Electronic Supplementary Information

Variable Coordination Geometries via an Amine-Enamidophosphinimine Ligand on Cobalt

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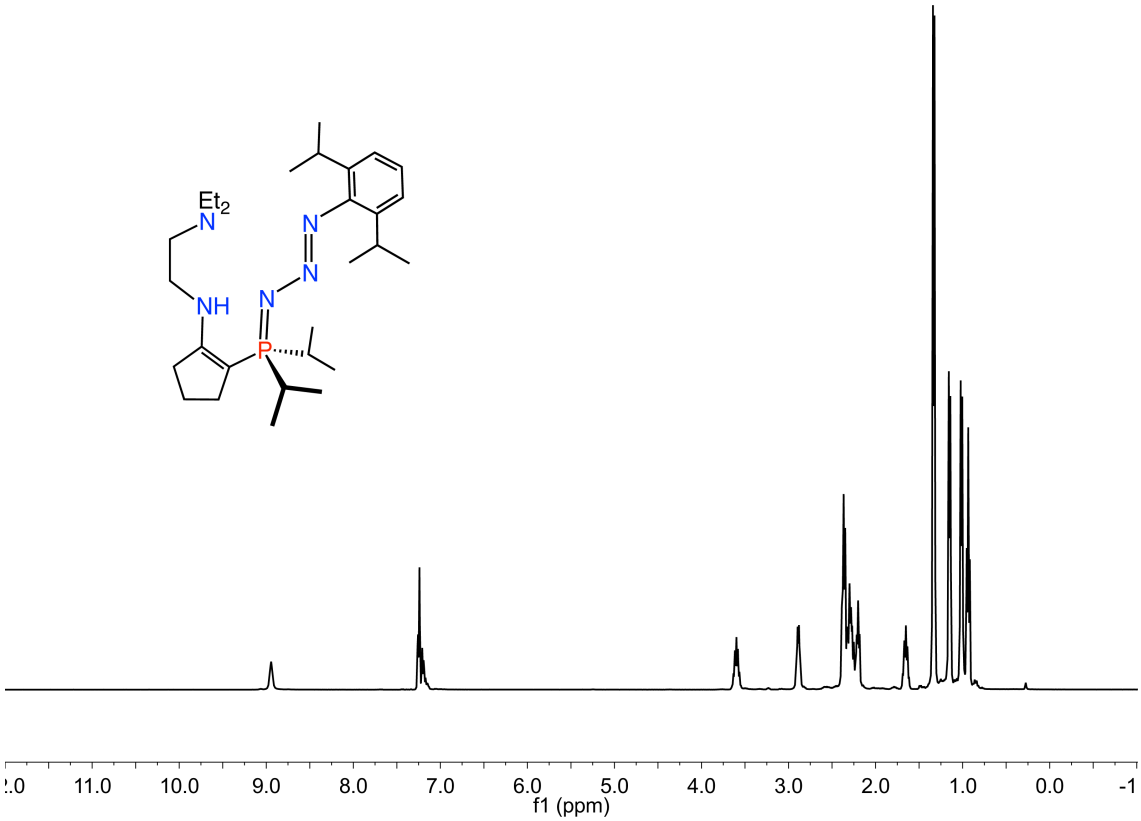

Figure S1. ^{1}H NMR spectrum of **2** in benzene-d_6.

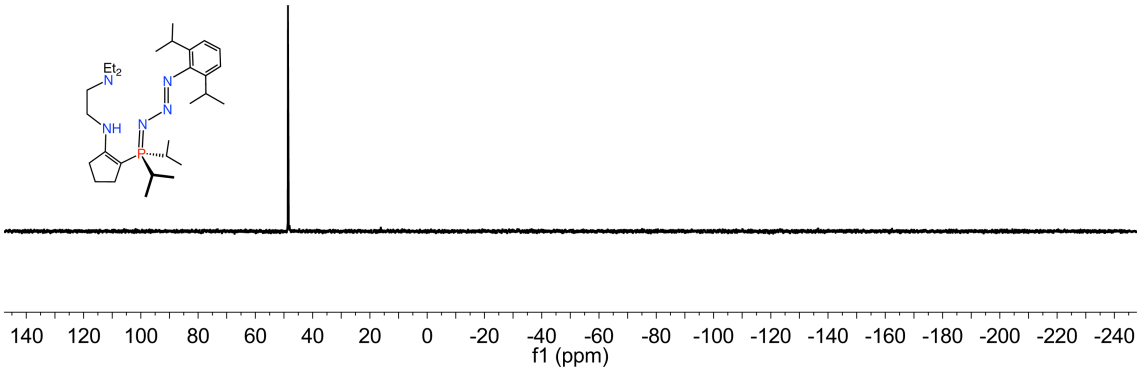

Figure S2. ^{31}P NMR spectrum of **2** in benzene-d_6.

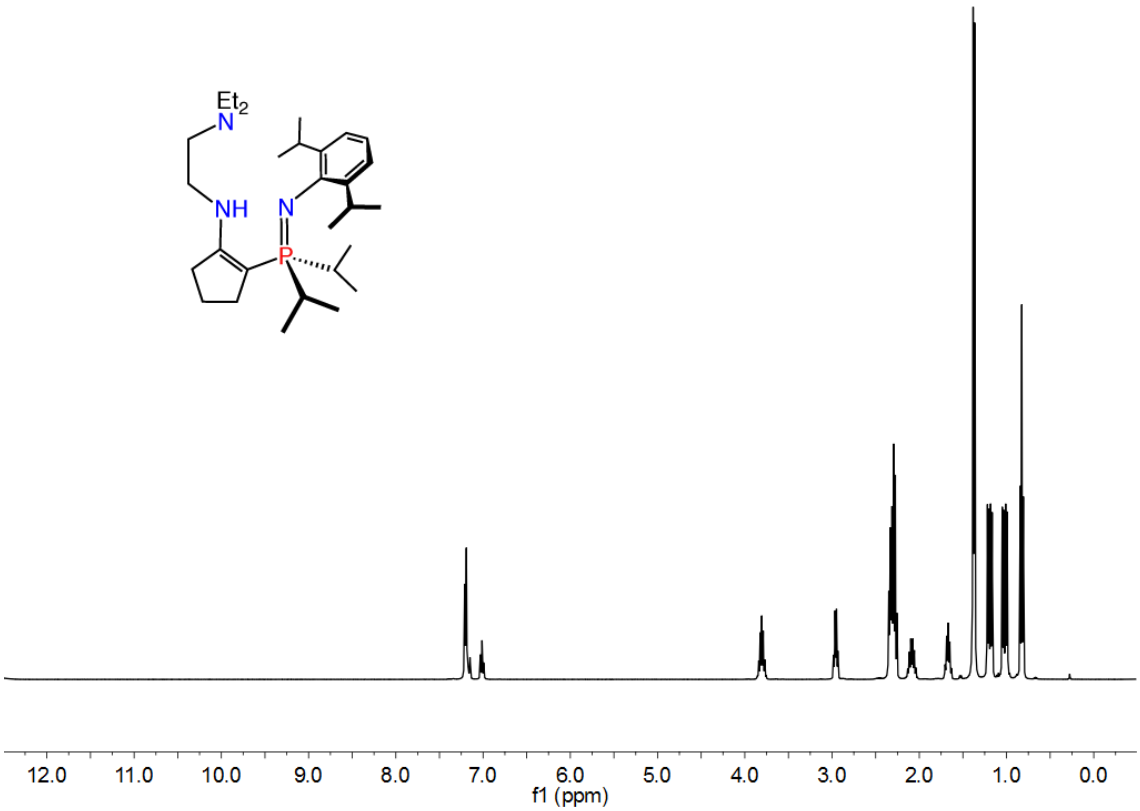

Figure S3. ^{1}H NMR spectrum of **3** in benzene-d_6.

