Electronic Supplementary Information for Dalton Transactions

Three-Coordinate Late Transition Metal Fluorinated Alkoxide Complexes

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Table S1. Selected Interatomic Distances and Angles for **1**.[a]

Compound	Distance	(Å)	Angle	(°)
1	K1—O1	2.746(2)	O1—K1—O4	80.28(6)
	K1—O3	2.689(2)	O1—K1—O3	82.17(6)
	K1—O4	2.745(2)	O1—K2—O3	83.18(7)
	K2—O1	2.686(2)	O1—K2—O2	80.48(6)
	K2—O2	2.698(2)	O1—K3—O4	83.27(6)
	K2—O3	2.695(2)	O1—K3—O2	81.36(6)
	K3—O1	2.658(2)	O2—K2—O3	82.48(6)
	K3—O2	2.677(2)	O2—K3—O4	82.70(7)
	K3—O4	2.670(2)	O2—K4—O4	81.27(7)
	K4—O2	2.695(2)	O3—K1—O4	82.39(6)
	K4—O3	2.740(2)	O2—K4—O3	81.70(6)
	K4—O4	2.729(2)	O3—K4—O4	81.77(6)
	O1—C1	1.345(3)		
	O2—C5	1.348(3)		
	O3—C9	1.348(3)		
	O4—C13	1.348(3)		
	K1···F5	3.032(2)		
	K1···F8	3.045(2)		
	K1···F24	3.063(2)		
	K1···F26	3.237(3)		
	K1···F28	3.050(2)		
	K1···F31	3.248(2)		

[a]Numbers in parentheses are estimated deviations of the last significant figure.

Table S2. Selected Interatomic Distances and Angles in $[MX_3]^-$ Compounds.[a]

Compound	X-ray		DFT	
	Distance	(Å)	Distance	(Å)
$[Co(OC_4F_9)_3]^-$	Co(1)-O(1)	1.9143(18)	Co-O	1.852
This work	Co(1)-O(2)	1.8810(19)	Co-O	1.820
	Co(1)-O(3)	1.9262(18)	Co-O	1.788
	Angle	(°)		
	O(1)-Co(1)-O(2)	128.38(9)	O-Co-O	114.55
	O(2)-Co(1)-O(3)	124.39(9)	O-Co-O	129.98
	O(1)-Co(1)-O(3)	107.23(8)	O-Co-O	115.47
$[Co(mes)_3]^-$			Co-C	2.100
No pub X-ray			Co-C	2.100
			Co-C	2.100
			C-Co-C	120.0
			C-Co-C	120.0
			C-Co-C	120.0
$[Co\{N(TMS)_2\}_3]^-$	Co(1)-N(1)	1.974		1.909
TEGCEN[b]	Co(1)-N(2)	1.980		1.910
	Co(1)-N(3)	1.974		1.910
	Angle	(°)		
	N(1)-Co(1)-N(2)	120.54		119.92
	N(2)-Co(1)-N(3)	119.13		120.01
	N(1)-Co(1)-N(3)	120.34		120.07

[a]Numbers in parentheses are estimated deviations of the last significant figure.

[b]M. A. Putzer, B. Neumueller, K. Behnicke, and J. Magull, *Chem. Ber.*, 1996, **129**, 715-719.

Table S3. Alpha and Beta Spin-Orbital Energies and Averages.

