Supporting Information

Heteronuclear assembly of Ni-Cu Dithiolato Complexes: Synthesis, Structures, and Reactivity Studies

Xiaoxiao Chu, Xin Xu, Hao Su, Sakthi Raje, Raja Angamuthu, Chen-Ho Tung and Wenguang Wang*

Part I. Figures

Part II. Tables

* *School of Chemistry and Chemical Engineering, Shandong University, Jinan 250100, PR China. E-mail: wwg@sdu.edu.cn; Tel: +86 531 88365545*

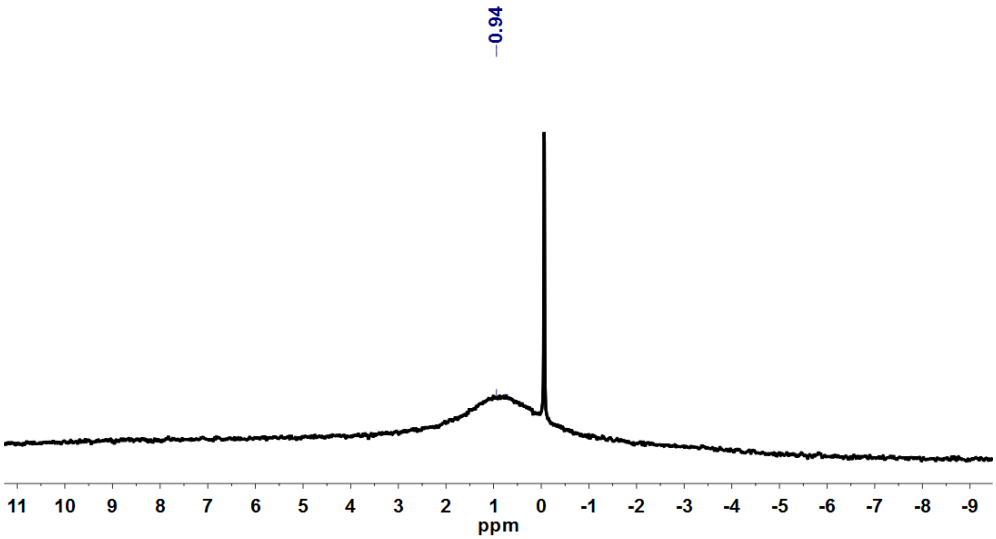

Figure S1. $^{31}P\{^{1}H\}$ NMR spectrum (121 MHz) of [Cu(dppe)$(MeCN)_2BF_4$] (**L1**) in MeCN solution (a capillary with 8% H_3PO_4 added as the internal standard).