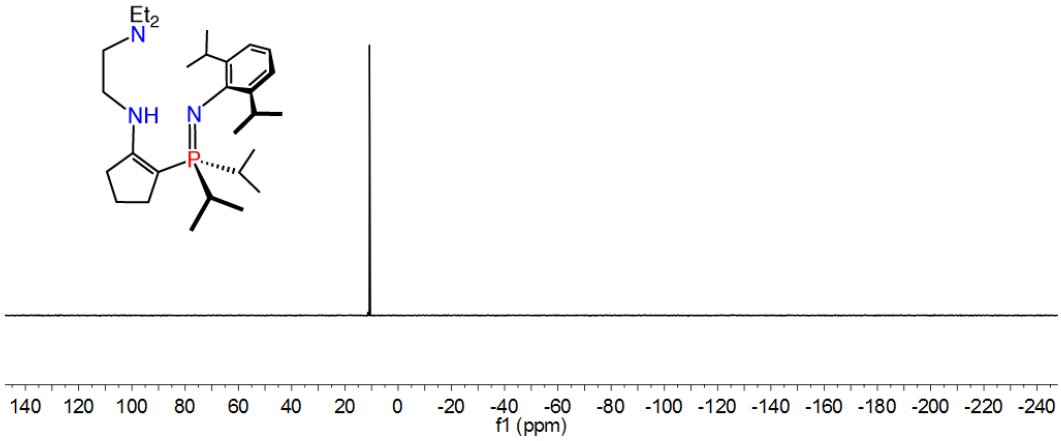

Figure S4. ^{31}P NMR spectrum of **3** in benzene-d_6.

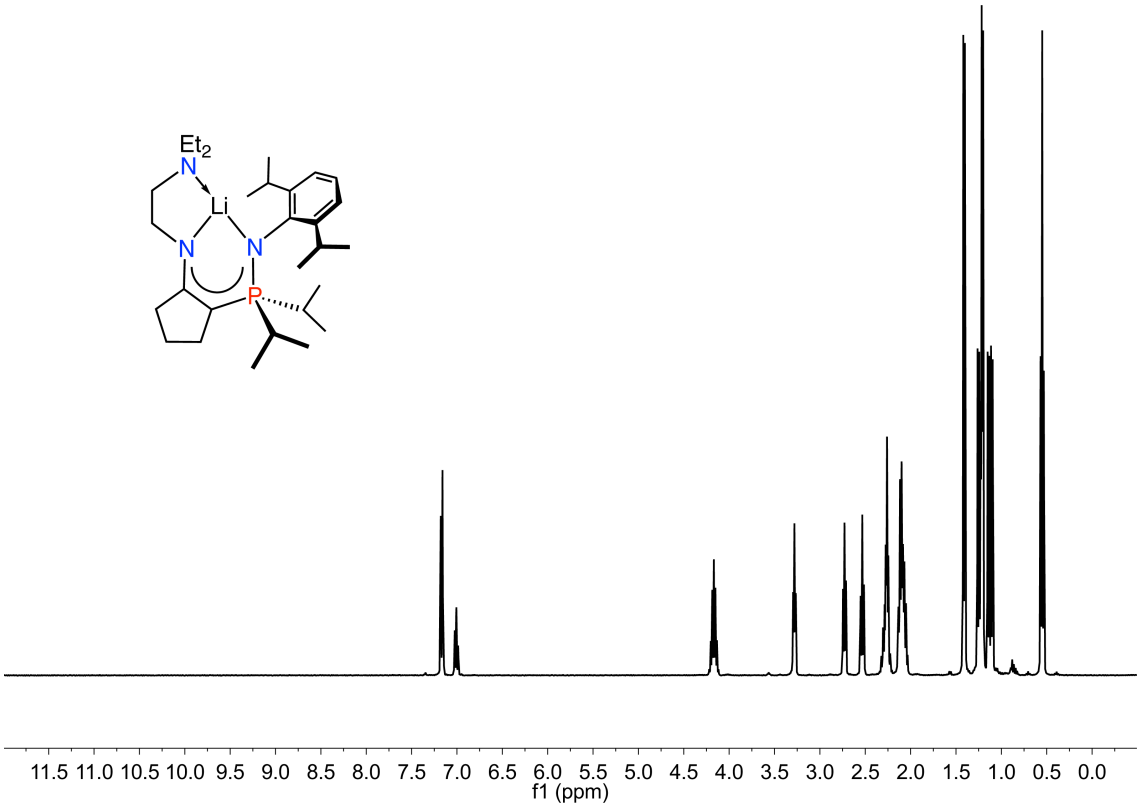

Figure S5. ^{1}H NMR spectrum of **4** in benzene-d_6.

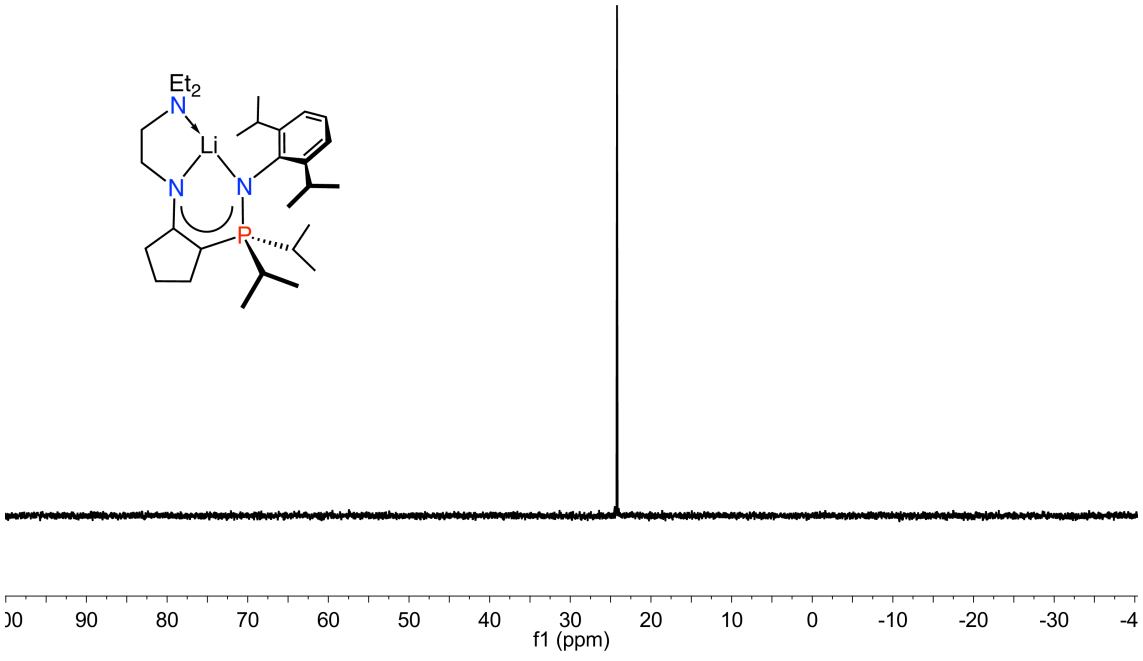

Figure S6. ^{31}P NMR spectrum of **4** in benzene-d_6.

