Supporting Information

Phosphine/Thiolate Containing Dinitrosyl Cobalt Complexes (DNCCs): Synthesis, Characterization, Interconversion, X-ray Diffraction Identification and Its NO Releasing

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Table S1. Crystal data and structure refinement for $(PPh_3)(CO)_2Co(NO)$ (**1**)

Identification code	ic17097	
Empirical formula	C20 H15 Co N O3 P	
Formula weight	407.23	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.1780(7) Å	α = 62.4838(14)°.
	b = 10.4315(7) Å	β = 78.8115(15)°.
	c = 10.9687(8) Å	γ = 64.1468(15)°.
Volume	929.42(11) $Å^3$	
Z	2	
Density (calculated)	1.455 Mg/m^3	
Absorption coefficient	1.028 mm^{-1}	
F(000)	416	
Crystal size	0.25 x 0.20 x 0.20 mm^3	
Theta range for data collection	2.09 to 27.50°.	
Index ranges	-13<=h<=13, -13<=k<=13, -14<=l<=14	
Reflections collected	12097	
Independent reflections	4269 [R(int) = 0.0302]	
Completeness to theta = 27.50°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8208 and 0.7832	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4269 / 0 / 235	
Goodness-of-fit on F^2	1.033	
Final R indices [I>2sigma(I)]	R1 = 0.0388, wR2 = 0.0946	
R indices (all data)	R1 = 0.0469, wR2 = 0.0993	
Largest diff. peak and hole	0.330 and -0.626 e.$Å^{-3}$	

Table S2. Bond lengths [Å] and angles [°] for **1**

Co-NC2	1.719(2)	C(1)-Co-P(1)	105.38(7)
Co-NC1	1.737(2)	C(8)-P(1)-C(14)	103.57(9)
Co-C(1)	1.771(2)	C(8)-P(1)-C(2)	102.83(9)
Co-P(1)	2.2181(5)	C(14)-P(1)-C(2)	103.56(9)
P(1)-C(8)	1.8216(19)	C(8)-P(1)-Co	116.91(6)
P(1)-C(14)	1.8232(19)	C(14)-P(1)-Co	114.73(6)
P(1)-C(2)	1.826(2)	C(2)-P(1)-Co	113.59(7)
C(1)-O(1)	1.134(3)	O(1)-C(1)-Co	178.6(2)
NC1-O(2)	1.141(3)	O(2)-NC1-Co	178.67(19)
NC2-O(3)	1.143(3)	O(3)-NC2-Co	177.9(3)
C(2)-C(7)	1.386(3)	C(7)-C(2)-C(3)	119.18(19)
C(2)-C(3)	1.391(3)	C(7)-C(2)-P(1)	123.20(17)
C(3)-C(4)	1.382(3)	C(3)-C(2)-P(1)	117.62(16)
C(4)-C(5)	1.369(4)	C(4)-C(3)-C(2)	120.1(2)
C(5)-C(6)	1.377(4)	C(5)-C(4)-C(3)	120.4(2)
C(6)-C(7)	1.387(3)	C(4)-C(5)-C(6)	120.0(2)
C(8)-C(9)	1.384(3)	C(5)-C(6)-C(7)	120.2(2)
C(8)-C(13)	1.389(3)	C(2)-C(7)-C(6)	120.1(2)
C(9)-C(10)	1.384(3)	C(9)-C(8)-C(13)	118.99(18)
C(10)-C(11)	1.373(3)	C(9)-C(8)-P(1)	122.02(15)
C(11)-C(12)	1.379(3)	C(13)-C(8)-P(1)	118.98(15)
C(12)-C(13)	1.381(3)	C(8)-C(9)-C(10)	120.4(2)
C(14)-C(15)	1.389(3)	C(11)-C(10)-C(9)	120.2(2)
C(14)-C(19)	1.397(3)	C(10)-C(11)-C(12)	119.9(2)
C(15)-C(16)	1.388(3)	C(11)-C(12)-C(13)	120.1(2)
C(16)-C(17)	1.377(3)	C(12)-C(13)-C(8)	120.4(2)
C(17)-C(18)	1.382(3)	C(15)-C(14)-C(19)	118.97(18)
C(18)-C(19)	1.377(3)	C(15)-C(14)-P(1)	122.64(15)
		C(19)-C(14)-P(1)	118.37(15)
NC2-Co-NC1	116.78(11)	C(16)-C(15)-C(14)	120.2(2)
NC2-Co-C(1)	113.47(11)	C(17)-C(16)-C(15)	120.2(2)
NC1-Co-C(1)	110.77(10)	C(16)-C(17)-C(18)	120.0(2)
NC2-Co-P(1)	105.06(7)	C(19)-C(18)-C(17)	120.2(2)
NC1-Co-P(1)	104.07(7)	C(18)-C(19)-C(14)	120.4(2)

Table S3. Crystal data and structure refinement for $(PPh_3)_2(CO)Co(NO)$ **(2)**

Identification code	ch17594	
Empirical formula	C37 H30 Co N O2 P2	
Formula weight	641.49	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 2/c	
Unit cell dimensions	a = 11.6879(3) Å	α = 90°.
	b = 8.1606(3) Å	β = 106.191(2)°.
	c = 17.0513(6) Å	γ = 90°.
Volume	1561.85(9) $Å^3$	
Z	2	
Density (calculated)	1.364 Mg/m^3	
Absorption coefficient	0.686 mm^{-1}	
F(000)	664	
Crystal size	0.30 x 0.28 x 0.04 mm^3	
Theta range for data collection	2.49 to 25.08°.	
Index ranges	-13<=h<=13, -8<=k<=9, -20<=l<=19	
Reflections collected	10581	
Independent reflections	2772 [R(int) = 0.0369]	
Completeness to theta = 25.08°	99.8 %	
Absorption correction	multi-scan	
Max. and min. transmission	0.9731 and 0.8206	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2772 / 0 / 203	
Goodness-of-fit on F^2	1.087	
Final R indices [I>2sigma(I)]	R1 = 0.0391, wR2 = 0.0896	
R indices (all data)	R1 = 0.0553, wR2 = 0.0978	
Largest diff. peak and hole	0.547 and -0.312 $e.Å^{-3}$	

Table S4. Bond lengths [Å] and angles [°] for **2**

C(2)-C(7)	1.390(3)	Co(1)-C(1)	1.605(9)
C(2)-C(3)	1.396(3)	Co(1)-N(1)#1	1.793(8)
C(2)-P(1)	1.833(2)	Co(1)-N(1)	1.793(8)
C(7)-C(6)	1.383(4)	Co(1)-P(1)	2.2213(6)
C(7)-H(7)	0.9500	Co(1)-P(1)#1	2.2213(6)
C(6)-C(5)	1.382(4)	C(1)-O(1)	1.14(3)
C(6)-H(6)	0.9500	N(1)-O(1')	1.20(3)
C(5)-C(4)	1.375(4)		
C(5)-H(5)	0.9500	C(7)-C(2)-C(3)	118.4(2)
C(4)-C(3)	1.388(4)	C(7)-C(2)-P(1)	118.51(18)
C(4)-H(4)	0.9500	C(3)-C(2)-P(1)	123.07(19)
C(3)-H(3)	0.9500	C(6)-C(7)-C(2)	121.1(2)
C(8)-C(9)	1.383(4)	C(6)-C(7)-H(7)	119.4
C(8)-C(13)	1.393(3)	C(2)-C(7)-H(7)	119.4
C(8)-P(1)	1.830(2)	C(5)-C(6)-C(7)	120.0(2)
C(9)-C(10)	1.386(4)	C(5)-C(6)-H(6)	120.0
C(9)-H(9)	0.9500	C(7)-C(6)-H(6)	120.0
C(10)-C(11)	1.375(4)	C(4)-C(5)-C(6)	119.5(3)
C(10)-H(10)	0.9500	C(4)-C(5)-H(5)	120.2
C(11)-C(12)	1.380(4)	C(6)-C(5)-H(5)	120.2
C(11)-H(11)	0.9500	C(5)-C(4)-C(3)	120.8(2)
C(12)-C(13)	1.377(4)	C(5)-C(4)-H(4)	119.6
C(12)-H(12)	0.9500	C(3)-C(4)-H(4)	119.6
C(13)-H(13)	0.9500	C(4)-C(3)-C(2)	120.0(2)
C(14)-C(15)	1.385(4)	C(4)-C(3)-H(3)	120.0
C(14)-C(19)	1.388(4)	C(2)-C(3)-H(3)	120.0
C(14)-P(1)	1.838(2)	C(9)-C(8)-C(13)	118.4(2)
C(15)-C(16)	1.387(4)	C(9)-C(8)-P(1)	123.75(19)
C(15)-H(15)	0.9500	C(13)-C(8)-P(1)	117.85(19)
C(16)-C(17)	1.368(5)	C(8)-C(9)-C(10)	120.7(3)
C(16)-H(16)	0.9500	C(8)-C(9)-H(9)	119.7
C(17)-C(18)	1.373(4)	C(10)-C(9)-H(9)	119.7
C(17)-H(17)	0.9500	C(11)-C(10)-C(9)	120.2(3)
C(18)-C(19)	1.387(4)	C(11)-C(10)-H(10)	119.9
C(18)-H(18)	0.9500	C(9)-C(10)-H(10)	119.9
C(19)-H(19)	0.9500	C(10)-C(11)-C(12)	119.9(3)
Co(1)-C(1)#1	1.605(9)	C(10)-C(11)-H(11)	120.0

