Supporting Information for:

Routes to Acetonitrile-Supported Trifluoromethyl and Perfluorometallacyclopentane Complexes of Cobalt

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NMR Spectral Data for All Compounds:

Figure S1: ^{19}F NMR of **5** in CD_3CN, collected on a spectrometer operating at 376 MHz, recorded at 25°C, and referenced to α,α,α-trifluorotoluene as an internal standard (δ = -63.7).

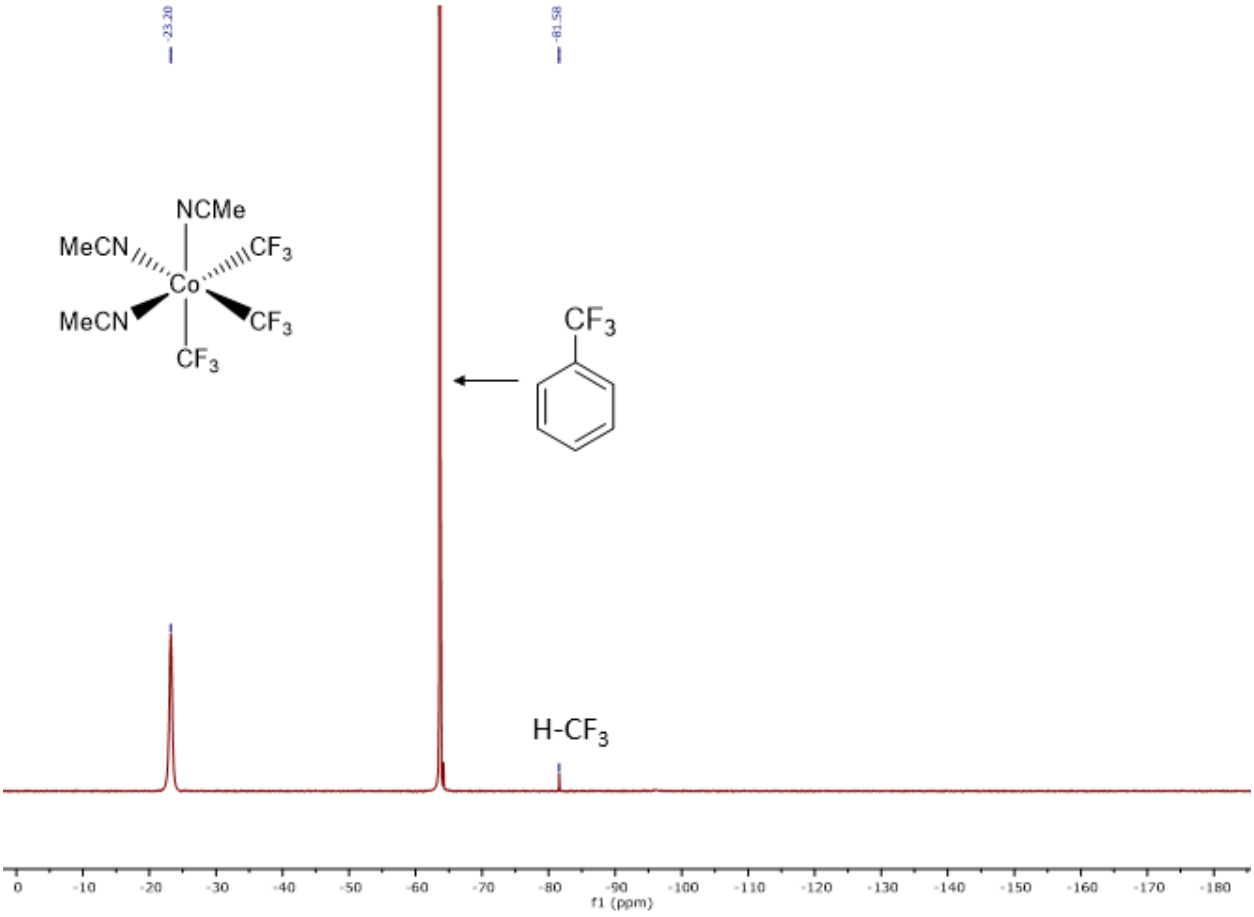

Figure S2: ^{19}F NMR of **11** in CD_3CN collected on a spectrometer operating at 376 MHz, recorded at 25°C, and referenced to α,α,α-trifluorotoluene as an internal standard (δ = -63.7).