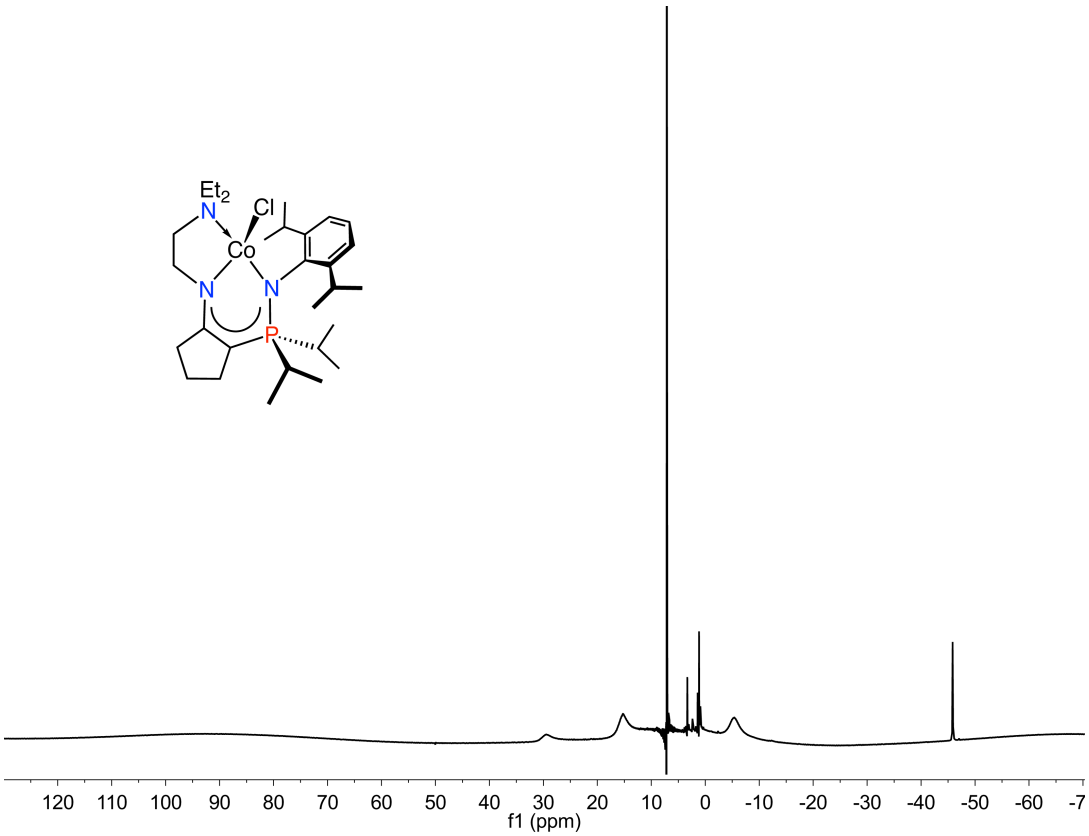

Figure S7. ^{1}H NMR spectrum of **5** in benzene-d_6.

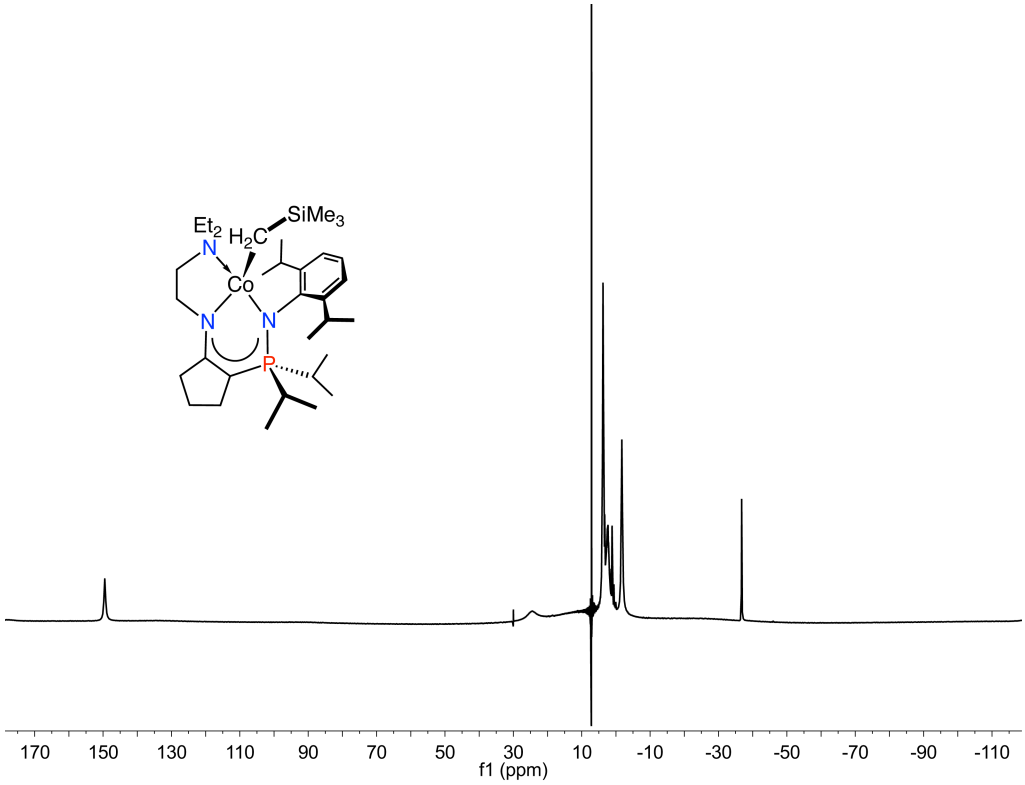

Figure S8. ^{1}H NMR spectrum of **6** in benzene-d_6.

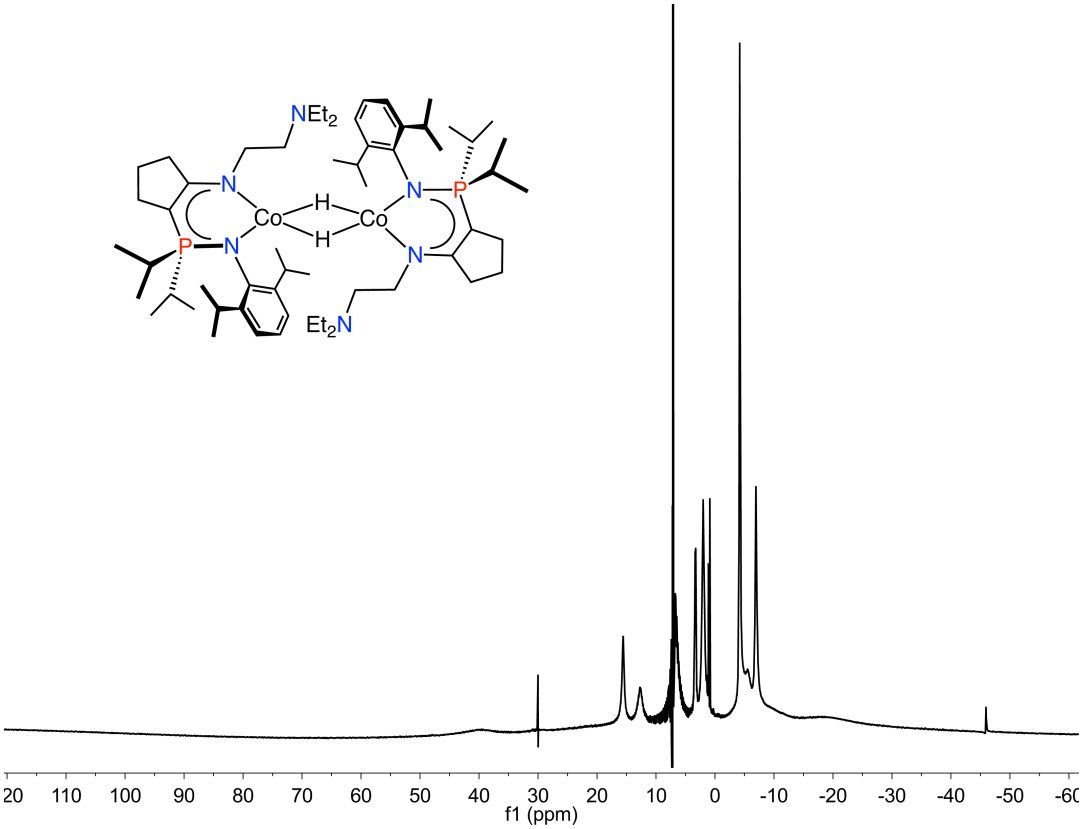

Figure S9. ^{1}H NMR spectrum of **7** in benzene-d_6.