C(12)-C(11)-H(11)	120.0	C(14)-C(19)-H(19)	119.6
C(13)-C(12)-C(11)	119.9(3)	C(1)#1-Co(1)-C(1)	112.6(6)
C(13)-C(12)-H(12)	120.0	C(1)#1-Co(1)-N(1)#1	7.9(4)
C(11)-C(12)-H(12)	120.0	C(1)-Co(1)-N(1)#1	118.6(3)
C(12)-C(13)-C(8)	121.0(2)	C(1)#1-Co(1)-N(1)	118.6(3)
C(12)-C(13)-H(13)	119.5	C(1)-Co(1)-N(1)	7.9(4)
C(8)-C(13)-H(13)	119.5	N(1)#1-Co(1)-N(1)	125.1(4)
C(15)-C(14)-C(19)	118.6(2)	C(1)#1-Co(1)-P(1)	107.4(3)
C(15)-C(14)-P(1)	122.8(2)	C(1)-Co(1)-P(1)	107.8(3)
C(19)-C(14)-P(1)	118.56(19)	N(1)#1-Co(1)-P(1)	108.8(2)
C(14)-C(15)-C(16)	120.3(3)	N(1)-Co(1)-P(1)	100.4(2)
C(14)-C(15)-H(15)	119.9	C(1)#1-Co(1)-P(1)#1	107.8(3)
C(16)-C(15)-H(15)	119.9	C(1)-Co(1)-P(1)#1	107.4(3)
C(17)-C(16)-C(15)	120.3(3)	N(1)#1-Co(1)-P(1)#1	100.4(2)
C(17)-C(16)-H(16)	119.8	N(1)-Co(1)-P(1)#1	108.8(2)
C(15)-C(16)-H(16)	119.8	P(1)-Co(1)-P(1)#1	113.95(4)
C(16)-C(17)-C(18)	120.3(3)	O(1)-C(1)-Co(1)	171.3(16)
C(16)-C(17)-H(17)	119.9	O(1')-N(1)-Co(1)	175.7(14)
C(18)-C(17)-H(17)	119.9	C(8)-P(1)-C(2)	102.72(11)
C(17)-C(18)-C(19)	119.7(3)	C(8)-P(1)-C(14)	102.53(11)
C(17)-C(18)-H(18)	120.1	C(2)-P(1)-C(14)	101.93(11)
C(19)-C(18)-H(18)	120.1	C(8)-P(1)-Co(1)	117.82(8)
C(18)-C(19)-C(14)	120.7(3)	C(2)-P(1)-Co(1)	119.74(8)
C(18)-C(19)-H(19)	119.6	C(14)-P(1)-Co(1)	109.73(8)

Table S5. Crystal data and structure refinement for $[(PPh_3)_2Co(NO)_2][BF_4]$ (**3**)

Identification code	ic17409	
Empirical formula	C36 H30 B Co F4 N2 O2 P2	
Formula weight	730.30	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 9.4268(5) Å	α = 90°.
	b = 18.2553(9) Å	β = 101.5090(10)°.
	c = 20.3429(9) Å	γ = 90°.
Volume	3430.4(3) $Å^3$	
Z	4	
Density (calculated)	1.414 Mg/m^3	
Absorption coefficient	0.651 mm^{-1}	
F(000)	1496	
Crystal size	0.50 x 0.45 x 0.08 mm^3	
Theta range for data collection	1.51 to 27.50°.	
Index ranges	-12<=h<=12, -23<=k<=23, -26<=l<=25	
Reflections collected	26169	
Independent reflections	7876 [R(int) = 0.0358]	
Completeness to theta = 27.50°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9498 and 0.7368	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7876 / 0 / 433	
Goodness-of-fit on F^2	1.017	
Final R indices [I>2sigma(I)]	R1 = 0.0405, wR2 = 0.0972	
R indices (all data)	R1 = 0.0520, wR2 = 0.1032	
Largest diff. peak and hole	0.475 and -0.214 $e.Å^{-3}$	

Table S6. Bond lengths [Å] and angles [°] for **3**

Co-N(1)	1.662(2)	C(25)-C(30)	1.390(3)
Co-N(2)	1.6629(19)	C(26)-C(27)	1.384(3)
Co-P(2)	2.2552(5)	C(27)-C(28)	1.376(3)
Co-P(1)	2.3039(6)	C(28)-C(29)	1.374(3)
P(1)-C(13)	1.814(2)	C(29)-C(30)	1.384(3)
P(1)-C(1)	1.823(2)	C(31)-C(36)	1.391(3)
P(1)-C(7)	1.8258(19)	C(31)-C(32)	1.395(3)
P(2)-C(31)	1.8092(19)	C(32)-C(33)	1.387(3)
P(2)-C(19)	1.809(2)	C(33)-C(34)	1.372(4)
P(2)-C(25)	1.8121(19)	C(34)-C(35)	1.381(4)
N(1)-O(1)	1.144(3)	C(35)-C(36)	1.380(3)
N(2)-O(2)	1.155(2)	B(1)-F(3)	1.366(4)
C(1)-C(2)	1.389(3)	B(1)-F(1)	1.367(4)
C(1)-C(6)	1.393(3)	B(1)-F(2)	1.369(3)
C(2)-C(3)	1.385(3)	B(1)-F(4)	1.371(4)
C(3)-C(4)	1.372(4)		
C(4)-C(5)	1.373(4)	N(1)-Co-N(2)	128.76(10)
C(5)-C(6)	1.382(3)	N(1)-Co-P(2)	98.23(7)
C(7)-C(8)	1.383(3)	N(2)-Co-P(2)	101.11(7)
C(7)-C(12)	1.393(3)	N(1)-Co-P(1)	107.52(7)
C(8)-C(9)	1.389(3)	N(2)-Co-P(1)	110.90(7)
C(9)-C(10)	1.372(3)	P(2)-Co-P(1)	107.52(2)
C(10)-C(11)	1.378(4)	C(13)-P(1)-C(1)	104.90(10)
C(11)-C(12)	1.381(3)	C(13)-P(1)-C(7)	104.57(9)
C(13)-C(18)	1.392(3)	C(1)-P(1)-C(7)	102.72(9)
C(13)-C(14)	1.396(3)	C(13)-P(1)-Co	113.29(6)
C(14)-C(15)	1.384(3)	C(1)-P(1)-Co	118.56(7)
C(15)-C(16)	1.383(4)	C(7)-P(1)-Co	111.40(7)
C(16)-C(17)	1.370(4)	C(31)-P(2)-C(19)	105.79(9)
C(17)-C(18)	1.387(3)	C(31)-P(2)-C(25)	105.82(9)
C(19)-C(24)	1.385(3)	C(19)-P(2)-C(25)	104.42(9)
C(19)-C(20)	1.390(3)	C(31)-P(2)-Co	114.95(6)
C(20)-C(21)	1.381(3)	C(19)-P(2)-Co	115.10(7)
C(21)-C(22)	1.372(4)	C(25)-P(2)-Co	109.85(6)
C(22)-C(23)	1.376(4)	O(1)-N(1)-Co	169.54(19)
C(23)-C(24)	1.388(3)	O(2)-N(2)-Co	171.05(19)
C(25)-C(26)	1.383(3)	C(2)-C(1)-C(6)	118.6(2)

C(2)-C(1)-P(1)	120.20(17)	C(22)-C(21)-C(20)	119.5(2)
C(6)-C(1)-P(1)	121.06(16)	C(21)-C(22)-C(23)	120.6(2)
C(3)-C(2)-C(1)	120.5(2)	C(22)-C(23)-C(24)	120.0(2)
C(4)-C(3)-C(2)	120.3(2)	C(19)-C(24)-C(23)	120.0(2)
C(3)-C(4)-C(5)	119.8(2)	C(26)-C(25)-C(30)	119.24(18)
C(4)-C(5)-C(6)	120.6(2)	C(26)-C(25)-P(2)	121.27(15)
C(5)-C(6)-C(1)	120.3(2)	C(30)-C(25)-P(2)	119.44(15)
C(8)-C(7)-C(12)	119.22(19)	C(25)-C(26)-C(27)	119.9(2)
C(8)-C(7)-P(1)	120.28(15)	C(28)-C(27)-C(26)	120.5(2)
C(12)-C(7)-P(1)	120.36(16)	C(29)-C(28)-C(27)	119.9(2)
C(7)-C(8)-C(9)	120.2(2)	C(28)-C(29)-C(30)	120.0(2)
C(10)-C(9)-C(8)	119.9(2)	C(29)-C(30)-C(25)	120.3(2)
C(9)-C(10)-C(11)	120.6(2)	C(36)-C(31)-C(32)	119.57(19)
C(10)-C(11)-C(12)	119.8(2)	C(36)-C(31)-P(2)	117.94(15)
C(11)-C(12)-C(7)	120.3(2)	C(32)-C(31)-P(2)	122.40(16)
C(18)-C(13)-C(14)	119.21(19)	C(33)-C(32)-C(31)	119.5(2)
C(18)-C(13)-P(1)	120.34(16)	C(34)-C(33)-C(32)	120.4(2)
C(14)-C(13)-P(1)	120.01(16)	C(33)-C(34)-C(35)	120.5(2)
C(15)-C(14)-C(13)	120.1(2)	C(36)-C(35)-C(34)	119.8(2)
C(16)-C(15)-C(14)	120.0(2)	C(35)-C(36)-C(31)	120.2(2)
C(17)-C(16)-C(15)	120.4(2)	F(3)-B(1)-F(1)	107.9(3)
C(16)-C(17)-C(18)	120.2(2)	F(3)-B(1)-F(2)	110.9(2)
C(17)-C(18)-C(13)	120.1(2)	F(1)-B(1)-F(2)	107.8(3)
C(24)-C(19)-C(20)	118.97(19)	F(3)-B(1)-F(4)	111.4(3)
C(24)-C(19)-P(2)	122.08(16)	F(1)-B(1)-F(4)	108.3(3)
C(20)-C(19)-P(2)	118.75(15)	F(2)-B(1)-F(4)	110.3(2)
C(21)-C(20)-C(19)	120.8(2)		

Table S7. Crystal data and structure refinement for $(PPh_3)(SPh)Co(NO)_2$ (**4**)

Identification code	ic17462	
Empirical formula	C24 H20 Co N2 O2 P S	
Formula weight	490.38	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 9.7624(3) Å	α = 90°.
	b = 25.1828(7) Å	β = 116.6725(12)°.
	c = 10.4527(3) Å	γ = 90°.
Volume	2296.28(12) $Å^3$	
Z	4	
Density (calculated)	1.418 Mg/m^3	
Absorption coefficient	0.931 mm^{-1}	
F(000)	1008	
Crystal size	0.200 x 0.150 x 0.060 mm^3	
Theta range for data collection	1.617 to 27.499°.	
Index ranges	-12<=h<=12, -25<=k<=32, -11<=l<=13	
Reflections collected	12760	
Independent reflections	5257 [R(int) = 0.0500]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.946 and 0.836	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5257 / 0 / 280	
Goodness-of-fit on F^2	0.991	
Final R indices [I>2sigma(I)]	R1 = 0.0413, wR2 = 0.0899	
R indices (all data)	R1 = 0.0887, wR2 = 0.1143	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.402 and -0.387 $e.Å^{-3}$	

