

Supporting information

Table 1S. ^1H NMR data (δ , ppm; $\Delta\nu_{1/2}$, Hz and $J_{\text{H-H}}$, Hz) for the complexes observed upon $\text{L}^{2\text{iPr}}\text{CoCl}_2$ activation with MAO, AlMe_3 and $\text{AlMe}_3/[\text{CPh}_3][\text{B}(\text{C}_6\text{F}_5)_4]$ (toluene- d_8 , 20 °C).

Complex		A Py- H_m	B Py- H_p	C Ar- H_m	D Me_2CH	E Ar- H_p	F N=C(<i>Me</i>)	G Me_2CH	H Me_2CH	Co- <i>Me</i>	μ - <i>Me</i>
$\text{L}^{2\text{iPr}}\text{Co}^{\text{II}}\text{Cl}_2$ ^a		116.5	49.4	10.0	-17.8	-8.8	4.4	-19.0	-84.6		
($\Delta\nu_{1/2}$, Hz)		(90)	(40)	(30)	(30)	(30)	(40)	(70)	(240)		
$[\text{L}^{2\text{iPr}}\text{Co}^{\text{II}}\text{Me}(\text{S})]^+[\text{Me-MAO}]^-$	2	19.4	45.9	NA	-2.4	12.4	-23.6	-15.2	-41.5	~152	
($\Delta\nu_{1/2}$, Hz)		(40)	(60)		(20)	(20)	(70)	(100)	(420)	(~940)	
$[\text{L}^{2\text{iPr}}\text{Co}^{\text{II}}\text{Me}(\text{S})]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$	2'	19.1	44.3	NA	-2.2	12.3	-23.3	-14.6	-40.0	~143	
($\Delta\nu_{1/2}$, Hz)		(50)	(60)		(30)	(20)	(70)	(120)	(520)	(~1600)	
$[\text{L}^{2\text{iPr}}\text{Co}^{\text{I}}(\text{S})]^+[\text{Me-MAO}]^-$	3	7.71	8.35	NA	1.20	NA	-0.80	1.03	2.44		
($J_{\text{H-H}}$, Hz)		(7.8)	(8.3)		(6.4)			(6.4)	(~6)		
$[\text{L}^{2\text{iPr}}\text{Co}^{\text{I}}(\text{S})]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$	3'	7.48	7.92	NA	1.15	NA	-0.81	0.91	2.44		
($J_{\text{H-H}}$, Hz)		(7.3)	(7.7)		(5.5)			(5.9)	(~5)		
$\text{L}^{2\text{iPr}}\text{Co}^{\text{I}}(\mu\text{-Me})(\mu\text{-Cl})\text{AlMe}_2$ ^b	4a	NA	8.1	NA	NA	NA	-0.07	0.8	3.1		-1.6
$\text{L}^{2\text{iPr}}\text{Co}^{\text{I}}(\mu\text{-Me})_2\text{AlMe}_2$ ^b	4b	7.5	9.7	NA	1.1	NA	N/O	0.6	3.1		-2.8
$[\text{L}^{2\text{iPr}}\text{Co}^{\text{I}}(\eta\text{-C}_2\text{H}_4)]^+[\text{AlMe}_3\text{Cl}]^-$ ^b	5	NA	8.1	NA	1.1	NA	0.6	0.8	3.1		
$[\text{L}^{2\text{iPr}}\text{Co}^{\text{I}}(\eta\text{-N}_2)]^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ ^c	3_{N2}	6.69	7.55	6.87	1.05	7.00	1.11	0.98	2.85		N/O
$[\text{L}^{2\text{iPr}}\text{Co}^{\text{I}}(\eta\text{-C}_2\text{H}_4)]^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ ^c	3_{C2H4}	~7.0	8.00	6.77	1.09	~7.0	0.75	0.76	3.02		N/O
$\text{L}^{2\text{iPr}}\text{Co}^{\text{I}}\text{Me}$ ^c		7.86	10.19	7.37	1.19	7.49	-1.14	0.62	3.13	N/O	
$\text{L}^{2\text{iPr}}\text{Co}^{\text{I}}\text{Cl}$ ^c		6.91	9.54	7.27	1.18	7.41	0.05	1.06	3.33		

^a Solution in CH_2Cl_2 . ^b Spectra recorded at -10 °C, only broad singlets in the each case. ^c The data from ref. ²¹. N/O – not observed. NA – not reliably assigned.