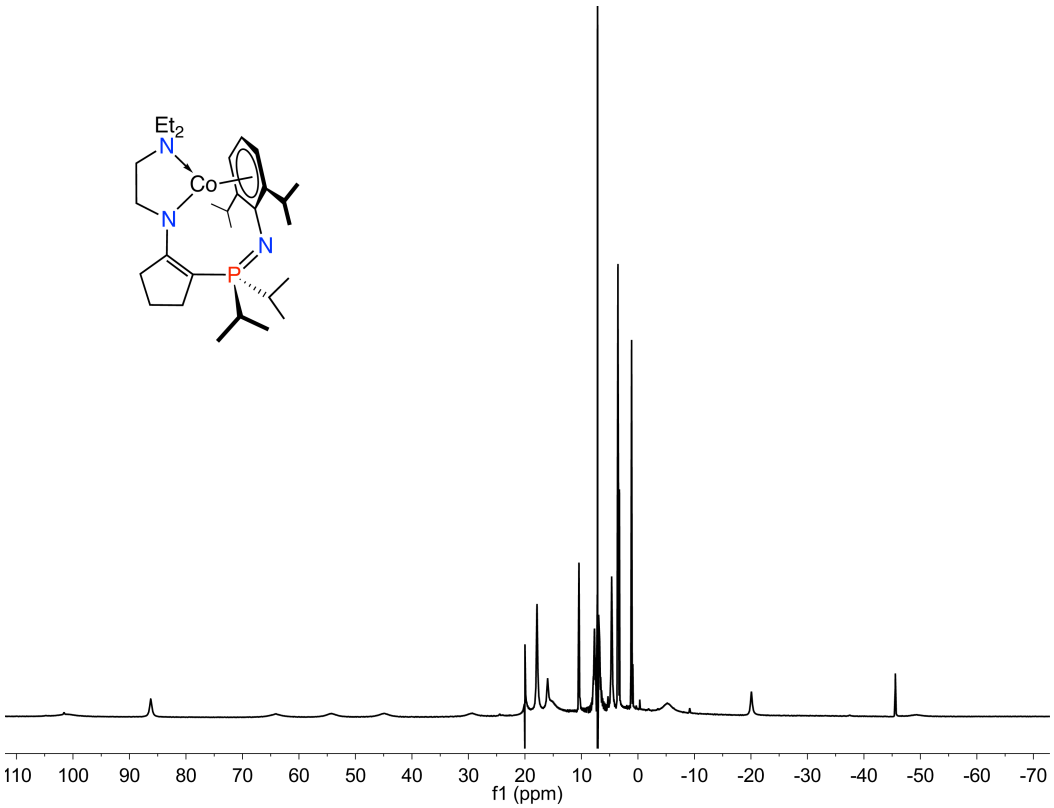

Figure S10. ^{1}H NMR spectrum of **8** in benzene-d_6.

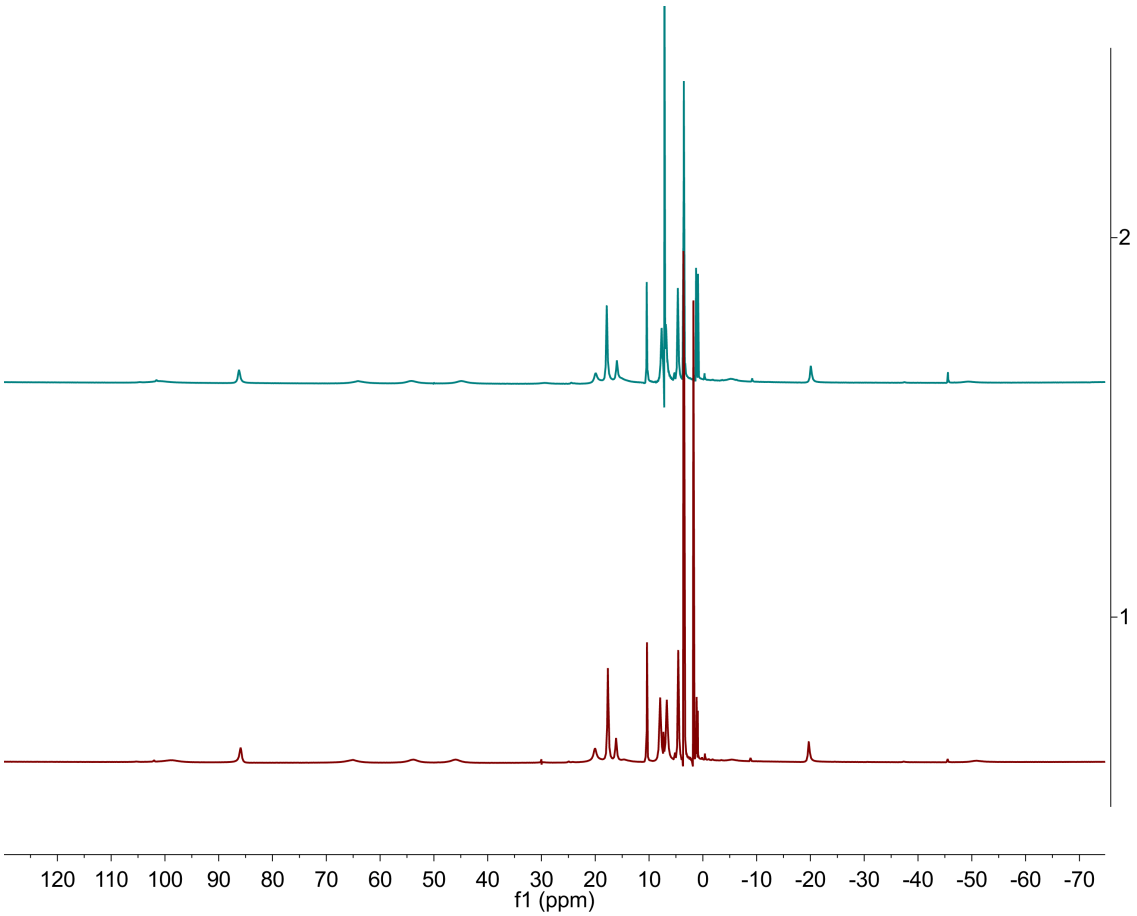

Figure S11. ^{1}H NMR spectra of **8** in benzene-d_6 (top) and in THF-d_8 (bottom).

Table S1. Crystallographic and structure refinement data for compounds **3**, **4**, **5**, **6**, **7** and **8**.