Table S8. Bond lengths [Å] and angles [°] for **4**

Co-N(2)	1.651(3)	N(1)-Co-P(1)	101.50(8)
Co-N(1)	1.663(3)	N(2)-Co-S(1)	112.10(8)
Co-P(1)	2.2419(8)	N(1)-Co-S(1)	115.95(9)
Co-S(1)	2.2633(8)	P(1)-Co-S(1)	91.27(3)
S(1)-C(1)	1.766(3)	C(1)-S(1)-Co	108.38(10)
P(1)-C(13)	1.816(3)	C(13)-P(1)-C(19)	104.70(12)
P(1)-C(19)	1.820(3)	C(13)-P(1)-C(7)	104.34(12)
P(1)-C(7)	1.823(3)	C(19)-P(1)-C(7)	106.05(12)
N(1)-O(1)	1.164(3)	C(13)-P(1)-Co	113.97(9)
N(2)-O(2)	1.162(3)	C(19)-P(1)-Co	112.50(9)
C(1)-C(2)	1.383(4)	C(7)-P(1)-Co	114.36(9)
C(1)-C(6)	1.395(4)	O(1)-N(1)-Co	163.0(2)
C(2)-C(3)	1.384(4)	O(2)-N(2)-Co	170.3(2)
C(3)-C(4)	1.379(4)	C(2)-C(1)-C(6)	118.3(3)
C(4)-C(5)	1.387(4)	C(2)-C(1)-S(1)	118.6(2)
C(5)-C(6)	1.388(4)	C(6)-C(1)-S(1)	123.0(2)
C(7)-C(12)	1.382(4)	C(1)-C(2)-C(3)	121.1(3)
C(7)-C(8)	1.394(4)	C(4)-C(3)-C(2)	120.4(3)
C(8)-C(9)	1.377(4)	C(3)-C(4)-C(5)	119.4(3)
C(9)-C(10)	1.378(4)	C(4)-C(5)-C(6)	120.1(3)
C(10)-C(11)	1.374(4)	C(5)-C(6)-C(1)	120.6(3)
C(11)-C(12)	1.389(4)	C(12)-C(7)-C(8)	119.5(3)
C(13)-C(14)	1.388(4)	C(12)-C(7)-P(1)	122.5(2)
C(13)-C(18)	1.402(4)	C(8)-C(7)-P(1)	118.0(2)
C(14)-C(15)	1.382(4)	C(9)-C(8)-C(7)	119.8(3)
C(15)-C(16)	1.365(4)	C(8)-C(9)-C(10)	120.5(3)
C(16)-C(17)	1.376(4)	C(11)-C(10)-C(9)	120.0(3)
C(17)-C(18)	1.384(4)	C(10)-C(11)-C(12)	120.1(3)
C(19)-C(20)	1.387(4)	C(7)-C(12)-C(11)	120.1(3)
C(19)-C(24)	1.392(4)	C(14)-C(13)-C(18)	119.0(3)
C(20)-C(21)	1.377(4)	C(14)-C(13)-P(1)	121.6(2)
C(21)-C(22)	1.383(4)	C(18)-C(13)-P(1)	119.1(2)
C(22)-C(23)	1.373(4)	C(15)-C(14)-C(13)	120.2(3)
C(23)-C(24)	1.381(4)	C(16)-C(15)-C(14)	120.7(3)
		C(15)-C(16)-C(17)	119.9(3)
N(2)-Co-N(1)	123.65(11)	C(16)-C(17)-C(18)	120.7(3)
N(2)-Co-P(1)	105.15(8)	C(17)-C(18)-C(13)	119.5(3)

C(20)-C(19)-C(24)	118.8(2)	C(20)-C(21)-C(22)	120.2(3)
C(20)-C(19)-P(1)	122.7(2)	C(23)-C(22)-C(21)	119.7(3)
C(24)-C(19)-P(1)	118.5(2)	C(22)-C(23)-C(24)	120.5(3)
C(21)-C(20)-C(19)	120.6(3)	C(23)-C(24)-C(19)	120.2(3)

Table S9. Crystal data and structure refinement for $[PPh_4][(SPh)_2Co(NO)_2]$ (**5**)

Identification code	a17474	
Empirical formula	C36 H30 Co N2 O2 P S2	
Formula weight	676.64	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 11.051(3) Å	α = 98.004(7)°.
	b = 16.554(5) Å	β = 92.466(6)°.
	c = 18.159(5) Å	γ = 97.493(7)°.
Volume	3255.1(17) $Å^3$	
Z	4	
Density (calculated)	1.381 Mg/m^3	
Absorption coefficient	0.740 mm^{-1}	
F(000)	1400	
Crystal size	0.29 x 0.14 x 0.02 mm^3	
Theta range for data collection	1.13 to 25.03°.	
Index ranges	-11<=h<=13, -19<=k<=18, -21<=l<=21	
Reflections collected	28704	
Independent reflections	11299 [R(int) = 0.0843]	
Completeness to theta = 25.03°	98.3 %	
Absorption correction	multi-scan	
Max. and min. transmission	0.9854 and 0.8140	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11299 / 3 / 793	
Goodness-of-fit on F^2	0.962	
Final R indices [I>2sigma(I)]	R1 = 0.0743, wR2 = 0.1051	
R indices (all data)	R1 = 0.1903, wR2 = 0.1345	
Largest diff. peak and hole	0.360 and -0.395 e.$Å^{-3}$	

Table S10. Bond lengths [Å] and angles [°] for **5**

C(1)-C(6)	1.374(7)	C(19)-C(24)	1.377(7)
C(1)-C(2)	1.374(7)	C(19)-S(4)	1.757(5)
C(1)-S(1)	1.760(6)	C(20)-C(21)	1.371(7)
C(2)-C(3)	1.369(7)	C(20)-H(20)	0.9500
C(2)-H(2)	0.9500	C(21)-C(22)	1.362(8)
C(3)-C(4)	1.350(7)	C(21)-H(21)	0.9500
C(3)-H(3)	0.9500	C(22)-C(23)	1.370(7)
C(4)-C(5)	1.352(9)	C(22)-H(22)	0.9500
C(4)-H(4)	0.9500	C(23)-C(24)	1.366(7)
C(5)-C(6)	1.380(9)	C(23)-H(23)	0.9500
C(5)-H(5)	0.9500	C(24)-H(24)	0.9500
C(6)-H(6)	0.9500	C(25)-C(30)	1.368(6)
C(7)-C(12)	1.381(7)	C(25)-C(26)	1.391(6)
C(7)-C(8)	1.382(6)	C(25)-P(1)	1.783(4)
C(7)-S(2)	1.745(6)	C(26)-C(27)	1.374(6)
C(8)-C(9)	1.384(7)	C(26)-H(26)	0.9500
C(8)-H(8)	0.9500	C(27)-C(28)	1.366(6)
C(9)-C(10)	1.365(8)	C(27)-H(27)	0.9500
C(9)-H(9)	0.9500	C(28)-C(29)	1.360(6)
C(10)-C(11)	1.343(8)	C(28)-H(28)	0.9500
C(10)-H(10)	0.9500	C(29)-C(30)	1.369(6)
C(11)-C(12)	1.388(7)	C(29)-H(29)	0.9500
C(11)-H(11)	0.9500	C(30)-H(30)	0.9500
C(12)-H(12)	0.9500	C(31)-C(32)	1.378(6)
C(13)-C(14)	1.377(7)	C(31)-C(36)	1.379(6)
C(13)-C(18)	1.394(7)	C(31)-P(1)	1.774(5)
C(13)-S(3)	1.748(6)	C(32)-C(33)	1.380(7)
C(14)-C(15)	1.378(7)	C(32)-H(32)	0.9500
C(14)-H(14)	0.9500	C(33)-C(34)	1.364(7)
C(15)-C(16)	1.362(7)	C(33)-H(33)	0.9500
C(15)-H(15)	0.9500	C(34)-C(35)	1.368(7)
C(16)-C(17)	1.385(8)	C(34)-H(34)	0.9500
C(16)-H(16)	0.9500	C(35)-C(36)	1.372(6)
C(17)-C(18)	1.373(8)	C(35)-H(35)	0.9500
C(17)-H(17)	0.9500	C(36)-H(36)	0.9500
C(18)-H(18)	0.9500	C(37)-C(42)	1.376(6)
C(19)-C(20)	1.370(6)	C(37)-C(38)	1.379(6)

C(37)-P(1)	1.784(5)	C(56)-H(56)	0.9500
C(38)-C(39)	1.369(6)	C(57)-C(58)	1.359(7)
C(38)-H(38)	0.9500	C(57)-H(57)	0.9500
C(39)-C(40)	1.359(7)	C(58)-C(59)	1.359(7)
C(39)-H(39)	0.9500	C(58)-H(58)	0.9500
C(40)-C(41)	1.365(7)	C(59)-C(60)	1.386(6)
C(40)-H(40)	0.9500	C(59)-H(59)	0.9500
C(41)-C(42)	1.378(7)	C(60)-H(60)	0.9500
C(41)-H(41)	0.9500	C(61)-C(62)	1.377(6)
C(42)-H(42)	0.9500	C(61)-C(66)	1.386(6)
C(43)-C(48)	1.383(6)	C(61)-P(2)	1.782(5)
C(43)-C(44)	1.385(5)	C(62)-C(63)	1.364(6)
C(43)-P(1)	1.779(5)	C(62)-H(62)	0.9500
C(44)-C(45)	1.373(6)	C(63)-C(64)	1.356(7)
C(44)-H(44)	0.9500	C(63)-H(63)	0.9500
C(45)-C(46)	1.368(6)	C(64)-C(65)	1.365(7)
C(45)-H(45)	0.9500	C(64)-H(64)	0.9500
C(46)-C(47)	1.363(6)	C(65)-C(66)	1.375(6)
C(46)-H(46)	0.9500	C(65)-H(65)	0.9500
C(47)-C(48)	1.374(6)	C(66)-H(66)	0.9500
C(47)-H(47)	0.9500	C(67)-C(72)	1.376(6)
C(48)-H(48)	0.9500	C(67)-C(68)	1.384(6)
C(49)-C(50)	1.374(6)	C(67)-P(2)	1.774(5)
C(49)-C(54)	1.383(6)	C(68)-C(69)	1.374(6)
C(49)-P(2)	1.787(5)	C(68)-H(68)	0.9500
C(50)-C(51)	1.370(6)	C(69)-C(70)	1.367(7)
C(50)-H(50)	0.9500	C(69)-H(69)	0.9500
C(51)-C(52)	1.370(7)	C(70)-C(71)	1.366(7)
C(51)-H(51)	0.9500	C(70)-H(70)	0.9500
C(52)-C(53)	1.348(7)	C(71)-C(72)	1.369(6)
C(52)-H(52)	0.9500	C(71)-H(71)	0.9500
C(53)-C(54)	1.382(7)	C(72)-H(72)	0.9500
C(53)-H(53)	0.9500	N(1)-O(1)	1.130(5)
C(54)-H(54)	0.9500	N(1)-Co(1)	1.624(6)
C(55)-C(60)	1.386(6)	N(2)-O(2)	1.116(5)
C(55)-C(56)	1.388(6)	N(2)-Co(1)	1.684(6)
C(55)-P(2)	1.773(5)	N(3)-O(3)	1.112(5)
C(56)-C(57)	1.371(6)	N(3)-Co(2)	1.637(6)