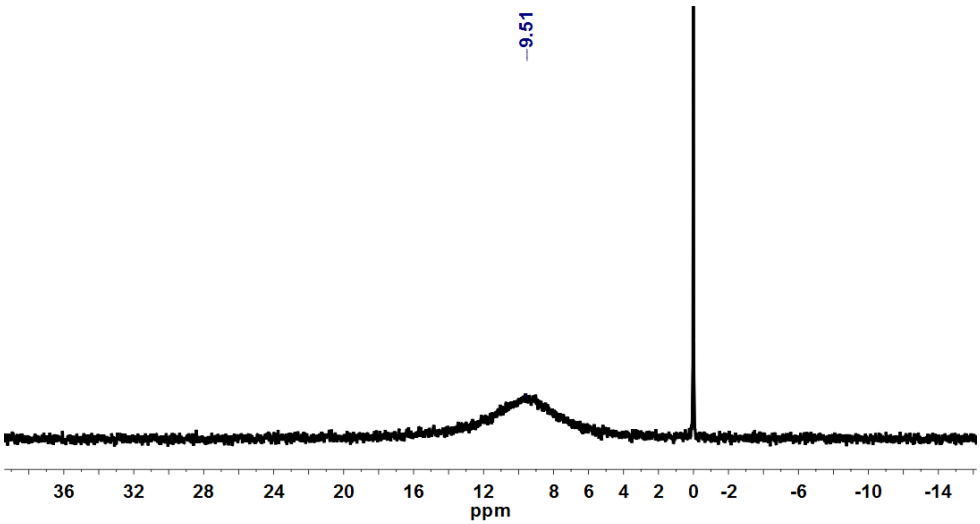

Figure S2. $^{31}P\{^{1}H\}$ NMR spectrum (121 MHz) of [Cu(dppbz)$(MeCN)_2BF_4$] (**L2**) in MeCN solution (a capillary with 8% H_3PO_4 added as the internal standard).

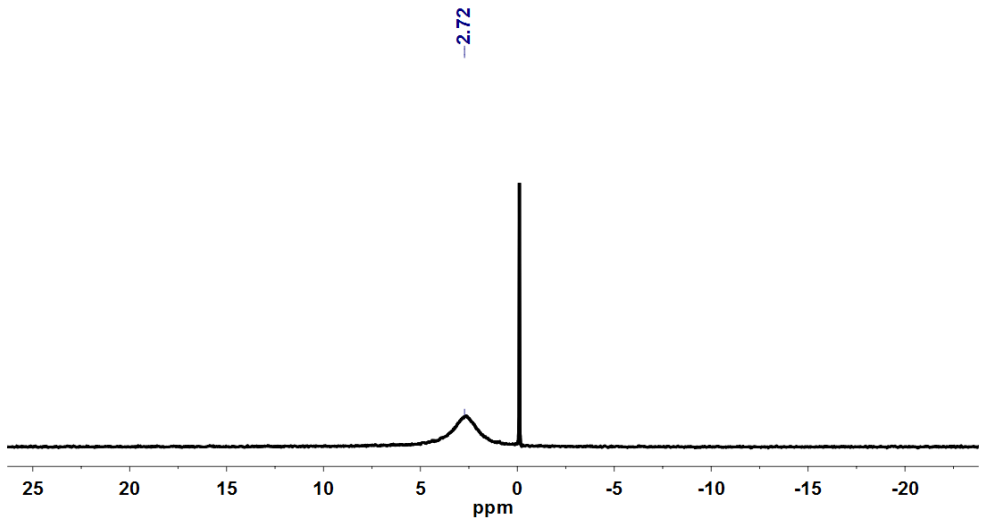

Figure S3. $^{31}P\{^{1}H\}$ NMR spectrum (121 MHz) of $[Cu(dcpe)(MeCN)_2BF_4]$ (**L3**) in MeCN solution (a capillary with 8% H_3PO_4 added as the internal standard).