Compound	Orbital	Dominant *d* Character	Alpha	Beta	Average
$[Co(OC_4H_9)_3]^-$	25a"	xz	-0.317548	1.024113	0.3532825
	52a'	xy	-0.576271	1.256097	0.339913
	51a'	x^2-y^2	-0.741358	1.208673	0.2336575
	24a"	yz	-0.937934	0.934854	-0.00154
	50a'	z^2	-1.016947	0.37322	-0.3218635
$[Co(OC_4F_9)_3]^-$	76a"	xz	-2.592487	-1.039124	-1.8158055
	109a'	x^2-y^2	-2.746703	-0.746396	-1.7465495
	108a'	xy	-3.056187	-0.991624	-2.0239055
	75a"	yz	-3.195316	-1.251635	-2.2234755
	107a'	z^2	-3.245534	-1.653905	-2.4497195
$[Co\{N(TMS)_2\}_3]^-$	149a	xy	-0.937711	0.701829	-0.117941
	148a	x^2-y^2	-0.940376	0.699222	-0.120577
	147a/145a	yz	-1.755208	-0.419265	-1.0872365
	146a	xz	-1.759261	-0.416847	-1.088054
	144a/147a	z^2	-2.650698	-0.278061	-1.4643795
$[Co(mes)_3]^-$	113a	xy	-0.442	0.692861	0.1254305
	112a	x^2-y^2	-0.44231	0.692701	0.1251955
	111a/109a	yz	-1.649726	-0.387672	-1.018699
	110a	xz	-1.64981	-0.387365	-1.0185875
	109a/111a	z^2	-2.158649	0.0088	-1.0749245

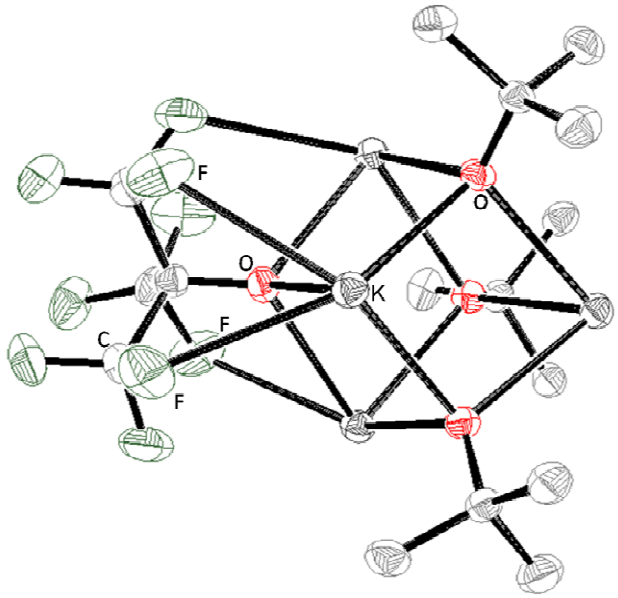

Figure S1. ORTEP of **1** with most F atoms removed for clarity. Ellipsoids are shown at the 50% probability level.

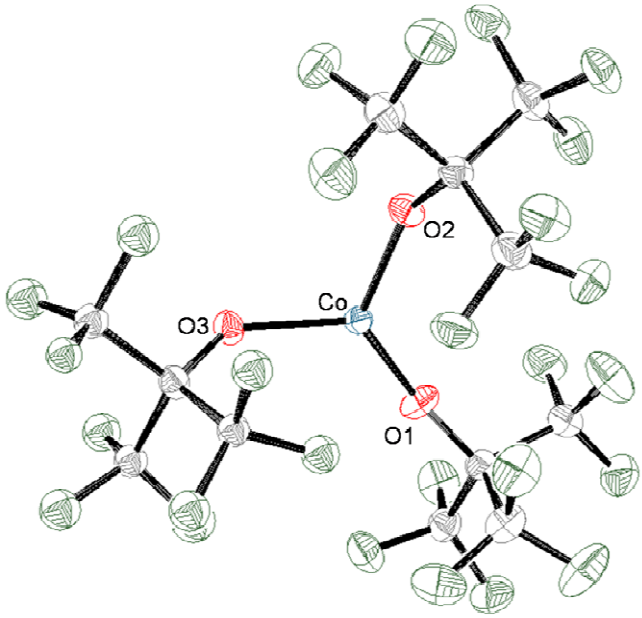

Figure S2. ORTEP of **4** with $\{K(18C6)\}^+$ cation removed for clarity. Ellipsoids are shown at the 50% probability level.