N(4)-O(4)	1.124(4)	C(10)-C(11)-H(11)	119.4
N(4)-Co(2)	1.650(5)	C(12)-C(11)-H(11)	119.4
S(1)-Co(1)	2.2544(19)	C(7)-C(12)-C(11)	121.3(5)
S(2)-Co(1)	2.2479(14)	C(7)-C(12)-H(12)	119.3
S(3)-Co(2)	2.2569(17)	C(11)-C(12)-H(12)	119.3
S(4)-Co(2)	2.2467(17)	C(14)-C(13)-C(18)	117.4(6)
		C(14)-C(13)-S(3)	123.8(5)
C(6)-C(1)-C(2)	117.4(6)	C(18)-C(13)-S(3)	118.8(6)
C(6)-C(1)-S(1)	118.0(6)	C(13)-C(14)-C(15)	121.3(6)
C(2)-C(1)-S(1)	124.5(5)	C(13)-C(14)-H(14)	119.3
C(3)-C(2)-C(1)	121.5(6)	C(15)-C(14)-H(14)	119.3
C(3)-C(2)-H(2)	119.2	C(16)-C(15)-C(14)	120.6(7)
C(1)-C(2)-H(2)	119.2	C(16)-C(15)-H(15)	119.7
C(4)-C(3)-C(2)	120.3(6)	C(14)-C(15)-H(15)	119.7
C(4)-C(3)-H(3)	119.8	C(15)-C(16)-C(17)	119.6(7)
C(2)-C(3)-H(3)	119.8	C(15)-C(16)-H(16)	120.2
C(3)-C(4)-C(5)	119.4(7)	C(17)-C(16)-H(16)	120.2
C(3)-C(4)-H(4)	120.3	C(18)-C(17)-C(16)	119.5(7)
C(5)-C(4)-H(4)	120.3	C(18)-C(17)-H(17)	120.2
C(4)-C(5)-C(6)	120.8(7)	C(16)-C(17)-H(17)	120.2
C(4)-C(5)-H(5)	119.6	C(17)-C(18)-C(13)	121.6(6)
C(6)-C(5)-H(5)	119.6	C(17)-C(18)-H(18)	119.2
C(1)-C(6)-C(5)	120.4(7)	C(13)-C(18)-H(18)	119.2
C(1)-C(6)-H(6)	119.8	C(20)-C(19)-C(24)	116.3(5)
C(5)-C(6)-H(6)	119.8	C(20)-C(19)-S(4)	120.2(5)
C(12)-C(7)-C(8)	116.8(5)	C(24)-C(19)-S(4)	123.4(5)
C(12)-C(7)-S(2)	124.2(4)	C(21)-C(20)-C(19)	122.4(5)
C(8)-C(7)-S(2)	119.0(5)	C(21)-C(20)-H(20)	118.8
C(9)-C(8)-C(7)	120.8(6)	C(19)-C(20)-H(20)	118.8
C(9)-C(8)-H(8)	119.6	C(22)-C(21)-C(20)	120.5(6)
C(7)-C(8)-H(8)	119.6	C(22)-C(21)-H(21)	119.7
C(10)-C(9)-C(8)	121.2(6)	C(20)-C(21)-H(21)	119.7
C(10)-C(9)-H(9)	119.4	C(21)-C(22)-C(23)	118.0(6)
C(8)-C(9)-H(9)	119.4	C(21)-C(22)-H(22)	121.0
C(11)-C(10)-C(9)	118.7(7)	C(23)-C(22)-H(22)	121.0
C(11)-C(10)-H(10)	120.7	C(24)-C(23)-C(22)	121.2(6)
C(9)-C(10)-H(10)	120.7	C(24)-C(23)-H(23)	119.4
C(10)-C(11)-C(12)	121.1(7)	C(22)-C(23)-H(23)	119.4

C(23)-C(24)-C(19)	121.5(5)	C(31)-C(36)-H(36)	119.3
C(23)-C(24)-H(24)	119.2	C(42)-C(37)-C(38)	119.5(5)
C(19)-C(24)-H(24)	119.2	C(42)-C(37)-P(1)	121.2(4)
C(30)-C(25)-C(26)	118.7(4)	C(38)-C(37)-P(1)	119.3(4)
C(30)-C(25)-P(1)	122.0(4)	C(39)-C(38)-C(37)	120.6(5)
C(26)-C(25)-P(1)	119.3(4)	C(39)-C(38)-H(38)	119.7
C(27)-C(26)-C(25)	120.2(5)	C(37)-C(38)-H(38)	119.7
C(27)-C(26)-H(26)	119.9	C(40)-C(39)-C(38)	119.6(6)
C(25)-C(26)-H(26)	119.9	C(40)-C(39)-H(39)	120.2
C(28)-C(27)-C(26)	120.0(5)	C(38)-C(39)-H(39)	120.2
C(28)-C(27)-H(27)	120.0	C(39)-C(40)-C(41)	120.6(6)
C(26)-C(27)-H(27)	120.0	C(39)-C(40)-H(40)	119.7
C(29)-C(28)-C(27)	120.0(5)	C(41)-C(40)-H(40)	119.7
C(29)-C(28)-H(28)	120.0	C(40)-C(41)-C(42)	120.4(6)
C(27)-C(28)-H(28)	120.0	C(40)-C(41)-H(41)	119.8
C(28)-C(29)-C(30)	120.5(5)	C(42)-C(41)-H(41)	119.8
C(28)-C(29)-H(29)	119.7	C(37)-C(42)-C(41)	119.3(5)
C(30)-C(29)-H(29)	119.7	C(37)-C(42)-H(42)	120.4
C(25)-C(30)-C(29)	120.5(5)	C(41)-C(42)-H(42)	120.4
C(25)-C(30)-H(30)	119.7	C(48)-C(43)-C(44)	118.8(4)
C(29)-C(30)-H(30)	119.7	C(48)-C(43)-P(1)	121.4(4)
C(32)-C(31)-C(36)	118.1(5)	C(44)-C(43)-P(1)	119.7(4)
C(32)-C(31)-P(1)	118.8(4)	C(45)-C(44)-C(43)	120.2(5)
C(36)-C(31)-P(1)	123.1(4)	C(45)-C(44)-H(44)	119.9
C(33)-C(32)-C(31)	120.5(5)	C(43)-C(44)-H(44)	119.9
C(33)-C(32)-H(32)	119.7	C(46)-C(45)-C(44)	120.5(5)
C(31)-C(32)-H(32)	119.7	C(46)-C(45)-H(45)	119.8
C(34)-C(33)-C(32)	120.3(6)	C(44)-C(45)-H(45)	119.8
C(34)-C(33)-H(33)	119.9	C(47)-C(46)-C(45)	119.7(5)
C(32)-C(33)-H(33)	119.9	C(47)-C(46)-H(46)	120.1
C(33)-C(34)-C(35)	120.1(6)	C(45)-C(46)-H(46)	120.1
C(33)-C(34)-H(34)	120.0	C(46)-C(47)-C(48)	120.6(5)
C(35)-C(34)-H(34)	120.0	C(46)-C(47)-H(47)	119.7
C(34)-C(35)-C(36)	119.6(6)	C(48)-C(47)-H(47)	119.7
C(34)-C(35)-H(35)	120.2	C(47)-C(48)-C(43)	120.2(4)
C(36)-C(35)-H(35)	120.2	C(47)-C(48)-H(48)	119.9
C(35)-C(36)-C(31)	121.4(5)	C(43)-C(48)-H(48)	119.9
C(35)-C(36)-H(36)	119.3	C(50)-C(49)-C(54)	118.8(4)

C(50)-C(49)-P(2)	120.5(4)	C(63)-C(62)-C(61)	120.4(5)
C(54)-C(49)-P(2)	120.7(4)	C(63)-C(62)-H(62)	119.8
C(51)-C(50)-C(49)	121.2(5)	C(61)-C(62)-H(62)	119.8
C(51)-C(50)-H(50)	119.4	C(64)-C(63)-C(62)	121.1(6)
C(49)-C(50)-H(50)	119.4	C(64)-C(63)-H(63)	119.4
C(50)-C(51)-C(52)	119.1(5)	C(62)-C(63)-H(63)	119.4
C(50)-C(51)-H(51)	120.4	C(63)-C(64)-C(65)	119.2(5)
C(52)-C(51)-H(51)	120.4	C(63)-C(64)-H(64)	120.4
C(53)-C(52)-C(51)	120.9(5)	C(65)-C(64)-H(64)	120.4
C(53)-C(52)-H(52)	119.5	C(64)-C(65)-C(66)	120.9(5)
C(51)-C(52)-H(52)	119.5	C(64)-C(65)-H(65)	119.6
C(52)-C(53)-C(54)	120.3(5)	C(66)-C(65)-H(65)	119.6
C(52)-C(53)-H(53)	119.9	C(65)-C(66)-C(61)	119.6(5)
C(54)-C(53)-H(53)	119.9	C(65)-C(66)-H(66)	120.2
C(53)-C(54)-C(49)	119.7(5)	C(61)-C(66)-H(66)	120.2
C(53)-C(54)-H(54)	120.1	C(72)-C(67)-C(68)	119.8(5)
C(49)-C(54)-H(54)	120.1	C(72)-C(67)-P(2)	120.8(4)
C(60)-C(55)-C(56)	118.7(5)	C(68)-C(67)-P(2)	119.1(4)
C(60)-C(55)-P(2)	123.1(4)	C(69)-C(68)-C(67)	119.7(5)
C(56)-C(55)-P(2)	118.2(4)	C(69)-C(68)-H(68)	120.2
C(57)-C(56)-C(55)	120.5(5)	C(67)-C(68)-H(68)	120.2
C(57)-C(56)-H(56)	119.7	C(70)-C(69)-C(68)	120.6(5)
C(55)-C(56)-H(56)	119.7	C(70)-C(69)-H(69)	119.7
C(58)-C(57)-C(56)	119.7(5)	C(68)-C(69)-H(69)	119.7
C(58)-C(57)-H(57)	120.2	C(69)-C(70)-C(71)	119.2(5)
C(56)-C(57)-H(57)	120.2	C(69)-C(70)-H(70)	120.4
C(57)-C(58)-C(59)	121.5(6)	C(71)-C(70)-H(70)	120.4
C(57)-C(58)-H(58)	119.2	C(70)-C(71)-C(72)	121.5(5)
C(59)-C(58)-H(58)	119.2	C(70)-C(71)-H(71)	119.2
C(58)-C(59)-C(60)	119.4(5)	C(72)-C(71)-H(71)	119.2
C(58)-C(59)-H(59)	120.3	C(71)-C(72)-C(67)	119.2(5)
C(60)-C(59)-H(59)	120.3	C(71)-C(72)-H(72)	120.4
C(55)-C(60)-C(59)	120.2(5)	C(67)-C(72)-H(72)	120.4
C(55)-C(60)-H(60)	119.9	O(1)-N(1)-Co(1)	175.9(5)
C(59)-C(60)-H(60)	119.9	O(2)-N(2)-Co(1)	156.9(5)
C(62)-C(61)-C(66)	118.8(5)	O(3)-N(3)-Co(2)	168.8(6)
C(62)-C(61)-P(2)	121.2(4)	O(4)-N(4)-Co(2)	168.1(5)
C(66)-C(61)-P(2)	120.0(4)	C(31)-P(1)-C(43)	108.7(2)