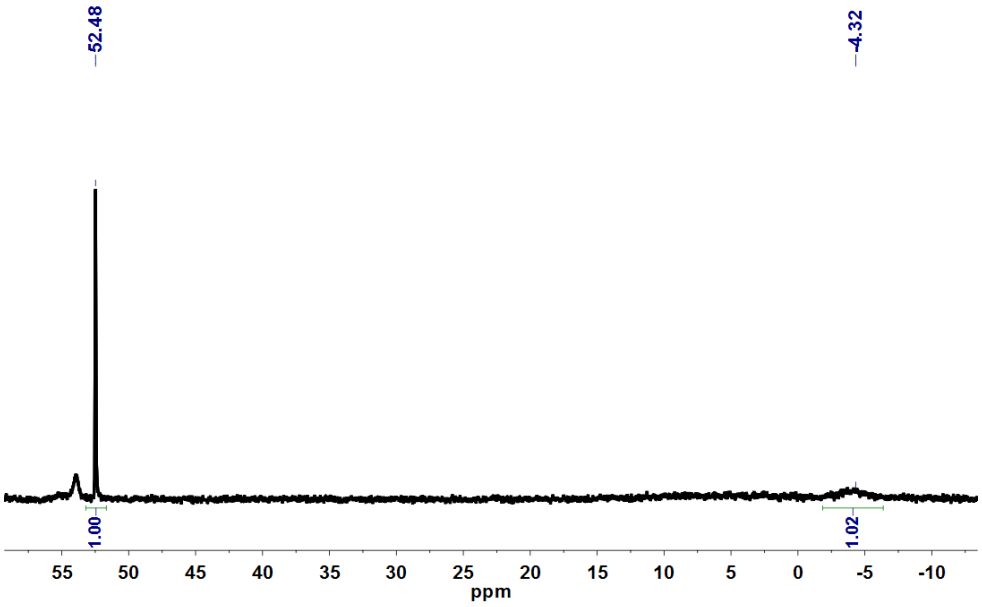

Figure S4. $^{31}P\{^{1}H\}$ NMR spectrum (121 MHz) of **1** in CD_2Cl_2 solution. The precursor Ni(pdt)(dppe) was observed at 54 ppm.

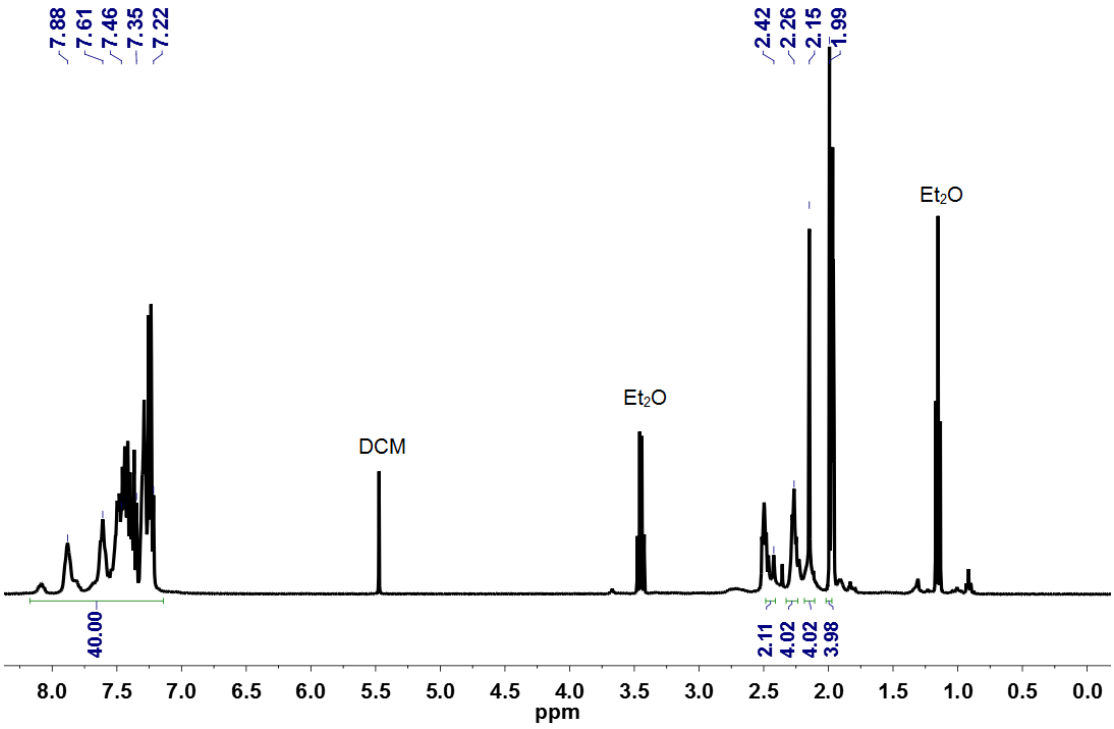

Figure S5. ^{1}H NMR spectrum (300 MHz) of **1** in CD_2Cl_2 solution.