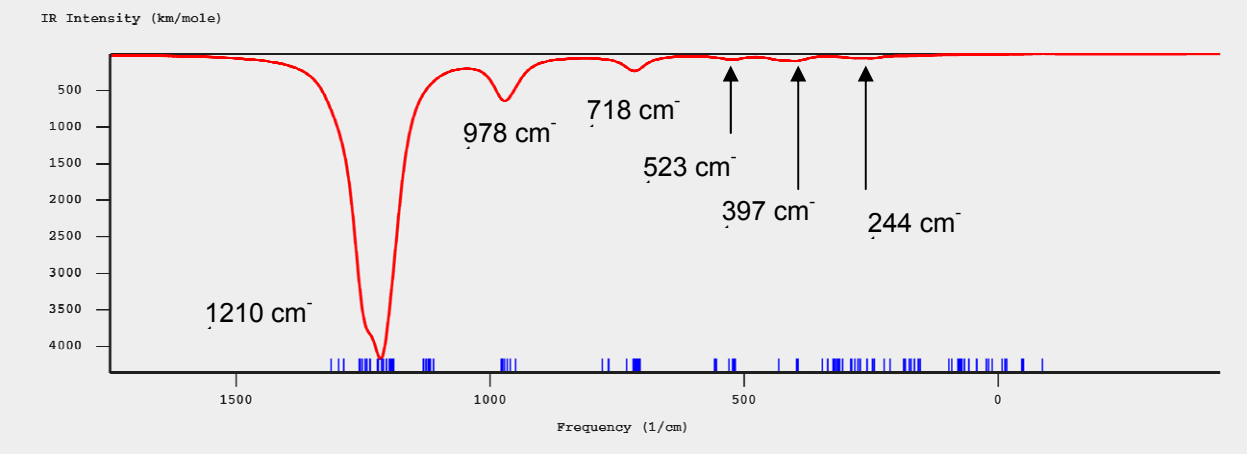

Figure S3. DFT frequency calculation of **4**.