C(31)-P(1)-C(25)	110.5(2)
C(43)-P(1)-C(25)	108.9(2)
C(31)-P(1)-C(37)	111.6(2)
C(43)-P(1)-C(37)	109.0(2)
C(25)-P(1)-C(37)	108.1(2)
C(55)-P(2)-C(67)	109.1(2)
C(55)-P(2)-C(61)	110.3(2)
C(67)-P(2)-C(61)	107.2(2)
C(55)-P(2)-C(49)	109.4(2)
C(67)-P(2)-C(49)	112.1(2)
C(61)-P(2)-C(49)	108.8(2)
C(1)-S(1)-Co(1)	109.5(2)
C(7)-S(2)-Co(1)	109.21(19)
C(13)-S(3)-Co(2)	109.0(2)
C(19)-S(4)-Co(2)	105.08(17)
N(1)-Co(1)-N(2)	114.7(3)
N(1)-Co(1)-S(2)	111.84(17)
N(2)-Co(1)-S(2)	110.30(17)
N(1)-Co(1)-S(1)	110.8(2)
N(2)-Co(1)-S(1)	116.67(18)
S(2)-Co(1)-S(1)	89.95(6)
N(3)-Co(2)-N(4)	112.9(3)
N(3)-Co(2)-S(4)	110.89(19)
N(4)-Co(2)-S(4)	112.57(18)
N(3)-Co(2)-S(3)	113.7(2)
N(4)-Co(2)-S(3)	113.29(16)
S(4)-Co(2)-S(3)	91.68(7)

Table S11. Crystal data and structure refinement for [(dppe)Co(NO)$_2$][BF$_4$] (dppe = 1,2-Bis(diphenylphosphino)ethan).

Identification code	ic17153	
Empirical formula	C27 H24 Co N O2 P2	
Formula weight	515.34	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 12.3657(7) Å	α= 90°.
	b = 15.6438(9) Å	β= 108.1441(12)°.
	c = 13.0824(7) Å	γ= 90°.
Volume	2404.9(2) Å^3	
Z	4	
Density (calculated)	1.423 Mg/m^3	
Absorption coefficient	0.872 mm^{-1}	
F(000)	1064	
Crystal size	0.28 x 0.14 x 0.12 mm^3	
Theta range for data collection	1.98 to 27.50°.	
Index ranges	-15<=h<=16, -20<=k<=20, -16<=l<=15	
Reflections collected	18341	
Independent reflections	5513 [R(int) = 0.0400]	
Completeness to theta = 27.50°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9026 and 0.7924	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5513 / 0 / 298	
Goodness-of-fit on F^2	1.129	
Final R indices [I>2sigma(I)]	R1 = 0.0412, wR2 = 0.0878	
R indices (all data)	R1 = 0.0483, wR2 = 0.0910	
Largest diff. peak and hole	0.445 and -0.272 e.Å^{-3}	

Table S12. Bond lengths [Å] and angles [°] for [(dppe)Co(NO)$_2$][BF$_4$] (dppe = 1,2-Bis(diphenylphosphino)ethan).

Co-N(1)	1.6454(19)	C(25)-C(26)	1.380(3)
Co-C(1)	1.763(2)	C(26)-C(27)	1.384(3)
Co-P(1)	2.1997(6)		
Co-P(2)	2.1998(6)	N(1)-Co-C(1)	121.88(10)
P(1)-C(4)	1.824(2)	N(1)-Co-P(1)	118.72(7)
P(1)-C(10)	1.830(2)	C(1)-Co-P(1)	102.36(8)
P(1)-C(2)	1.840(2)	N(1)-Co-P(2)	121.50(7)
P(2)-C(22)	1.826(2)	C(1)-Co-P(2)	97.86(7)
P(2)-C(16)	1.827(2)	P(1)-Co-P(2)	87.66(2)
P(2)-C(3)	1.843(2)	C(4)-P(1)-C(10)	104.00(10)
N(1)-O(2)	1.178(2)	C(4)-P(1)-C(2)	105.19(10)
C(1)-O(1)	1.152(3)	C(10)-P(1)-C(2)	103.76(10)
C(2)-C(3)	1.533(3)	C(4)-P(1)-Co	119.98(7)
C(4)-C(5)	1.395(3)	C(10)-P(1)-Co	116.07(7)
C(4)-C(9)	1.396(3)	C(2)-P(1)-Co	106.24(7)
C(5)-C(6)	1.387(3)	C(22)-P(2)-C(16)	101.88(9)
C(6)-C(7)	1.378(3)	C(22)-P(2)-C(3)	104.20(10)
C(7)-C(8)	1.380(4)	C(16)-P(2)-C(3)	106.01(10)
C(8)-C(9)	1.384(3)	C(22)-P(2)-Co	120.52(7)
C(10)-C(15)	1.389(3)	C(16)-P(2)-Co	114.73(7)
C(10)-C(11)	1.391(3)	C(3)-P(2)-Co	108.21(7)
C(11)-C(12)	1.389(3)	O(2)-N(1)-Co	178.4(2)
C(12)-C(13)	1.373(4)	O(1)-C(1)-Co	177.9(2)
C(13)-C(14)	1.380(4)	C(3)-C(2)-P(1)	107.38(14)
C(14)-C(15)	1.387(3)	C(2)-C(3)-P(2)	109.27(14)
C(16)-C(17)	1.386(3)	C(5)-C(4)-C(9)	118.9(2)
C(16)-C(21)	1.395(3)	C(5)-C(4)-P(1)	117.71(16)
C(17)-C(18)	1.392(3)	C(9)-C(4)-P(1)	123.39(17)
C(18)-C(19)	1.376(4)	C(6)-C(5)-C(4)	120.4(2)
C(19)-C(20)	1.379(4)	C(7)-C(6)-C(5)	120.2(2)
C(20)-C(21)	1.385(3)	C(6)-C(7)-C(8)	119.9(2)
C(22)-C(23)	1.385(3)	C(7)-C(8)-C(9)	120.6(2)
C(22)-C(27)	1.392(3)	C(8)-C(9)-C(4)	120.1(2)
C(23)-C(24)	1.387(3)	C(15)-C(10)-C(11)	118.6(2)
C(24)-C(25)	1.384(4)	C(15)-C(10)-P(1)	118.30(16)

C(11)-C(10)-P(1)	123.11(18)	C(18)-C(19)-C(20)	119.8(2)
C(12)-C(11)-C(10)	120.4(2)	C(19)-C(20)-C(21)	120.1(2)
C(13)-C(12)-C(11)	120.3(2)	C(20)-C(21)-C(16)	120.7(2)
C(12)-C(13)-C(14)	120.0(2)	C(23)-C(22)-C(27)	119.1(2)
C(13)-C(14)-C(15)	120.0(3)	C(23)-C(22)-P(2)	120.31(17)
C(14)-C(15)-C(10)	120.8(2)	C(27)-C(22)-P(2)	120.63(16)
C(17)-C(16)-C(21)	118.7(2)	C(22)-C(23)-C(24)	120.5(2)
C(17)-C(16)-P(2)	124.47(17)	C(25)-C(24)-C(23)	120.1(2)
C(21)-C(16)-P(2)	116.78(17)	C(26)-C(25)-C(24)	119.8(2)
C(16)-C(17)-C(18)	120.3(2)	C(25)-C(26)-C(27)	120.2(2)
C(19)-C(18)-C(17)	120.4(2)	C(26)-C(27)-C(22)	120.4(2)

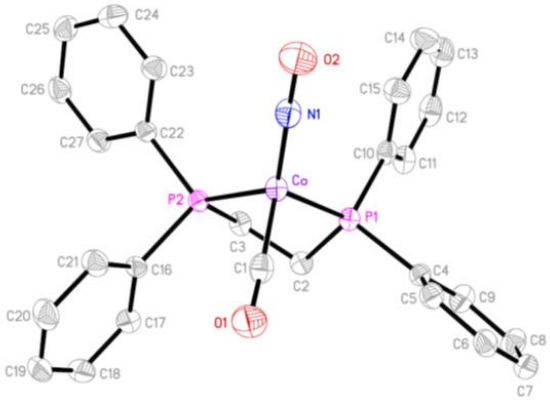

Figure S1. The Molecular Structure of $[(dppe)Co(NO)_2][BF_4]$ (dppe = 1,2-Bis(diphenylphosphino)ethan)

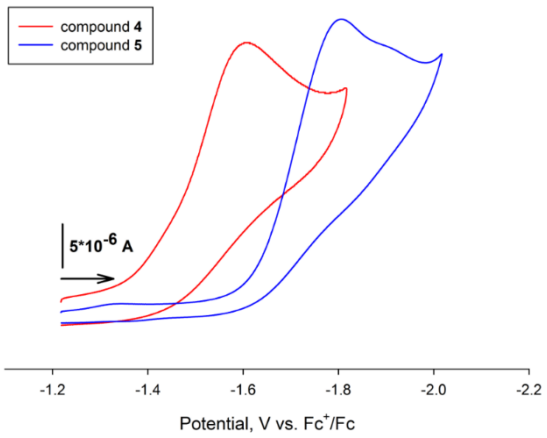

Figure S2. Overlay of cyclic voltammograms of complexes **4** (red) and complex **5** (blue) at scan rate 100 mV/s in 2 mM CH_2Cl_2 solution, referenced to Fc/Fc^+.