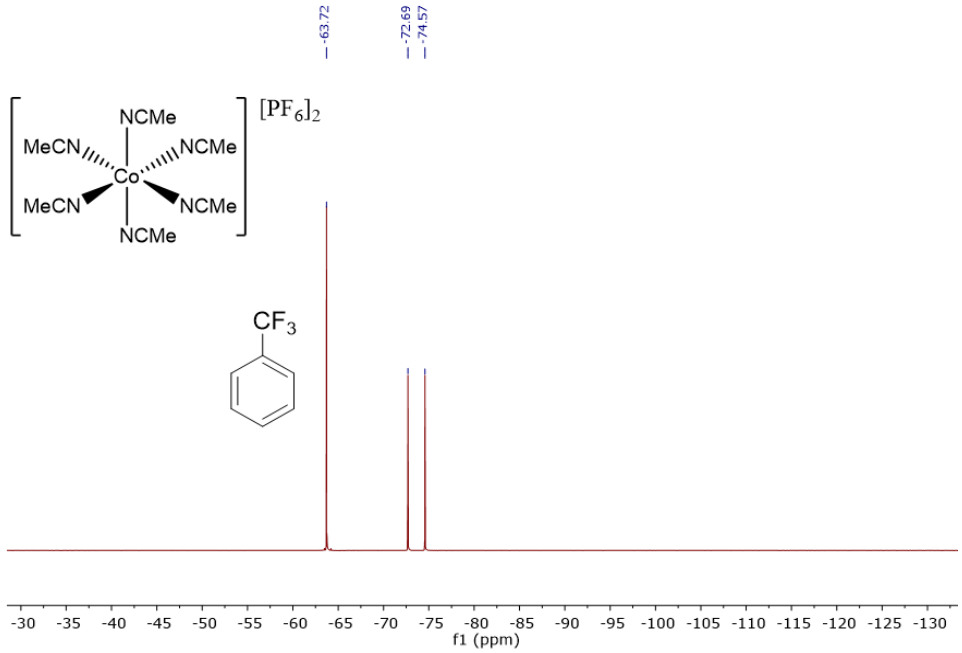

Figure S3: ^{19}F NMR of **12** in CD_3CN, collected on a spectrometer operating at 376 MHz, recorded at 25°C, and referenced to α,α,α-trifluorotoluene as an internal standard (δ = -63.7).