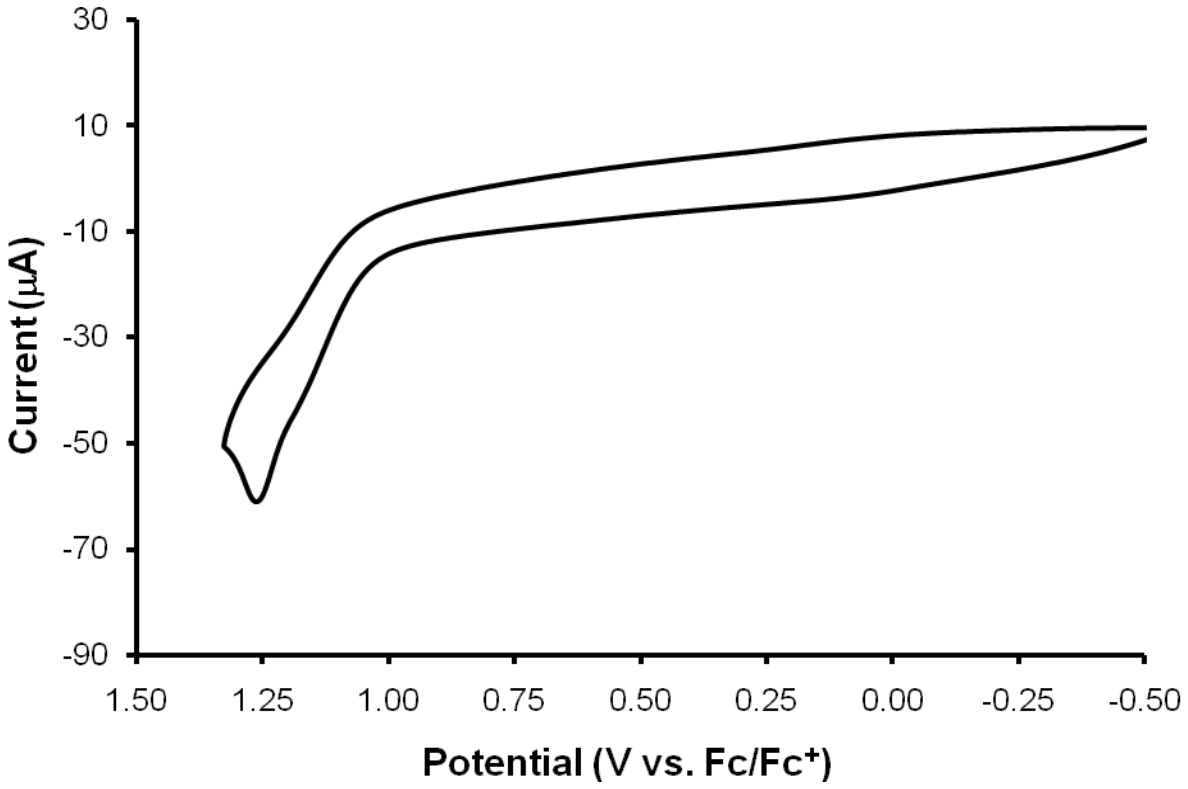

Figure S4. Cyclic voltammogram of 5 mM KOC_4F_9, **1**, in 0.1 M $TBAPF_6/CH_2Cl_2$ (scan rate 100 mVs^{-1}).