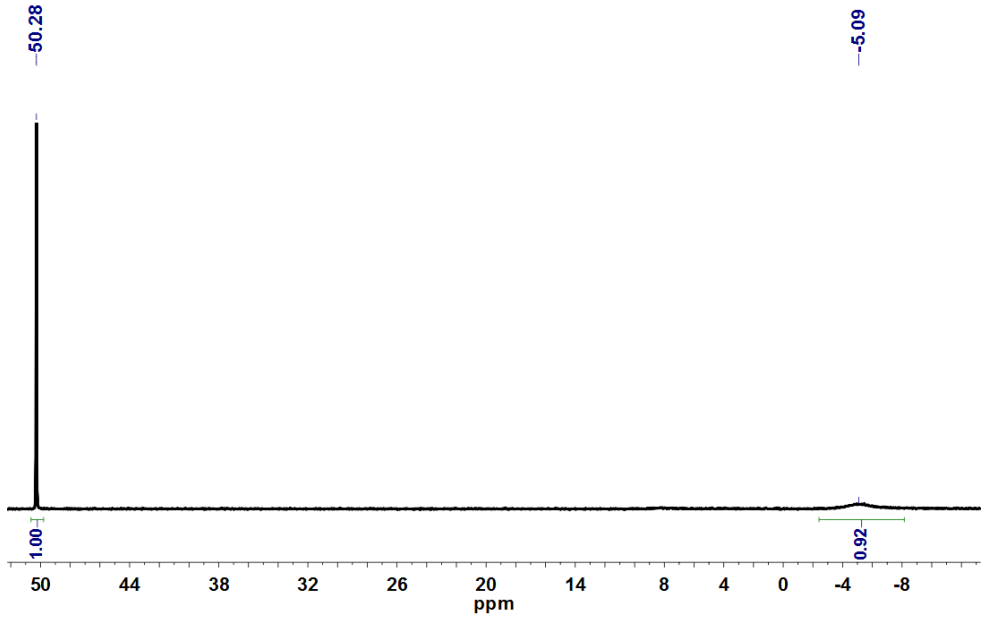

Figure S6. $^{31}P\{^{1}H\}$ NMR spectrum (121 MHz) of **2** in CD_2Cl_2 solution.