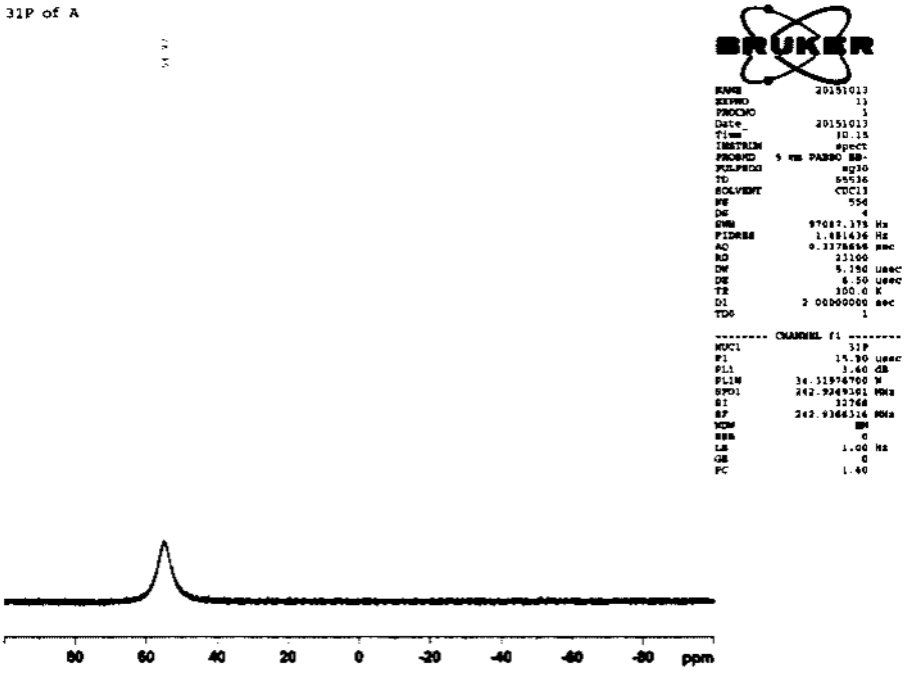

Figure S3P. The ^{31}P NMR spectrum of complex **1** in $CDCl_3$

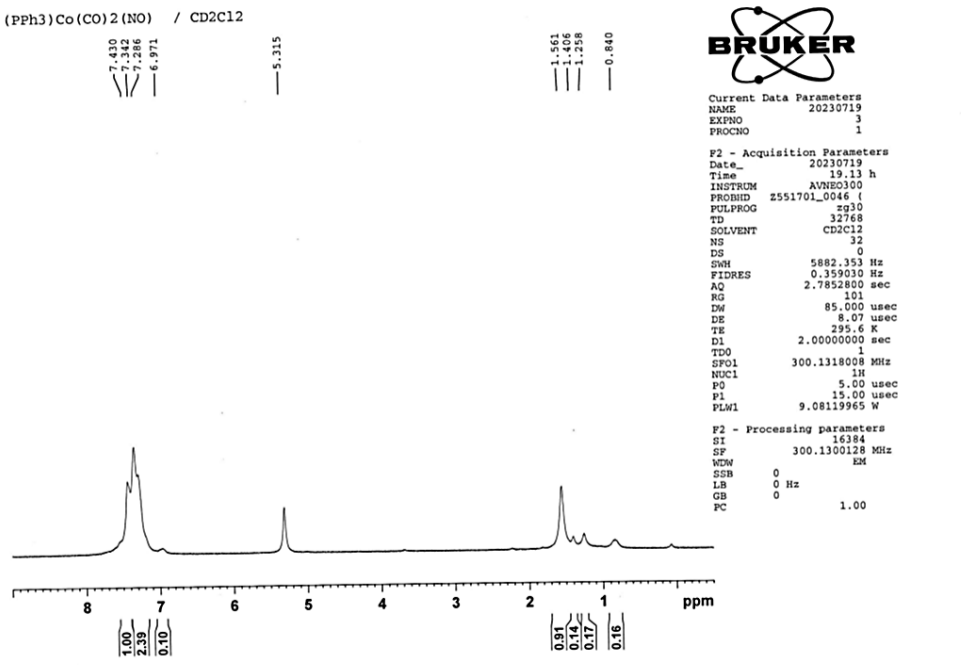

Figure S3H. The ^{1}H NMR spectrum of complex **1** in CD_2Cl_2

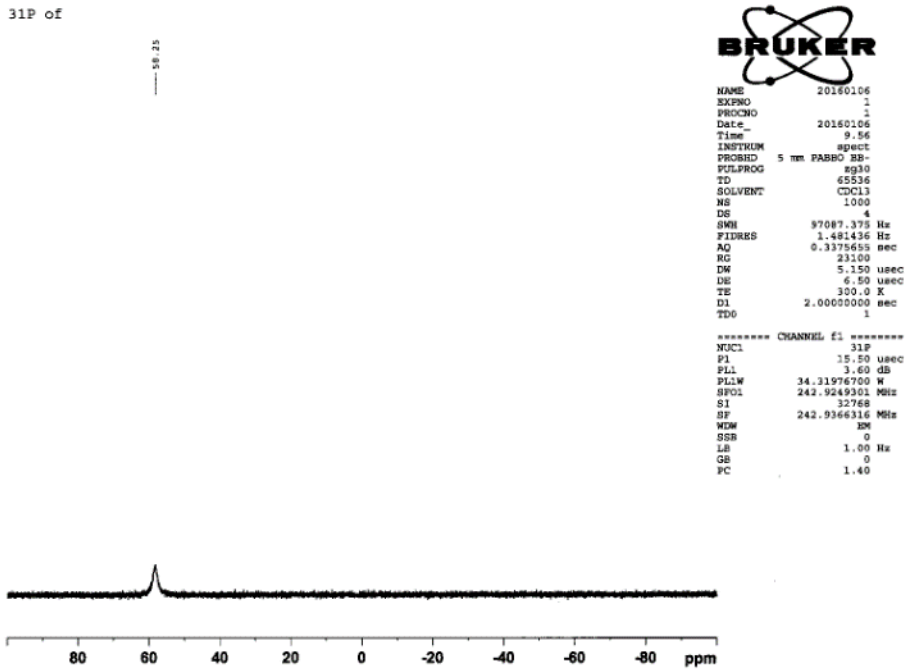

Figure S4P. The ^{31}P NMR spectrum of complex **2** in $CDCl_3$

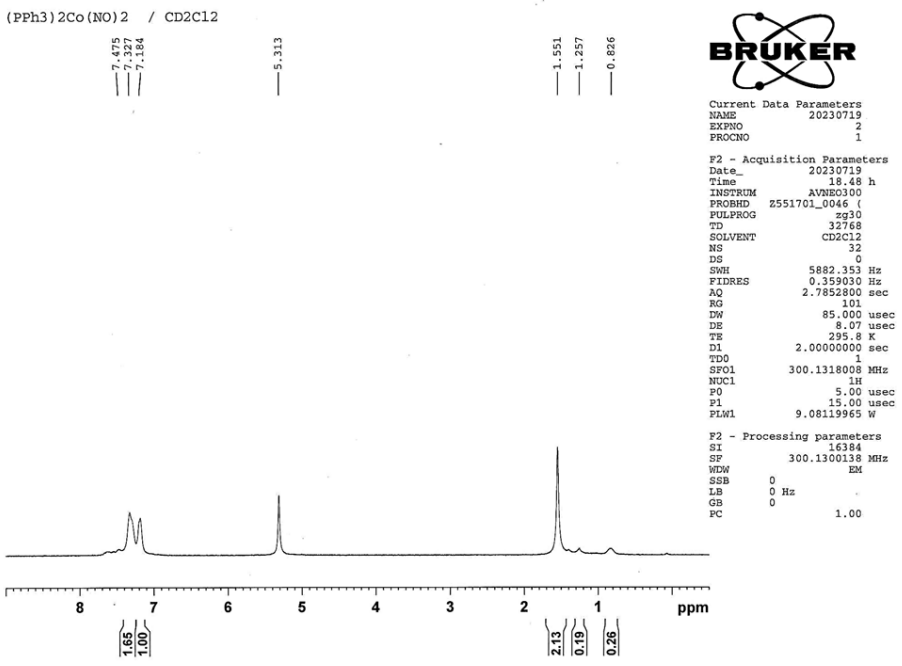

Figure S4H. The ^{1}H NMR spectrum of complex **2** in CD_2Cl_2

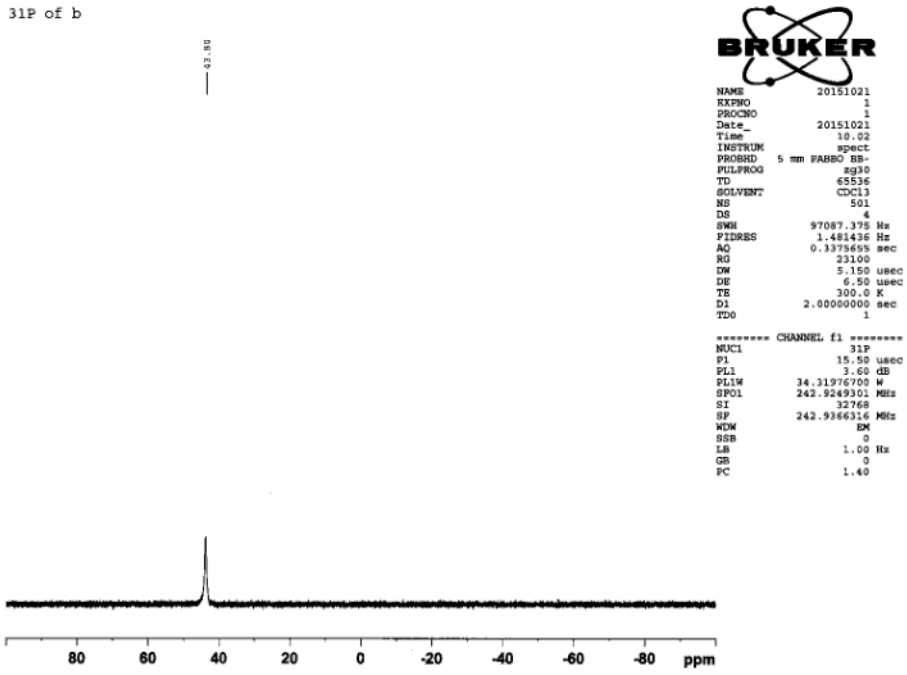

Figure S5P. The ^{31}P NMR spectrum of complex **3** in $CDCl_3$

