_2$	$C_{52}H_{63}Co_6F_{12}N_{29}O_{10}P_2$
Formula weight	1039.52	1960.09	1897.83
Crystal system	Orthorhombic	Tetragonal	Tetragonal
Space group	P *bca*	$P\text{-}42_1c$	$P\text{-}42_1c$
a / Å	14.5714(10)	22.2776(10)	22.0251(11)
b / Å	19.7339(13)	-	-
c / Å	33.610(2)	14.7609(6)	14.7509(7)
β °	-	-	-
V / Å^3	9664.5(11)	7325.7(6)	7155.7(6)
Z	8	4	4
Dc / Mg m^{-3}	1.429	1.777	1.762
T	100(2)	100(2)	100(2)
Dimensions / mm	0.33×0.13×0.08	0.37×0.16×0.12	0.34×0.18×0.14
μ(Mo-Kα) / mm^{-1}	1.128	1.587	1.511
F(000)	4224	3944	3832
Reflections collected / unique	104791/11122	81831/8382	79790/8301
Used reflections with $I > 2\sigma(I)$	6973	6829	7139
Parameters	650	483	476
[a]GOF on F^2	0.927	1.030	1.042
[b]R [$I > 2\sigma(I)$]	0.00537	0.0503	0.0427
[c]wR (F^2) [all data]	0.1609	0.1346	0.1098

[a] $\mathrm{GOF} = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$ (n; number of reflections, p; total number of parameters refined), [b] $R1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$, [c] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.