Compound	$HNNpN^{DIPP}$	$LiNNpN^{DIPP}$	κ^3-$(NNpN^{DIPP})CoCl$	$[\kappa^2$-$(NNpN^{DIPP})Co]_2(\mu$-$H)_2$	κ^3-$(NNpN^{DIPP})Co(CH_2SiMe_3)$	$\kappa^2:\eta^6$-$(NNpN^{DIPP})Co$
Chemical formula	$C_{29}H_{52}N_3P$	$C_{29}H_{51}LiN_3P$	$C_{29}H_{51}N_3PCoCl\ 0.5(C_4H_{10}O)$	$C_{58}H_{104}Co_2N_6P_2$	$C_{33}H_{62}CoN_3PSi$	$C_{29}H_{51}CoN_3P$
Formula weight	473.70	479.63	604.13	1065.33	618.15	529.61
Temp (K)	90	90	90	90	90	90
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$	P-1	C2/c	$P2_1/n$	$P2_1/c$
a / Å	11.2330(10)	13.8468(9)	12.7531(15)	27.716(7)	9.9978(5)	15.0712(4)
b / Å	17.5636(15)	13.3188(9)	15.1301(18)	10.304(3)	20.9247(11)	9.4570(3)
c / Å	14.7023(13)	15.9724(11)	18.634(2)	25.239(9)	16.7898(9)	19.8154(5)
α / °			105.750(6)			
β / °	93.445(2)	95.626(4)	107.780(6)	122.438(5)	93.751(2)	95.7230(10)
γ / °			90.106(6)			
V / Å^3	2895.4(4)	2931.5(3)	3281.1(7)	6083(3)	3504(3)	2810(14)
Z	4	4	4	4	4	4
D_{calc}/g cm^{-3}	1.087	1.084	1.223	1.1632	1.173	1.252
μ(Mo-Kα) / mm^{-1}	0.115	0.114	0.678	0.637	0.594	0.689
F(000)	1048	1056	1304	2316	1348	1144
Reflections collected	34799	85130	34822	52628	28373	16600
Independent reflections	8522	11949	11225	7013	7191	6244
R(int)	0.0472	0.0383	0.0484	0.0359	0.0468	0.0333
R1 ($I > 2\sigma(I)$)	0.0405	0.0568	0.0885	0.0284	0.0471	0.0349
R1 (all)	0.0575	0.0791	0.1090	0.0348	0.0587	0.0449
w*R*2 (all)	0.1044	0.1747	0.2446	0.0745	0.1284	0.0846
GOF	1.030	1.027	1.046	1.050	1.067	1.048
CCD number	1502794	1522303	1522304	1522305	1502796	1502795

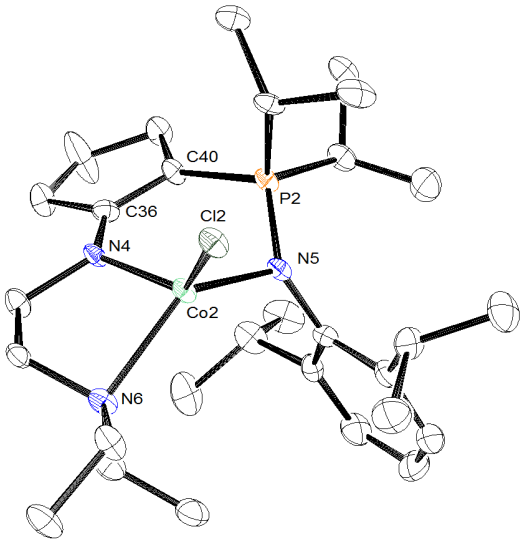

Figure S12. ORTEP diagram of the other independent molecule of κ^3-$(NNpN^{DIPP})CoCl$ **5**; selected bond lengths (Å) and bond angles (˚): Co2–Cl2 2.2643(15), Co2–N6 2.163(5), Co2–N4 1.951(4), Co2–N5 2.021(5), P2–C40 1.754(6), C36–C40 1.384(8), N4–C36 1.350(7), N6–Co2–Cl2 101.40(13), N4–Co2–Cl2 127.93(15), N4–Co2–N6 84.70(19), N4–Co2–N5 98.01(19), N5–Co2–Cl2 112.13(14), N5–Co2–N6 133.62(19).