Table 2S. ^1H NMR data (δ , ppm; $\Delta\nu_{1/2}$, Hz and $J_{\text{H-H}}$, Hz) for the complexes observed upon $\text{L}^{3\text{Me}}\text{CoCl}_2$ activation with MAO, AlMe_3 and $\text{AlMe}_3/[\text{CPh}_3][\text{B}(\text{C}_6\text{F}_5)_4]$ (toluene- d_8).

Complex	T, °C	A Py- H_m	B Py- H_p	C Ar- H_m	D Ar- Me_o	E Ar- Me_p	F N=C(Me)	Co-Me	AlMe_2
$\text{L}^{3\text{Me}}\text{Co}^{\text{II}}\text{Cl}_2$ ^a	+20	110.7	36.3	6.5	-26.5	17.0	-0.5		
($\Delta\nu_{1/2}$, Hz)		(520)	(210)	(60)	(210)	(80)	(100)		
$\text{L}^{3\text{Me}}\text{Co}^{\text{II}}\text{Cl}_2$ ^a	-20	141.5	49.3	6.5	-38.1	21.5	-0.5		
($\Delta\nu_{1/2}$, Hz)		(1100)	(570)	(110)	(540)	(230)	(110)		
$[\text{L}^{3\text{Me}}\text{Co}^{\text{II}}(\mu\text{-Me})_2\text{AlMe}_2]^+[\text{Me-MAO}]^-$	6 -20	147.6	37.5	34.4	-7.9	43.4	-5.6	N/O	55.2
($\Delta\nu_{1/2}$, Hz)		(130)	(50)	(60)	(260)	(40)	(170)		(120)
$[\text{L}^{3\text{Me}}\text{Co}^{\text{II}}(\mu\text{-Me})_2\text{AlMe}_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$	6' -20	147.8	36.3	35.3	-8.1	43.4	-3.9	N/O	57.2
($\Delta\nu_{1/2}$, Hz)		(60)	(30)	(20)	(160)	(20)	(60)		(60)
$[\text{L}^{3\text{Me}}\text{Co}^{\text{II}}\text{Me}(\text{S})]^+[\text{Me-MAO}]^-$	7 -20	21.7	52.0	NA	-26.3	NA	-31.7	N/O ^b	
($\Delta\nu_{1/2}$, Hz)		(80)	(170)		(340)		(170)		
$[\text{L}^{3\text{Me}}\text{Co}^{\text{II}}\text{Me}(\text{S})]^+[\text{Me-MAO}]^-$	7 +20	20.2	46.4	NA	-22.5	NA	-24.9	N/O ^b	
($\Delta\nu_{1/2}$, Hz)		(60)	(60)		(140)		(100)		
$[\text{L}^{3\text{Me}}\text{Co}^{\text{II}}\text{Me}(\text{S})]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$	7' -20	21.6	50.4	NA	-25.5	NA	-30.6	N/O	
($\Delta\nu_{1/2}$, Hz)		(100)	(70)		(260)		(140)		
$[\text{L}^{3\text{Me}}\text{Co}^{\text{I}}(\text{S})]^+[\text{Me-MAO}]^-$	8 +20	7.61	8.19	6.71	1.88	1.86	-0.71		
($J_{\text{H-H}}$, Hz)		(8.3)	(7.3)						
$[\text{L}^{3\text{Me}}\text{Co}^{\text{I}}(\text{S})]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$	8' +20	7.42	7.89	6.66	1.80	1.76	-0.72		
($J_{\text{H-H}}$, Hz)		(6.4)	(6.8)						
$\text{L}^{3\text{Me}}\text{Co}^{\text{I}}(\mu\text{-Me})(\mu\text{-Cl})\text{AlMe}_2$	9a +10	7.5	12.2	6.78	1.52	2.43	-1.64	N/O	N/O
$\text{L}^{3\text{Me}}\text{Co}^{\text{I}}(\mu\text{-Me})_2\text{AlMe}_2$	9b +10	7.6	12.6	6.82	1.41	2.43	-1.85	N/O	N/O
$[\text{L}^{3\text{Me}}\text{Co}^{\text{I}}(\eta\text{-C}_2\text{H}_4)]^+[\text{AlMe}_3\text{Cl}]^-$	10 +10	7.2	8.35	6.54	1.57	2.03	0.36		
$\text{L}^{3\text{Me}}\text{Co}^{\text{I}}\text{Me}$ ^c	+20	7.88	10.08	6.99	1.93	2.28	-1.21	0.46	
$\text{L}^{3\text{Me}}\text{Co}^{\text{I}}\text{Cl}$ ^c	+20	6.90	9.49	6.93	2.19	2.18	-0.06		
($J_{\text{H-H}}$, Hz)		(7.7)	(7.7)						