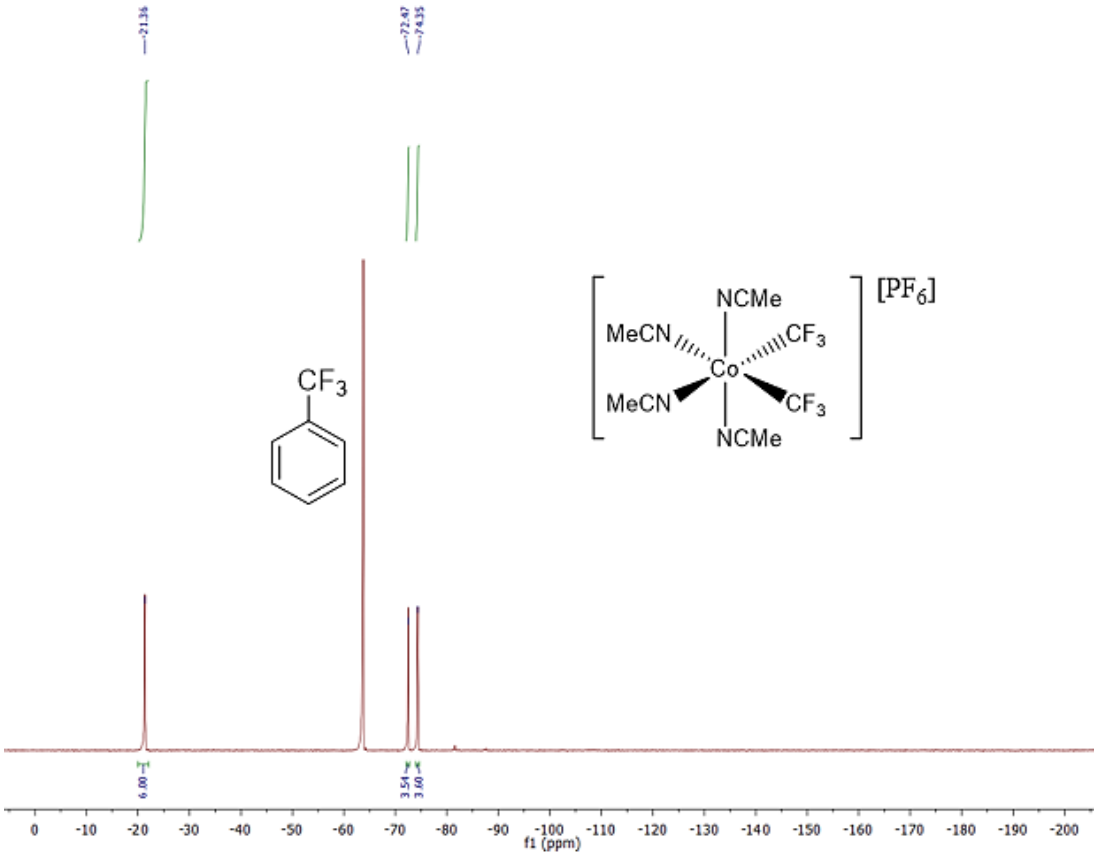

Figure S4: ^{19}F NMR of **13-14** in CD_3CN, collected on a spectrometer operating at 376 MHz, recorded at 25°C, and referenced to α,α,α-trifluorotoluene as an internal standard (δ = -63.7).

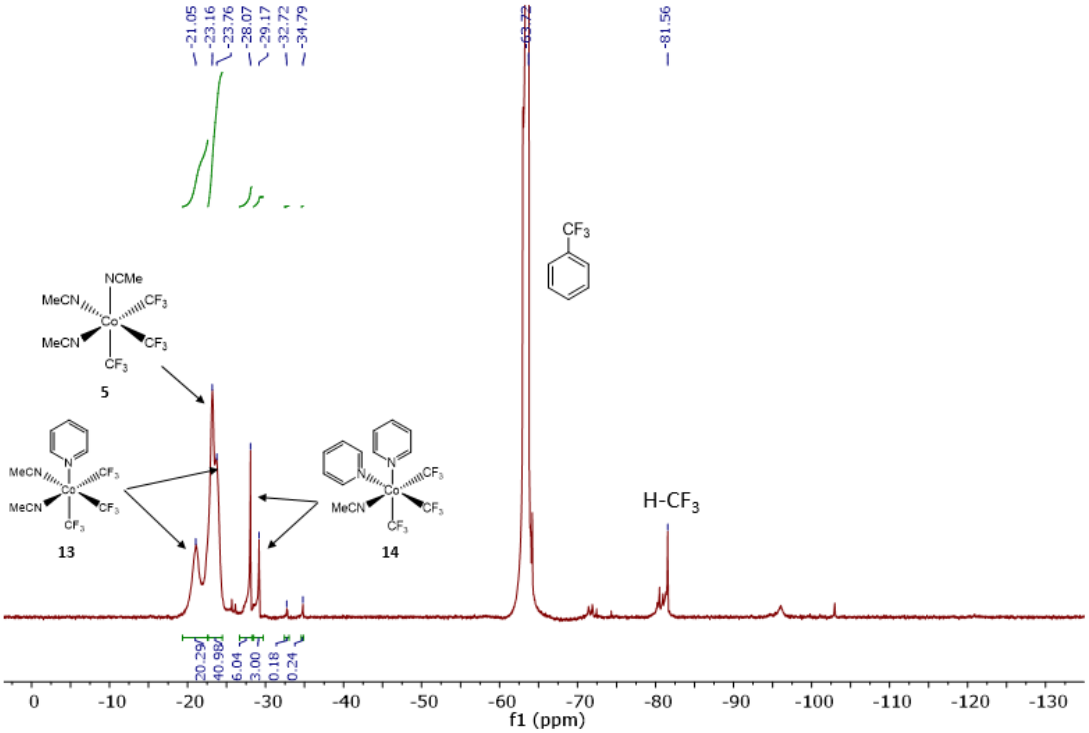

Figure S5: ^{19}F NMR of **16** in CD_3CN, collected on a spectrometer operating at 376 MHz, recorded at 25°C, and referenced to α,α,α-trifluorotoluene as an internal standard (δ = -63.7).