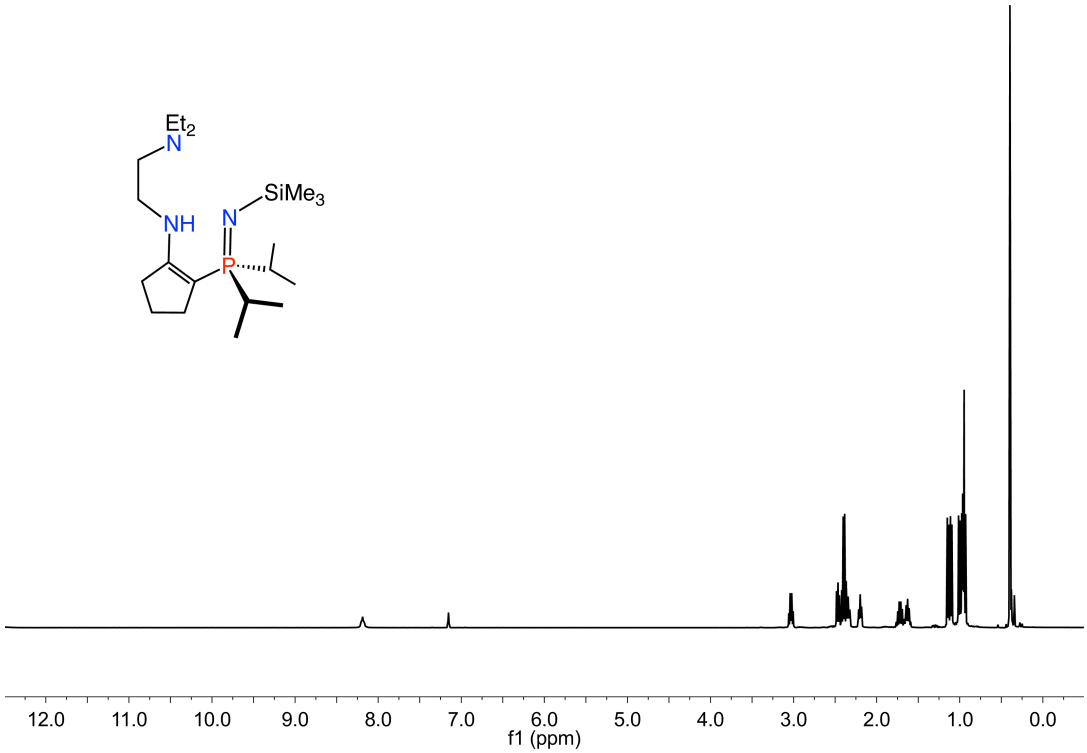

Figure S13. ^{1}H NMR spectrum of **9** in benzene-d_6

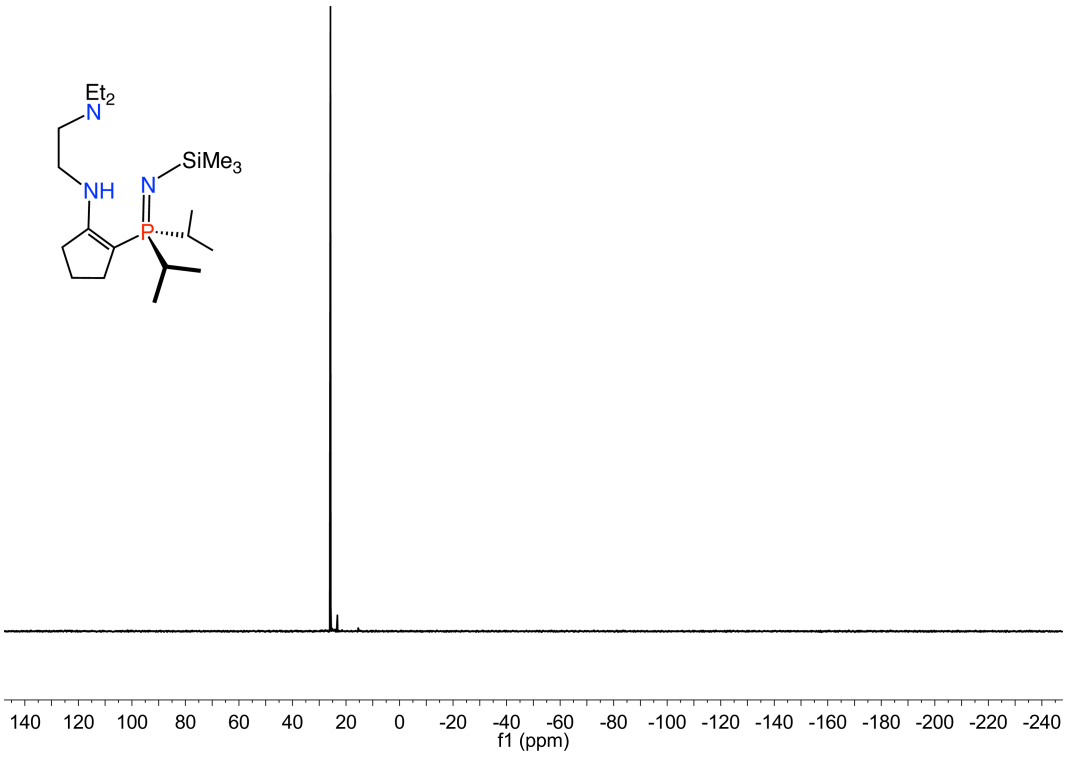

Figure S14. ^{31}P NMR spectrum of **9** in benzene-d_6

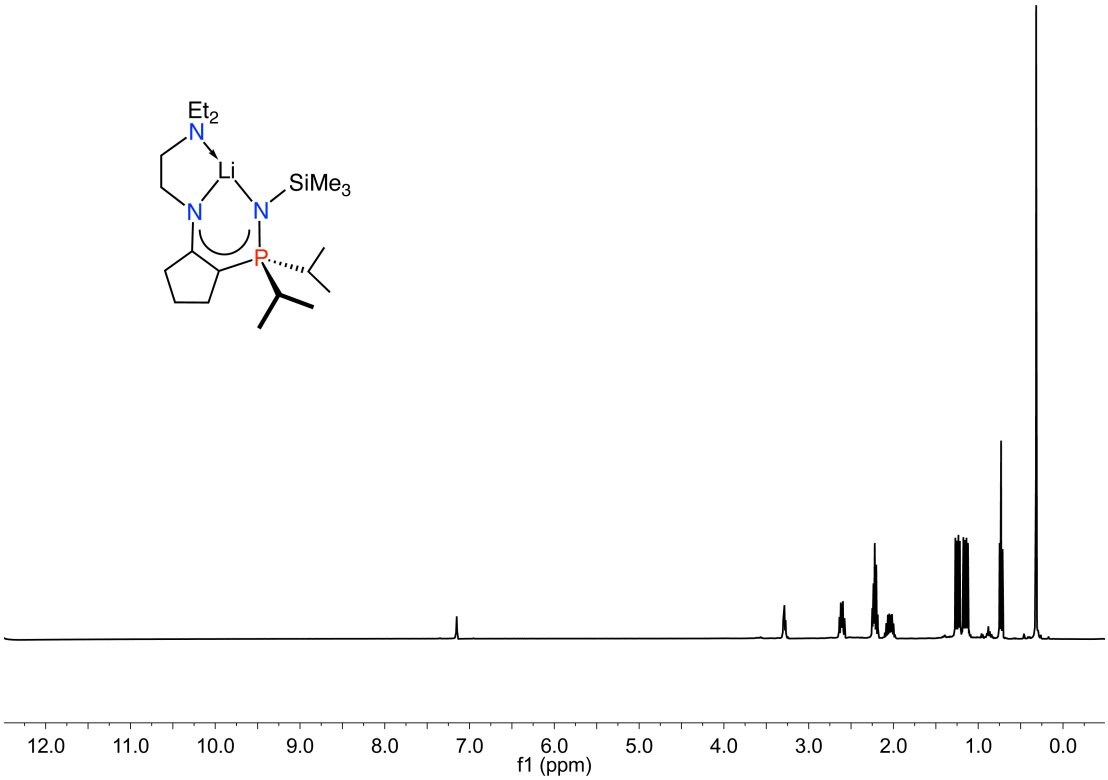

Figure S15. ^{1}H NMR spectrum of **10** in benzene-d_6.

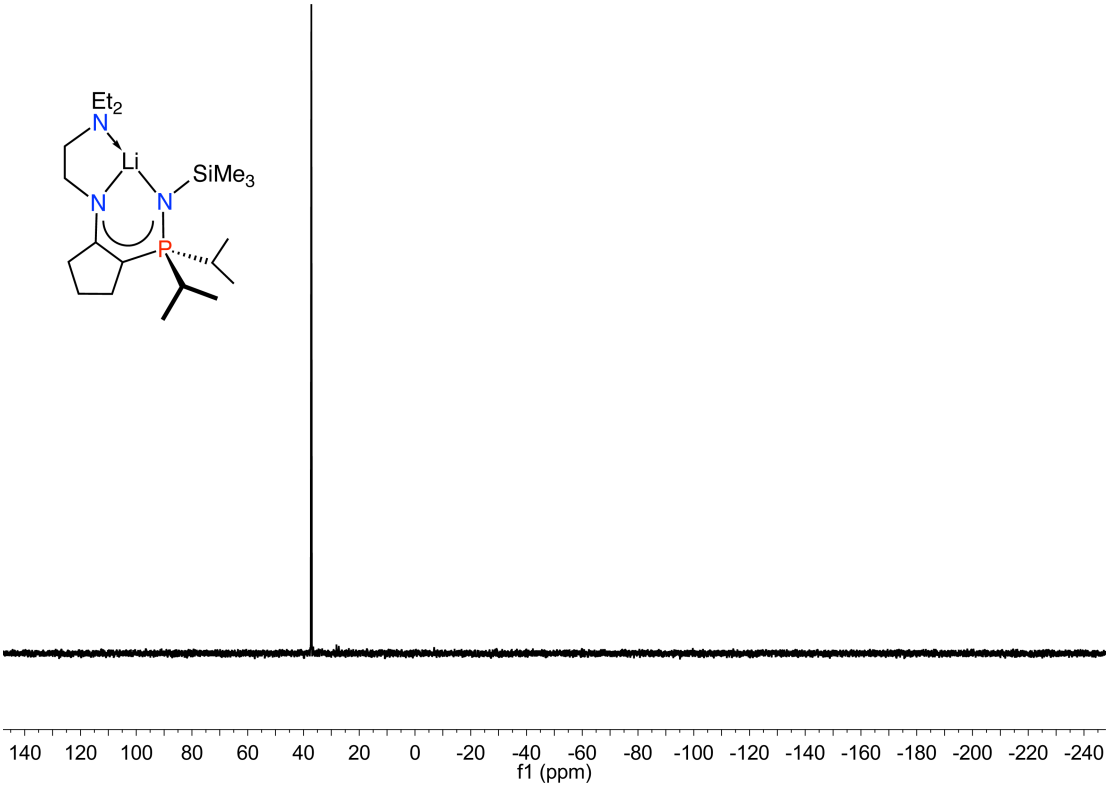

Figure S16. ^{31}P NMR spectrum of **10** in benzene-d_6.