^a Solution in CH_2Cl_2 . ^b A broad singlet ($\delta \sim 171$, $\Delta\nu_{1/2} \sim 600$ Hz) was observed at 0 °C after prolonged ^1H NMR spectrum accumulating. ^c The data from ref. ²¹. N/O – not observed. NA – not reliably assigned.

Table 3S. ^1H NMR data (δ , ppm; $\Delta\nu_{1/2}$, Hz and $J_{\text{H-H}}$, Hz) for the complexes observed upon $\text{L}^{\text{tBu}}\text{Co}^{\text{II}}\text{Cl}_2$ activation with MAO, AlMe_3 , and $\text{AlMe}_3/[\text{CPh}_3][\text{B}(\text{C}_6\text{F}_5)_4]$ (toluene- d_8).

Complex	T, °C	A Py- H_m	B Py- H_p	C Ar- H	D C(CH_3) $_3$	E Ar- H	F N=C(Me)	G Ar- H	H Ar- H	Co-Me	AlMe_2
$\text{L}^{\text{tBu}}\text{Co}^{\text{II}}\text{Cl}_2$ ^a	−20	141.6	65.4	14.6	−36.5	N/O	N/O	−16.1	−110.7		
($\Delta\nu_{1/2}$, Hz)		(860)	(480)	(190)	(410)			(130)	(780)		
$\text{L}^{\text{tBu}}\text{Co}^{\text{II}}\text{Cl}_2$ ^a	+20	111.8	50.9	12.6	−26.0	1.6	10.4	−11.8	−85.8		
($\Delta\nu_{1/2}$, Hz)		(180)	(150)	(100)	(190)	(30)	(350)	(40)	(280)		
$[\text{L}^{\text{tBu}}\text{Co}^{\text{II}}(\mu\text{-Me})_2\text{AlMe}_2]^+[\text{Me-MAO}]^-$	11 −20	138.6	44.1	30.7	−35.8	−6.0	−10.1	29.8	NA	N/O	48.3
($\Delta\nu_{1/2}$, Hz)		(100)	(70)	(70)	(270)	(30)	(70)	(50)			(120)
$[\text{L}^{\text{tBu}}\text{Co}^{\text{II}}\text{Me}(\text{S})]^+[\text{Me-MAO}]^-$	12 −20	~17.6	~51.4	NA	−14.7	NA	−32.8	NA	NA	N/O	
($\Delta\nu_{1/2}$, Hz)		(170)	(220)		(840)		(520)				
$[\text{L}^{\text{tBu}}\text{Co}^{\text{II}}\text{Me}(\text{S})]^+[\text{Me-MAO}]^-$	12 +20	16.5	44.6	NA	−12.7	NA	−26.5	NA	NA	~139	
($\Delta\nu_{1/2}$, Hz)		(120)	(480)		(400)		(250)			broad	
$[\text{L}^{\text{tBu}}\text{Co}^{\text{II}}(\mu\text{-Me})_2\text{AlMe}_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$	11' −20	140.2	44.6	31.0	−36.4	−6.3	−10.6	29.7	NA	N/O	48.9
($\Delta\nu_{1/2}$, Hz)		(80)	(30)	(30)	(170)	(30)	(50)	(30)			(60)
$[\text{L}^{\text{tBu}}\text{Co}^{\text{II}}(\mu\text{-Me})_2\text{AlMe}_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$	11' +20	118.3	37.7	26.9	−28.7	−4.8	−8.2	25.6	NA	N/O	40.9
($\Delta\nu_{1/2}$, Hz)		(50)	(20)	(30)	(120)	(30)	(50)	(30)			(40)
$[\text{L}^{\text{tBu}}\text{Co}^{\text{II}}\text{Me}(\text{S})]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$	12' +20	16.5	44.3	NA	−13.2	NA	−26.2	NA	NA	N/O	
($\Delta\nu_{1/2}$, Hz)		(180)	(110)		(240)		(170)				
$[\text{L}^{\text{tBu}}\text{Co}^{\text{I}}(\text{S})]^+[\text{Me-MAO}]^-$	13 +20	7.64	8.27	NA	1.17/1.14	NA	−0.70	7.23	6.63		
($J_{\text{H-H}}$, Hz)		(7.77)	(7.54)					(7.99)	(6.62)		
$[\text{L}^{\text{tBu}}\text{Co}^{\text{I}}(\eta\text{-C}_2\text{H}_4)]^+[\text{AlMe}_3\text{Cl}]^-$ ^b	14 −30	7.21	8.03	NA	0.79	NA	0.85	NA	NA		
($J_{\text{H-H}}$, Hz)		(5.87)	(6.84)								