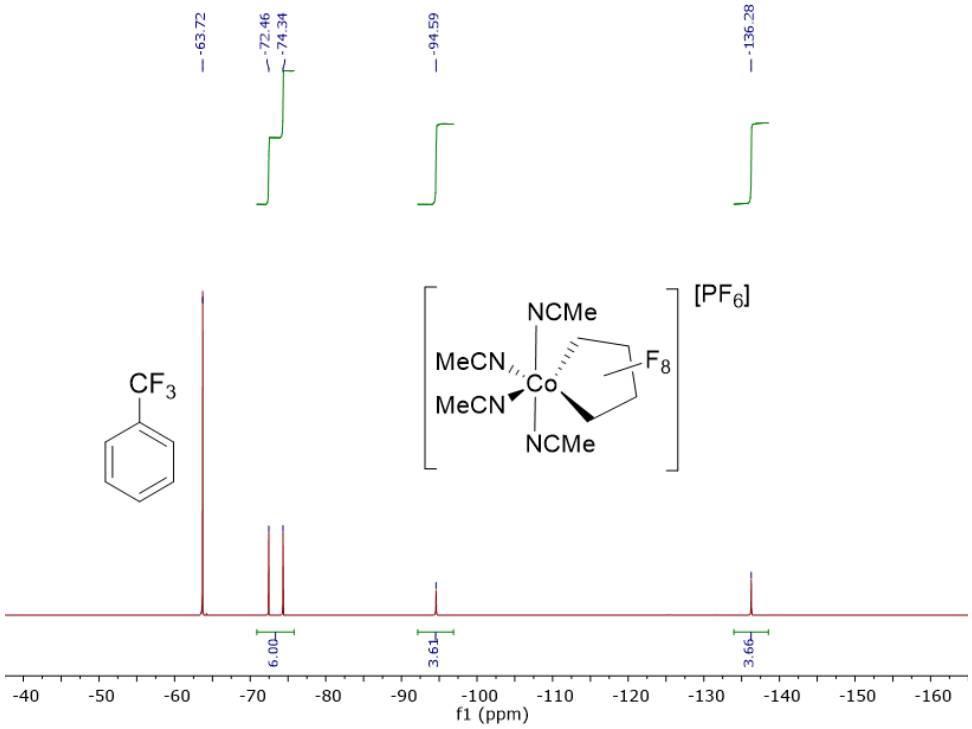

Table S1. Number of H···F contacts shorter than the sum of van der Waals radii of F and H.

Compound	*# of H···F contacts shorter than the sum of van der Waals radii of F and H*
5	4
12	8
13	13
14	8
16	8

Hydrogen contacts for Compound **5** with donor (D) and acceptor (A) designations as determined by the SHELX program:

Hydrogen bonds with H..A < r(A) + 2.000 Angstroms and <DHA > 110 deg.

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A
C5-H5B	0.980	2.505	136.45	3.285	F6 [x-1/2, -y+3/2, z]
C9-H9A	0.980	2.568	141.45	3.389	F6 [-x+3/2, y+1/2, z-1/2]
C9-H9B	0.980	2.613	151.37	3.504	F2 [x-1/2, -y+3/2, z]
C9-H9C	0.980	2.604	127.47	3.293	F7 [-x+1, -y+1, z-1/2]

Hydrogen contacts for Compound **12** with donor (D) and acceptor (A) designations as determined by the SHELX program:

Hydrogen bonds with H..A < r(A) + 2.000 Angstroms and <DHA > 110 deg.