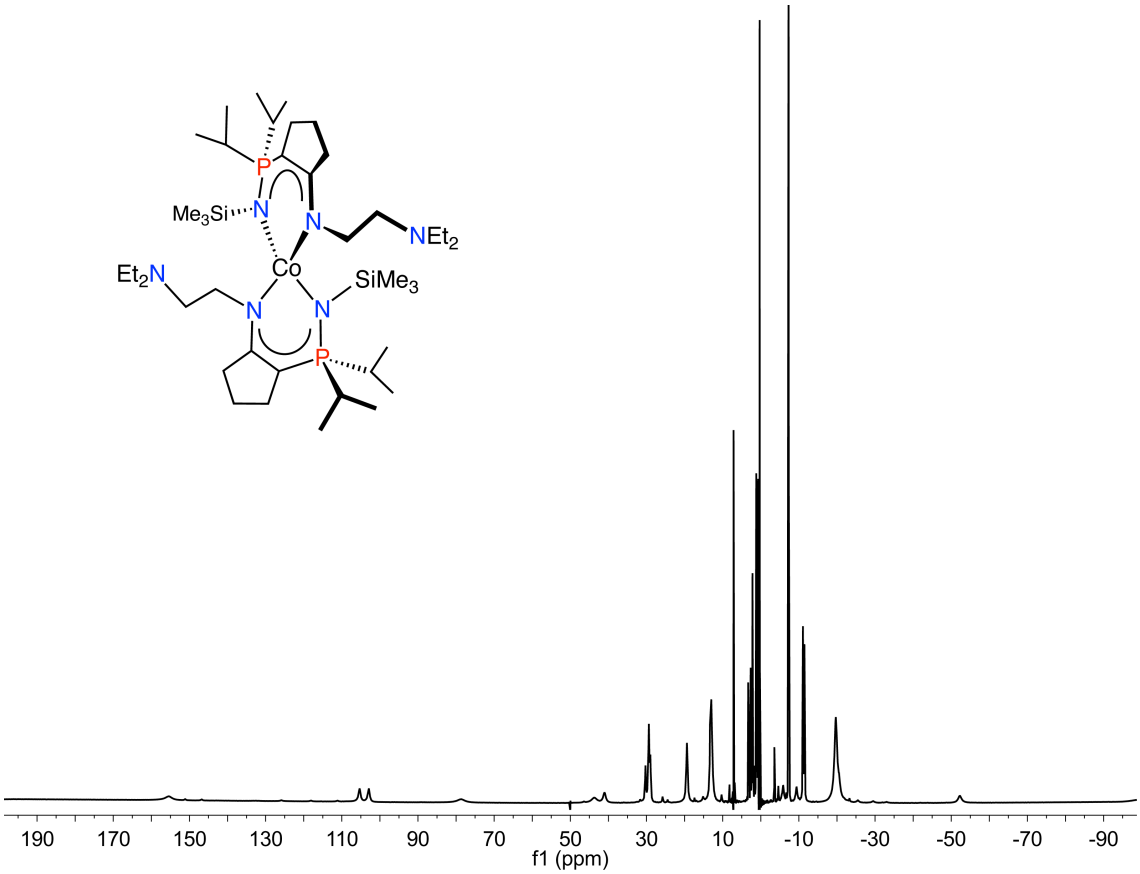

Figure S17. [1]H NMR spectrum of **11** in benzene-d_6.

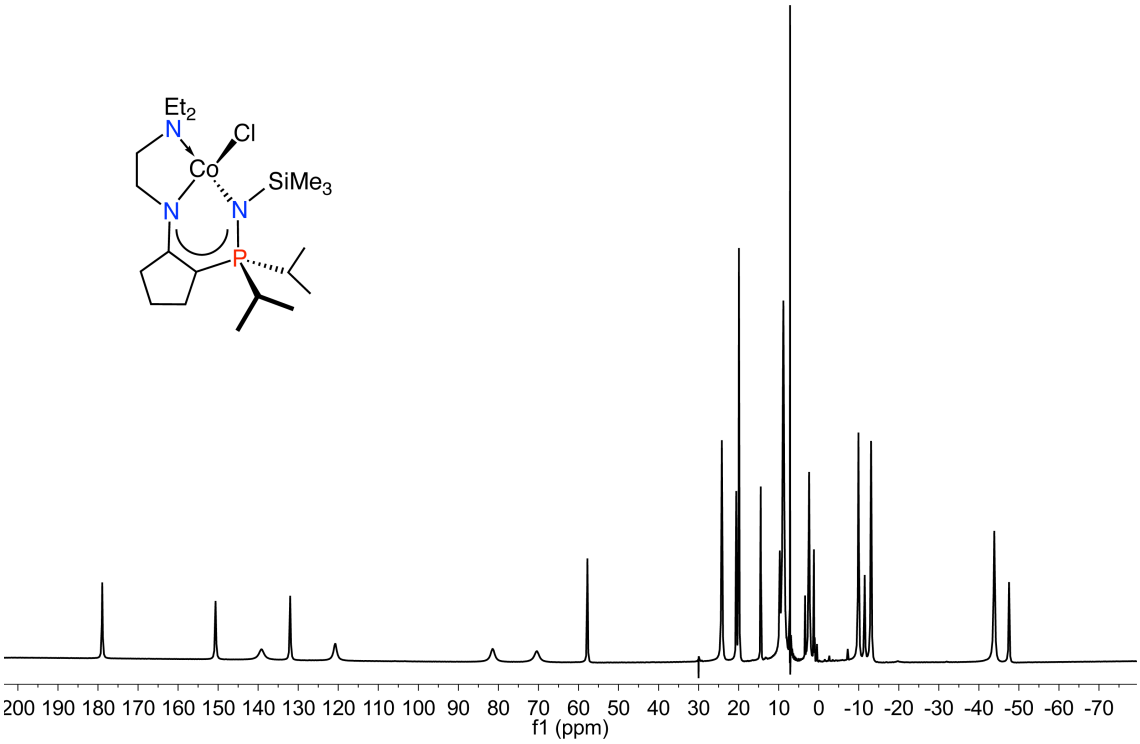

Figure S18. [1]H NMR spectrum of **12** in benzene-d_6. Because this complex is tetrahedral and asymmetric, one would expect 21 resonances; although we are unable to assign the peaks, the number of peaks approximates that predicted and so confirms the structure in solution.

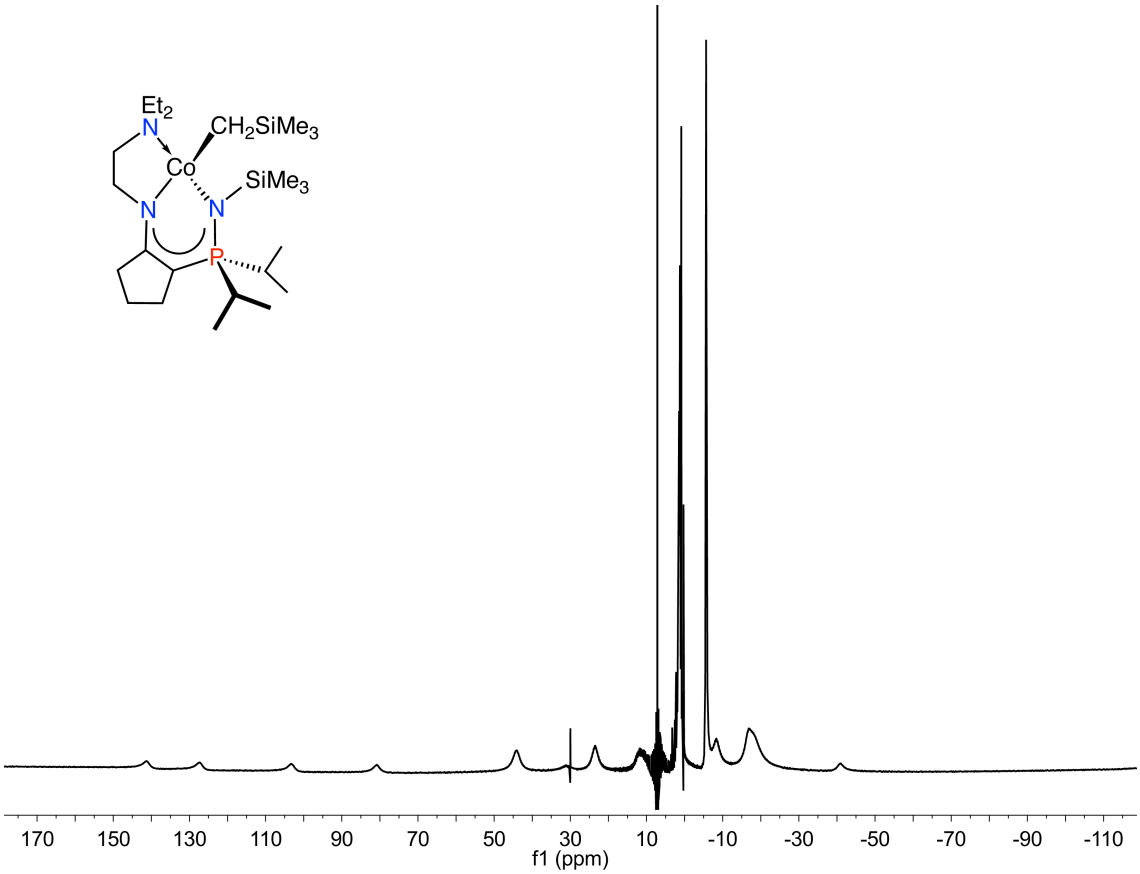

Figure S19. ^{1}H NMR spectrum of **13** in benzene-d_6.