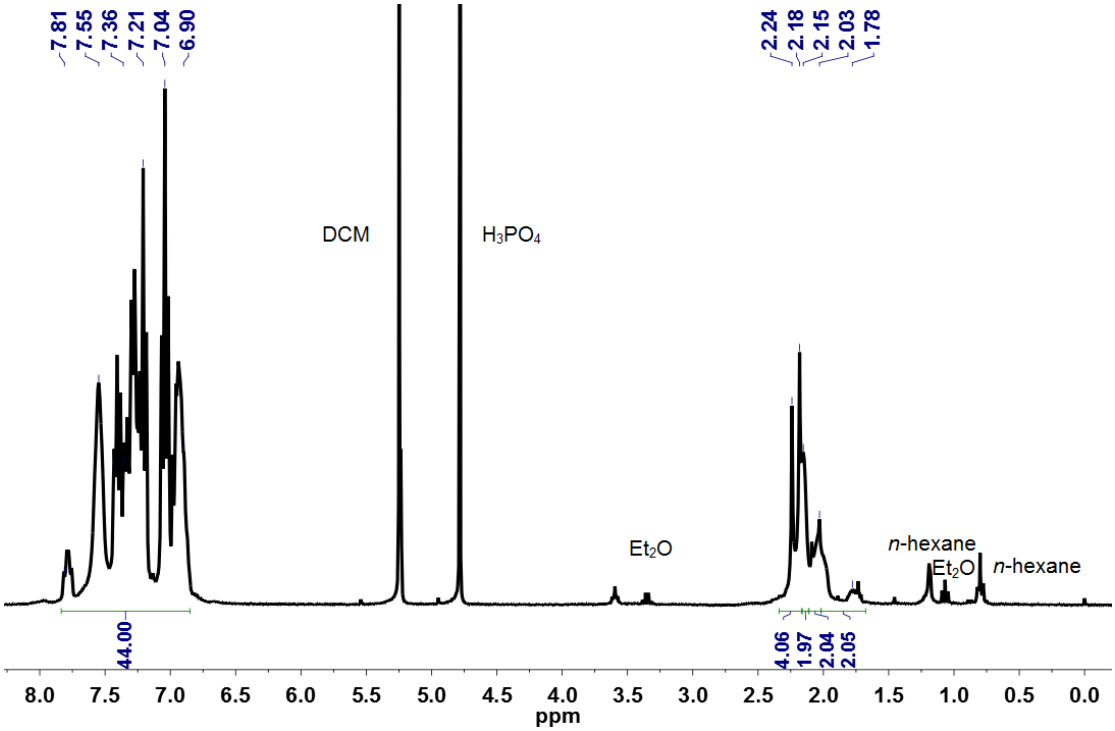

Figure S7. ^{1}H NMR spectrum (300 MHz) of **2** in CD_2Cl_2 solution.

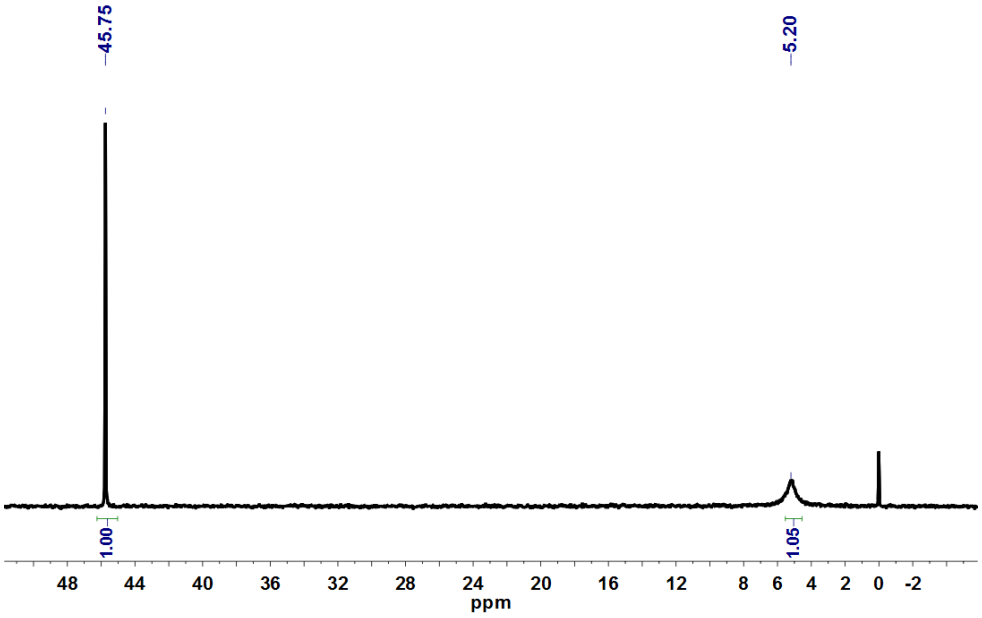

Figure S8. $^{31}P\{^{1}H\}$ NMR spectrum (121 MHz) of **3** in CD_2Cl_2 solution (a capillary with 8% H_3PO_4 added as the internal standard).