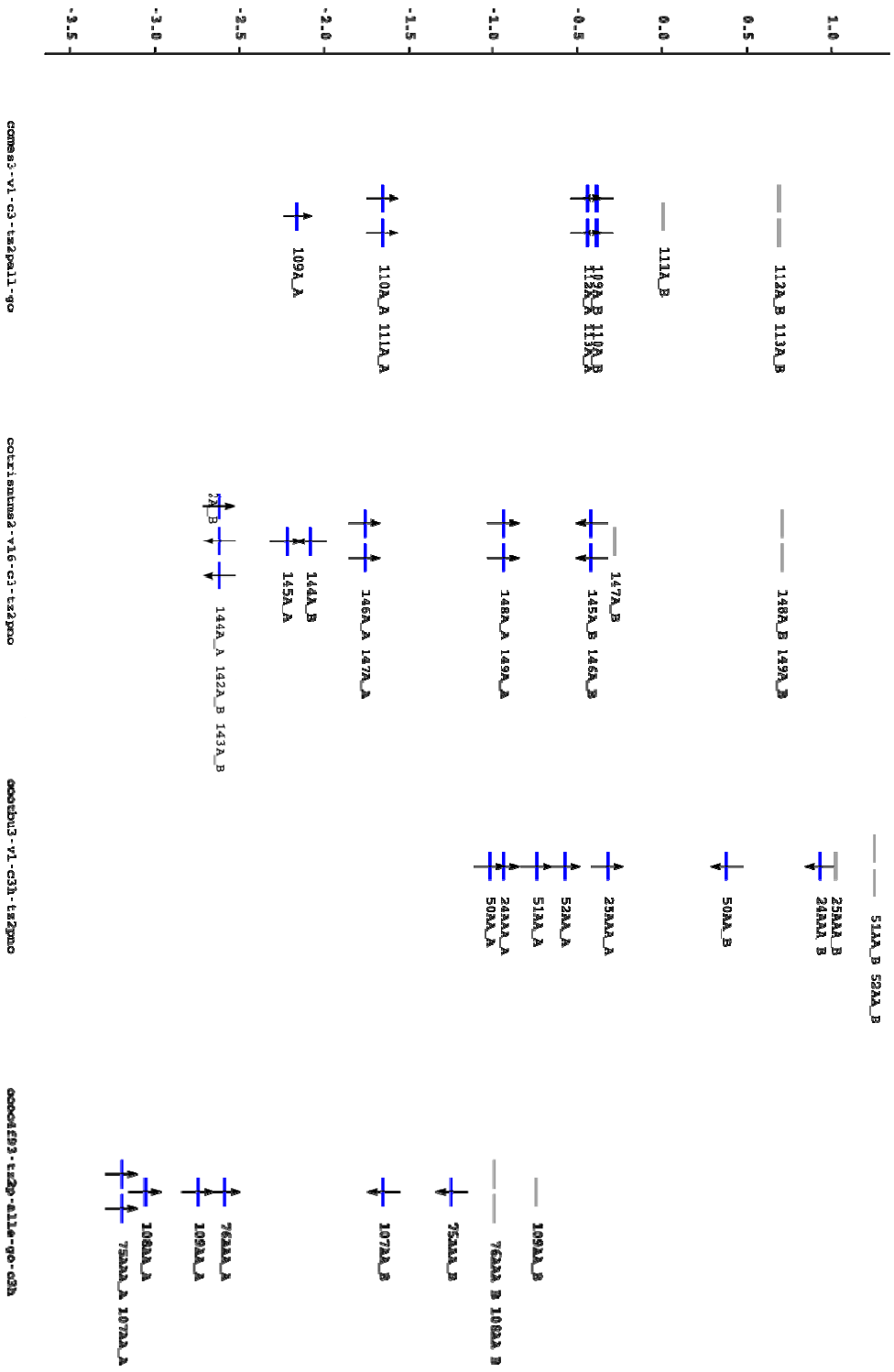

Figure S5. Comparison of *d*-manifold spin-orbital energies among four $[CoX_3]^-$ species. See tabulation in Table S3 for exact energies and *d*-character assignments.

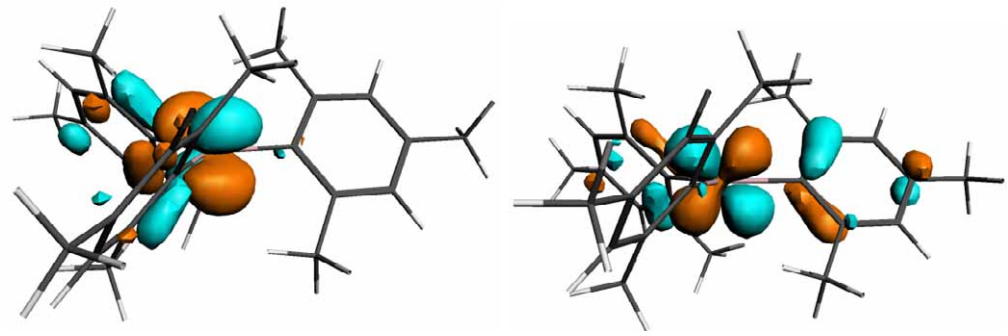

Figure S6. $[Co(mes)_3]^-$ spin orbitals 110a (α d_{xz}) (left) and 111a (α-d_{yz}) (right).

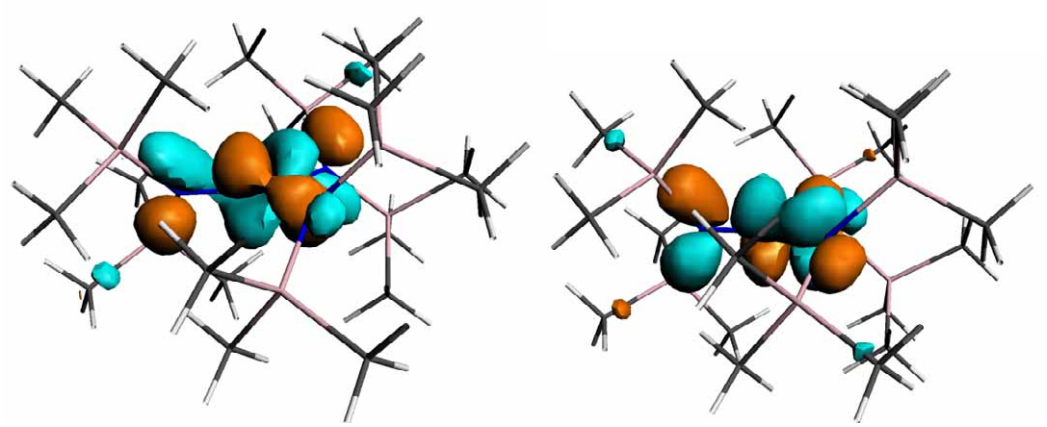

Figure S7. $[Co\{N(TMS)_2\}_3]^-$ spin orbitals 146a (α d_{xz}) (left) and 147a (α d_{yz}) (right).