^a Solution in CH_2Cl_2 . ^b The signal of $\eta\text{-C}_2\text{H}_4$ at δ 4.82 was observed. N/O – not observed. NA – not reliably assigned.

Table 4S. ^1H NMR data (δ , ppm; $\Delta\nu_{1/2}$, Hz) for the complexes observed upon $\text{L}^{\text{CF}_3}\text{Co}^{\text{II}}\text{Cl}_2$ activation with MAO and $\text{AlMe}_3/[\text{CPh}_3][\text{B}(\text{C}_6\text{F}_5)_4]$ (toluene- d_8).

Complex	T, °C	A <u>Py-H_m</u>	B <u>Py-H_p</u>	C <u>N=C(<i>Me</i>)</u>	D <u>Ar-H_m</u>	E <u>Ar-H_m</u>	F <u>Ar-H</u>	G <u>Ar-H</u>	<u>AlMe_2</u>
$\text{L}^{\text{CF}_3}\text{Co}^{\text{II}}\text{Cl}_2$ ^a	−40	158.3	67.9	13.6	17.8; −4.5; −16.4; NA				
($\Delta\nu_{1/2}$, Hz)		(210)	(140)	(110)	ND				
	+20	113.8	47.1	9.3	14.4; −4.0; −10.3; NA				
($\Delta\nu_{1/2}$, Hz)		(240)	(120)	(190)	ND				
$[\text{L}^{\text{CF}_3}\text{Co}^{\text{II}}(\mu\text{-Me})_2\text{AlMe}_2]^+[\text{Me-MAO}]^-$	15 −40	156.7	45.8	−16.1	37.0	31.0	−6.3	NA	58.5
($\Delta\nu_{1/2}$, Hz)		(700)	(310)	(230)	(240)	(250)	ND	ND	(360)
	+20	114.9	37.4	−8.4	24.7	23.8	−5.9	10.3	38.8
$[\text{L}^{\text{CF}_3}\text{Co}^{\text{II}}(\mu\text{-Me})_2\text{AlMe}_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$	15' −40	150.3	43.6	−15.6	35.8	29.5	−6.2	NA	56.7
($\Delta\nu_{1/2}$, Hz)		(110)	(110)	(140)	(90)	(90)	(50)	ND	(140)

^a Solution in CDCl_3 , N/O – not observed. NA – not reliably assigned. ND –not detected.