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A
C4-H4A	0.980	2.373	150.40	3.261	F8 [-x+1, -y+1, -z+1]
C4-H4B	0.980	2.443	151.87	3.339	F9 [x-1/2, -y+3/2, -z+1]
C4-H4B	0.980	2.408	141.17	3.231	F11 [x-1/2, -y+3/2, -z+1]
C4-H4C	0.980	2.489	124.53	3.150	F8
C8-H6	0.989	2.428	174.14	3.413	F6 [-x+3/2, y-1/2, z]
C10-H10A	0.980	2.581	133.09	3.328	F6 [-x+1, y-1/2, -z+1/2]
C10-H10B	0.980	2.587	135.94	3.361	F9 [-x+1, -y+1, -z+1]
C10-H10C	0.980	2.513	132.00	3.251	F10 [-x+3/2, y-1/2, z]

Hydrogen contacts for Compound **13** with donor (D) and acceptor (A) designations as determined by the SHELX program:

Hydrogen bonds with H..A < r(A) + 2.000 Angstroms and <DHA > 110 deg.

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A
C5-H5	0.950	2.632	121.32	3.230	F1 [-x+1, y+1/2, -z+3/2]
C7-H7	0.950	2.637	111.17	3.109	F6 [-x, -y+1, -z+1]
C8-H8	0.950	2.355	136.85	3.117	F6
C8-H8	0.950	2.318	126.47	2.982	F6 [-x, -y+1, -z+1]
C10-H10A	0.980	2.628	159.08	3.561	F2 [x+1, y, z]
C10-H10A	0.980	2.589	114.85	3.130	F3 [x+1, y, z]
C10-H10B	0.980	2.356	143.78	3.200	F5 [-x+1, y-1/2, -z+3/2]
C10-H10B	0.980	2.520	136.49	3.300	F7 [-x+1, y-1/2, -z+3/2]
C10-H10C	0.980	2.602	137.08	3.386	F8 [-x+1, -y+1, -z+2]
C10-H10C	0.980	2.635	158.10	3.563	F9 [-x+1, -y+1, -z+2]
C12-H12B	0.980	2.563	164.81	3.518	F5 [-x, -y+1, -z+1]
C12-H12C	0.980	2.489	144.29	3.334	F4 [-x, y-1/2, -z+3/2]
C12-H12C	0.980	2.524	139.04	3.326	F9 [-x, y-1/2, -z+3/2]

Hydrogen contacts for Compound **14** with donor (D) and acceptor (A) designations as determined by the SHELX program:

Hydrogen bonds with H..A < r(A) + 2.000 Angstroms and <DHA > 110 deg.

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A
C5-H5A	0.980	2.560	127.94	3.255	F1 [x, -y+1/2, z-1/2]
C5-H5A	0.980	2.596	122.75	3.233	F4 [x, -y+1/2, z-1/2]
C5-H5A	0.980	2.531	155.63	3.447	F7 [x, -y+1/2, z-1/2]
C5-H5B	0.980	2.406	166.74	3.367	F8 [x, y-1, z]
C6-H6	0.950	2.477	125.64	3.127	F6

C7-H7	0.950	2.429	148.57	3.277	F4 [-x+2, y+1/2, -z+3/2]
C10-H10	0.950	2.597	131.38	3.302	F2 [x, -y+1/2, z-1/2]
C11-H11	0.950	2.429	134.25	3.166	F8

Hydrogen contacts for Compound **16** with donor (D) and acceptor (A) designations as determined by the SHELX program:

Hydrogen bonds with H..A < r(A) + 2.000 Angstroms and <DHA > 110 deg.

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A
C6-H6A	0.980	2.520	125.67	3.192	F1 [-x+2, -y+1, -z+1]
C6-H6C	0.980	2.599	129.69	3.312	F10 [-x+1, -y+1, -z]
C8-H8A	0.980	2.518	170.72	3.489	F12 [-x+1, -y+1, -z+1]
C8-H8B	0.980	2.553	143.55	3.391	F13
C8-H8C	0.980	2.469	158.91	3.402	F8 [x, -y+3/2, z+1/2]
C10-H10B	0.980	2.612	113.72	3.137	F7 [-x+1, -y+1, -z]
C12-H12B	0.980	2.427	142.56	3.260	F9 [-x+1, -y+1, -z+1]
C12-H12C	0.980	2.639	123.95	3.289	F5 [-x+2, -y+1, -z+1]