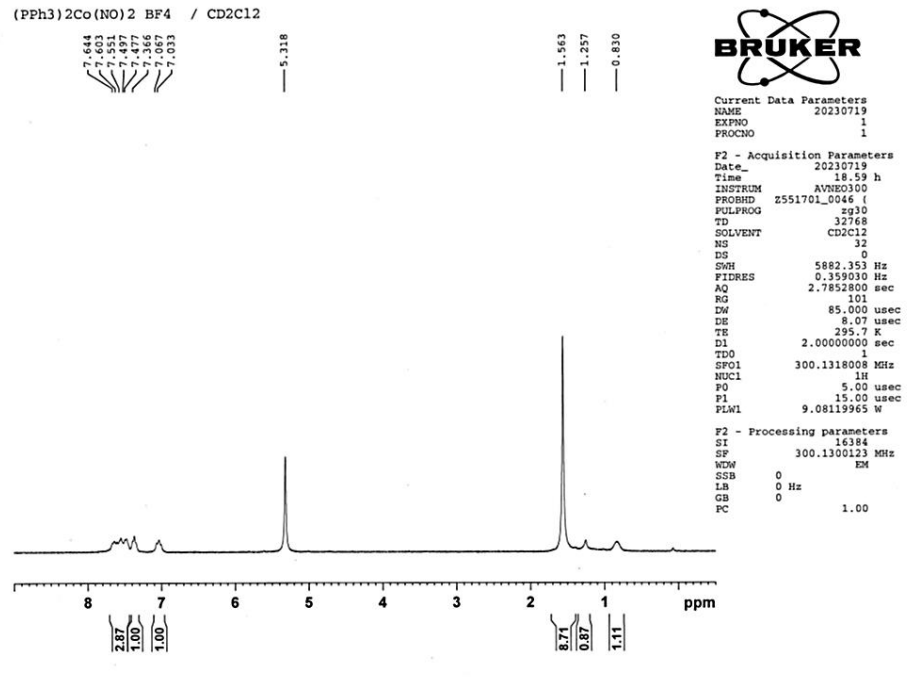

Figure S5H. The ^{1}H NMR spectrum of complex **3** in CD_2Cl_2

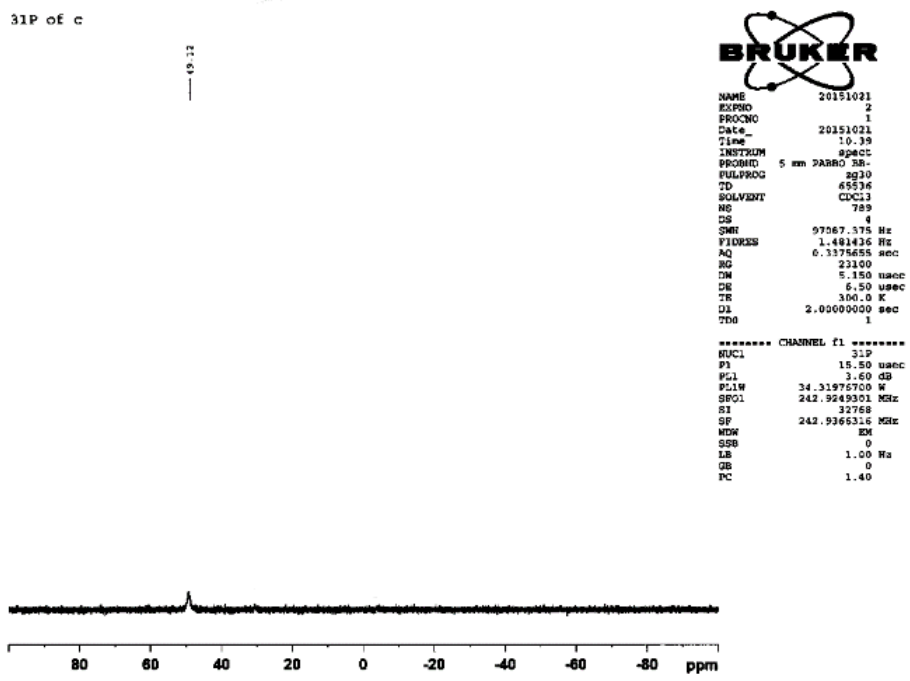

Figure S5P. The ^{31}P NMR spectrum of complex **4** in $CDCl_3$

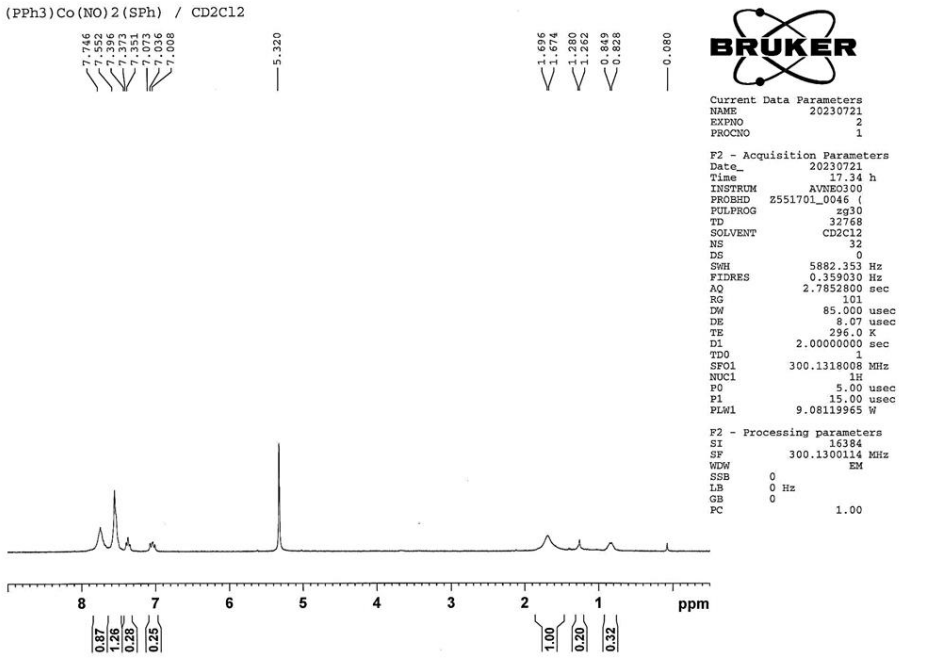

Figure S5H. The ^{1}H NMR spectrum of complex **4** in CD_2Cl_2

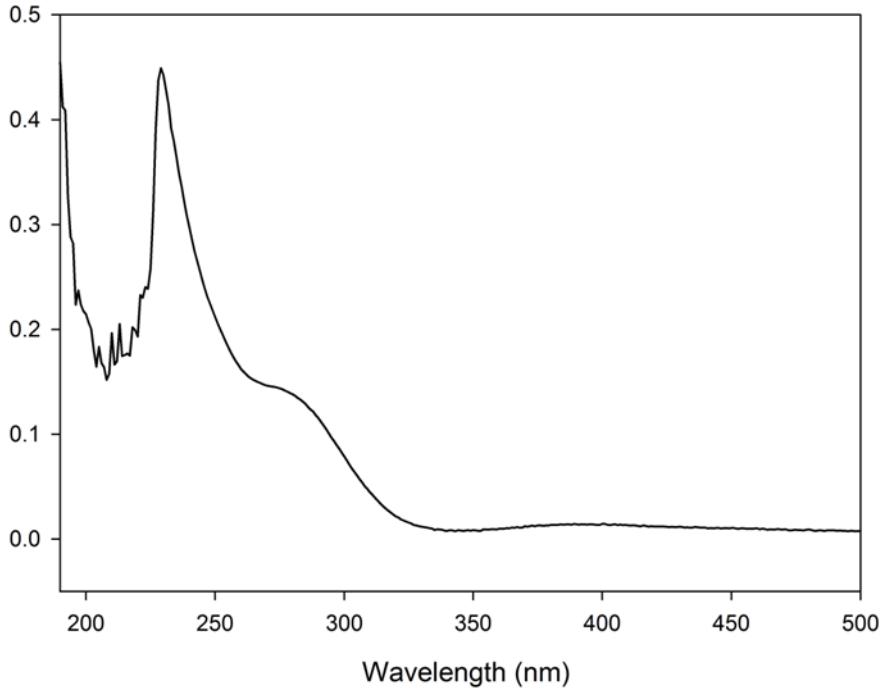

Figure S6. The UV spectrum of complex **1** in CH_2Cl_2 solution.

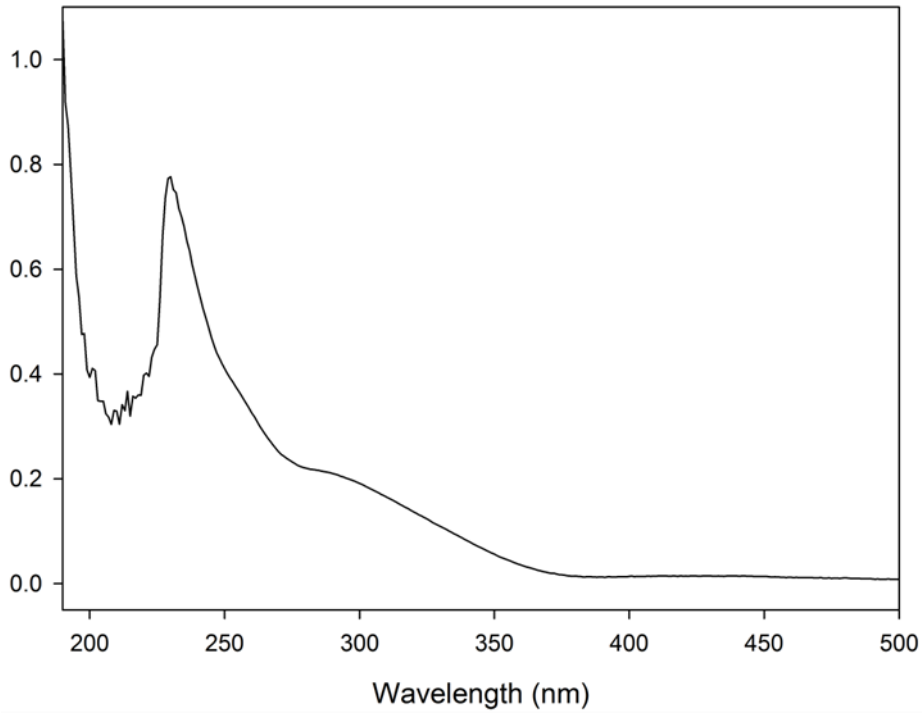

Figure S7. The UV spectrum of complex **2** in CH_2Cl_2 solution.