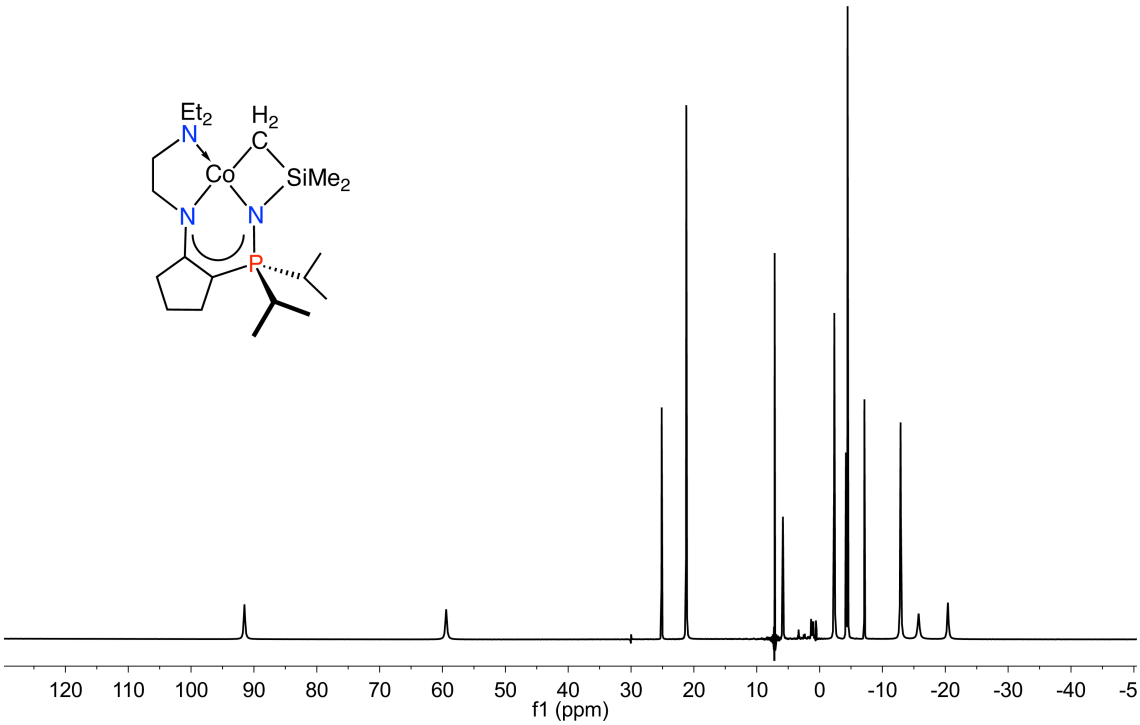

Figure S20. ^{1}H NMR spectrum of **14** in benzene-d_6. Because this complex is square planar, one would expect 12 distinct resonances; although we are unable to assign the peaks, the number of peaks approximates that predicted and so confirms the structure in solution.

Table S2. Crystallographic and structure refinement data for compounds **10**, **11**, **13** and **14**.

Compound	Li(NNpN^{TMS})	κ^2-(NNpN^{TMS})$_2$Co	κ^3-(NNpN^{TMS})Co(CH$_2$SiMe$_3$)	κ^4-(NNpNSiMe$_2$CH$_2$)Co
Chemical formula	$C_{20}H_{43}LiN_3PSi$	$C_{20}H_{43}Co_{0.5}N_3PSi$	$C_{24}H_{54}N_3CoPSi_2$	$C_{20}H_{42}CoN_3PSi$
Formula weight	391.58	414.10	530.79	442.55
Temp (K)	90	90	90	90
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic
Space group	P-1	$P2_1/c$	P-1	$P2_1/c$
a / Å	8.9369(5)	18.6761(9)	10.9373(5)	12.8978(12)
b / Å	10.3626(6)	10.0679(4)	11.4001(5)	10.1985(10)
c / Å	13.9495(7)	25.3409(12)	12.5228(6)	18.5025(18)
α / °	98.205(2)		81.580(2)	
β / °	95.099(2)	96.5240(10)	84.062(2)	107.622(3)
γ / °	110.635(11)		80.956(2)	
V / Å^3	1182(11)	4734(4)	1520.21(12)	2319.6(4)
Z	2	8	2	4
D_{calc}/g cm^{-3}	1.0993	1.162	1.1595	1.267
μ(Mo-Kα) / mm^{-1}	0.175	0.514	0.712	0.870
F(000)	432.5	1812	579.4	956
Reflections collected	18376	113854	40788	72213
Independent reflections	4835	28474	9904	17933
R(int)	0.0276	0.0740	0.0549	0.0555
R1 ($I > 2\sigma(I)$)	0.0295	0.0446	0.0367	0.0357
R1 (all)	0.0329	0.0858	0.0549	0.0617
w*R*2 (all)	0.0785	0.1133	0.0881	0.0871
GOF	1.036	1.030	1.025	1.018
CCD number	1522306	1522309	1522307	1522308

Table S3. Selected bond distances in the N1–C7–C11–P1–N2 ligand backbone for the indicated complexes

	3	**4**	**5**	**6**	**7**	**8**	**10**	**11**	**13**	**14**
N1–C7	1.3611(15)	1.3228(17)	1.350(7) 1.345(8)	1.337(3)	1.3405(18)	1.359(2)	1.3259(15)	1.3349(13) 1.3497(13)	1.3328(18)	1.3381(9)
C7–C11	1.3623(16)	1.4050(16)	1.384(8) 1.396(8)	1.384(3)	1.390(2)	1.379(2)	1.4003(16)	1.3924(15) 1.3827(15)	1.3842(19)	1.3880(10)
C11–P1	1.7783(12)	1.7544(12)	1.754(6) 1.755(6)	1.763(2)	1.7498(15)	1.7714(17)	1.7552(12)	1.7439(11) 1.7563(11)	1.7584(14)	1.7382(8)
P1–N2	1.5626(10)	1.6093(11)	1.624(5) 1.627(5)	1.6271(19)	1.6195(11)	1.5820(15)	1.5994(10)	1.6181(9) 1.6202(9)	1.6137(12)	1.5940(6)

X-ray Crystallographic Structure and Refinement Data

Single crystal X-ray diffraction data was collected on a Bruker (X8 or DUO) Apex II diffractometer equipped with a graphite (X8) or TRIUMPH (DUO) monochromator, using Mo Kα radiation (λ = 0.71073 Å), and integrated using the Bruker SAINT software package.[1] Suitable single crystals were selected, coated in Fomblin oil and mounted on a glass fiber. All absorption corrections were performed using the multi-scan technique (SADABS).[2] Structures were solved by direct methods and refined using the SHELXL[3] and OLEX2[4] software packages. All non-hydrogen atoms were refined anisotropically unless otherwise noted. All hydrogen atoms were placed in calculated positions and assigned to an isotropic displacement parameter, unless otherwise noted; hydrogen atoms so specified were located in the difference map and were refined isotropically.

(1) SAINT. Version 7.03A. Bruker AXS Inc. Madison, Wisconsin, USA (1997-2003).
(2) SADABS. Bruker Nonius area detector scaling and absorption correction - V2.10. Bruker AXS Inc. Madison, Wisconsin, USA (2003).
(3) G. Sheldrick, *Acta Crystallogr. A* **2008**, *64*, 112.
(4) O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard, H. Puschmann, *J. Appl. Cryst.* **2009**, *42*, 229.