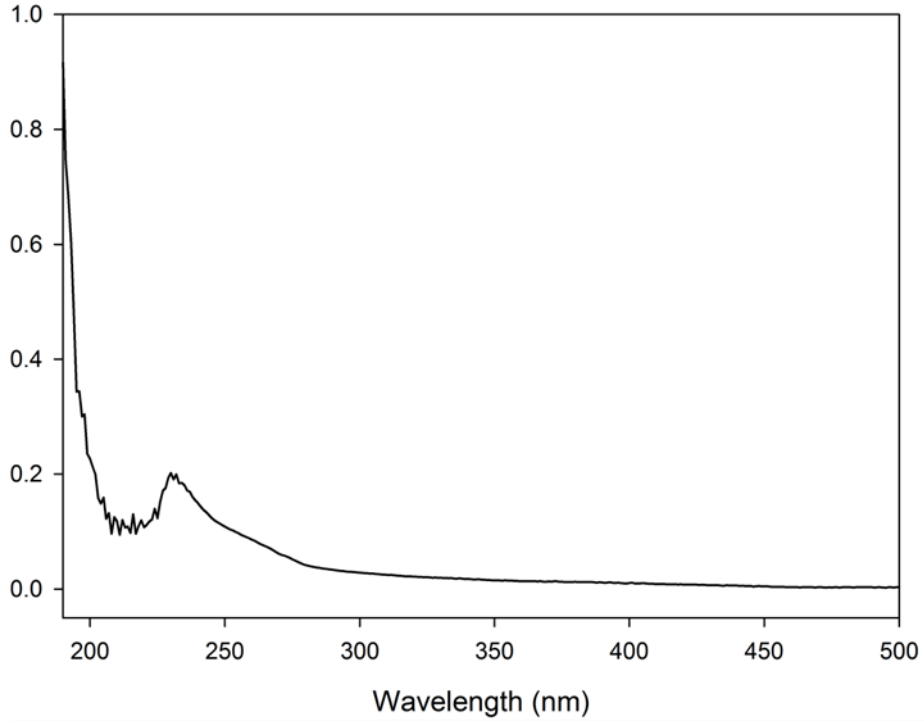

Figure S6. The UV spectrum of complex **3** in CH_2Cl_2 solution.

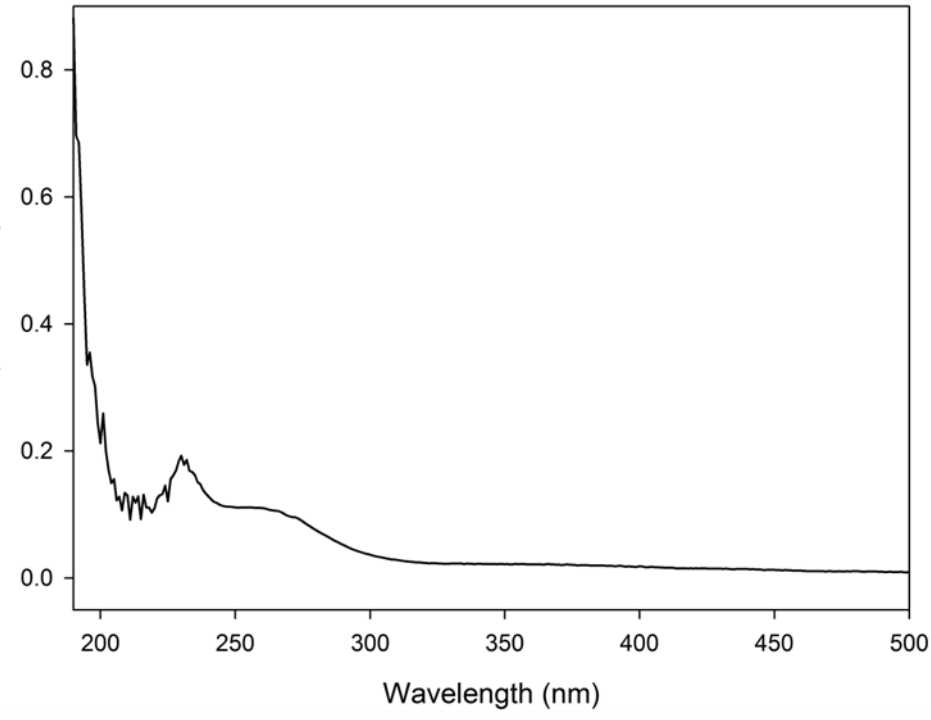

Figure S7. The UV spectrum of complex **4** in CH_2Cl_2 solution.

NO trapping experiments

Reaction of {Co(NO)}^{10} complexes 1 and 2 with [Fe(TPP)Cl]. In a Schlenk flask, a 10 mL CH_2Cl_2 solution of the complex (2.5 mM, 0.011 g/100 ml for complex **1** or 0.016 g/100 ml for complex **2**) was conveyed via a cannula to another Schlenk flask containing a 10 mL CH_2Cl_2 solution of [Fe(TPP)Cl] (5,10,15,20-Tetraphenyl-21H,23H-porphine iron(III) chloride) (2.5 mM, 0.0177 g/100 ml). This mixture was stirred at 0°C. Throughout the reaction, IR spectroscopy was utilized for monitoring. However, no observable changes in the spectra were detected over time. Following this, the reaction temperature was raised to room temperature, and the reaction was allowed to continue for 6 hours. IR analysis confirmed that no reaction occurred.

Reaction of {Co(NO)$_2$}^{10} complex 3-5 with [Fe(TPP)Cl]. In the reaction of {Co(NO)2}10 complexes **3-5** with [Fe(TPP)Cl], a 10 mL CH_2Cl_2 solution of the complex (2.5 mM, 0.018 g/100 ml for complex **3**, 0.012 g/100 ml for complex **4**, and 0.017 g/100 ml for complex **5**) was transferred from a Schlenk flask via a cannula into another Schlenk flask. This flask contained a 10 mL CH_2Cl_2 solution of [Fe(TPP)Cl] (5,10,15,20-Tetraphenyl-21H,23H-porphine iron(III) chloride) at a concentration of 5.0 mM (0.036 g/100 ml). This mixture was then stirred at 0°C for 3 hours. IR analysis confirmed that no reaction occurred for complex **3**. The reaction of complex **4** was monitored over time, with **Figure S8** showing an overlay IR spectrum of the reaction at 3 hours (red line) and 6 hours (black line). Approximately 50% of complex **4** remained, indicating that the **NOs** transfer reaction was not fully completed. In the case of complex **5**, **Figure S9** presents an overlay of the IR spectrum of the reaction at 3 hours (red line) and 6 hours (black line). The shift of the NO bands to 1672 cm^{-1} indicates that the formation of [Fe(TPP)Cl] is complete. A byproduct, diphenyl disulfide, was isolated using short column chromatography (with silica gel and diethyl ether as the eluent) and characterized by ^{1}H NMR spectroscopy. A dark-black, insoluble solid was observed adhering to the top of the short column during the chromatography. process.

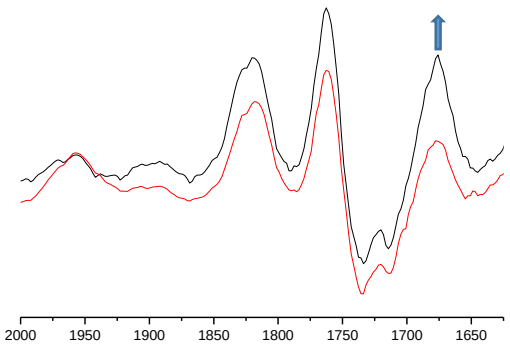

Figure S8. An overlaid IR spectrum from the reaction between complex **4** and [Fe(TPP)Cl], showing spectral data at both 3 hours (red line) and 6 hours (black line).

The appearance of [Fe(TPP)NO] is indicated by a blue arrow.

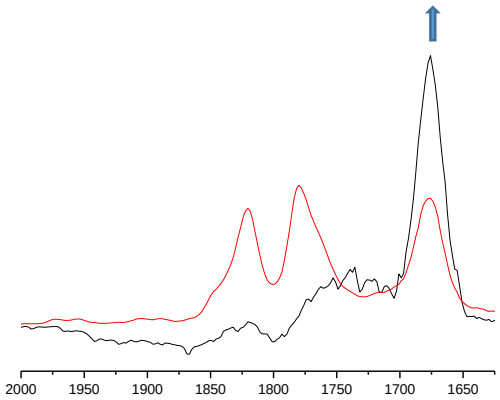

Figure S9. An overlaid IR spectrum from the reaction between complex **5** and [Fe(TPP)Cl], showing spectral data at both 3 hours (red line) and 6 hours (black line). The appearance of [Fe(TPP)NO] is indicated by a blue arrow.

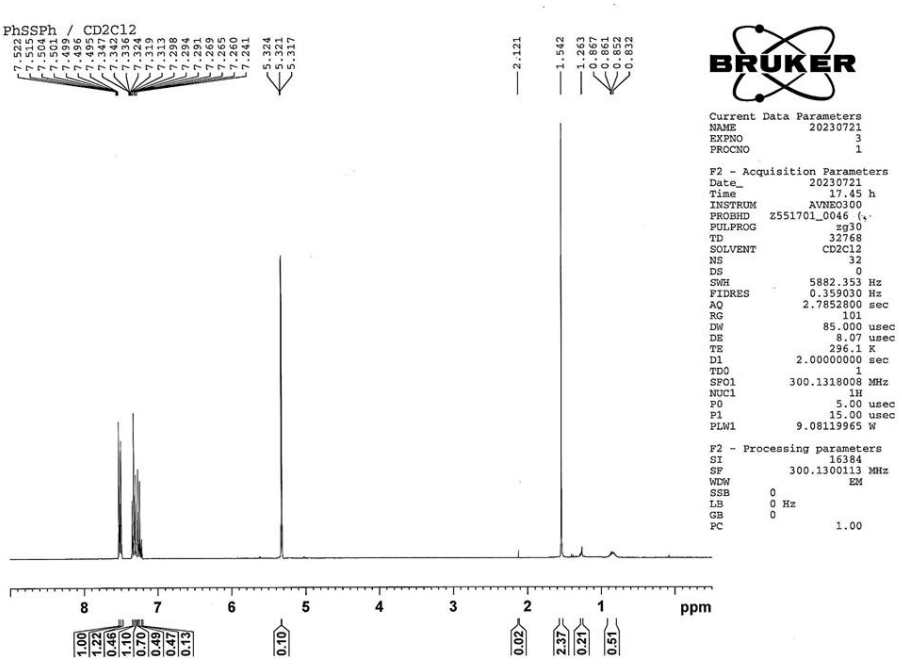

Figure S10. The ^{1}H NMR of isolated diphenyl disulfide in CD_2Cl_2