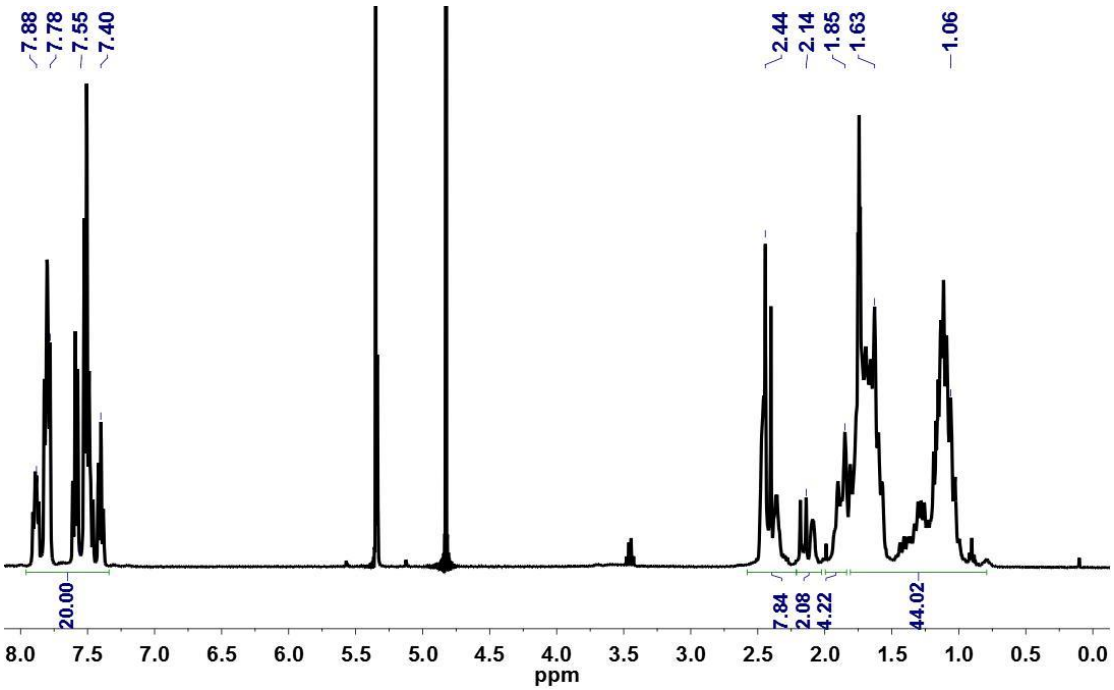

Figure S9. ^{1}H NMR spectrum (300 MHz) of **3** in CD_2Cl_2 solution.

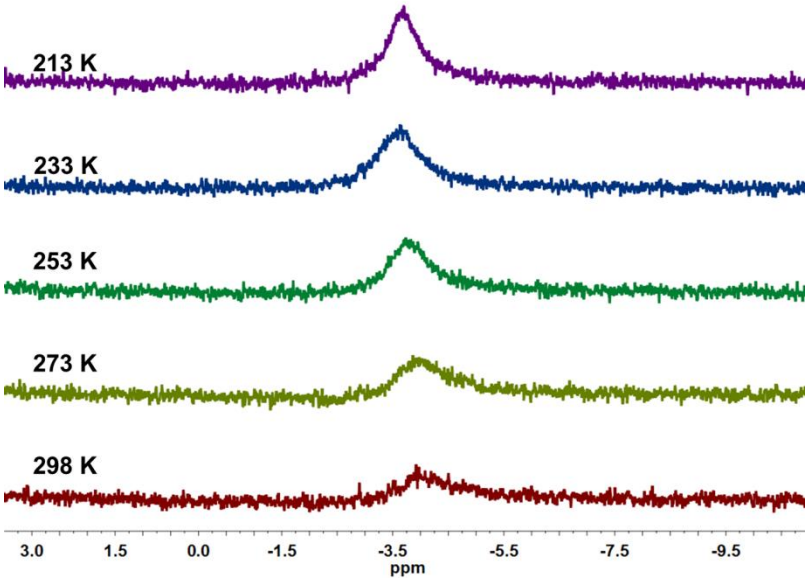

Figure S10 ^{31}P NMR spectra recorded for complex **1** in CD_2Cl_2 at various temperatures from 298 K to 213 K.

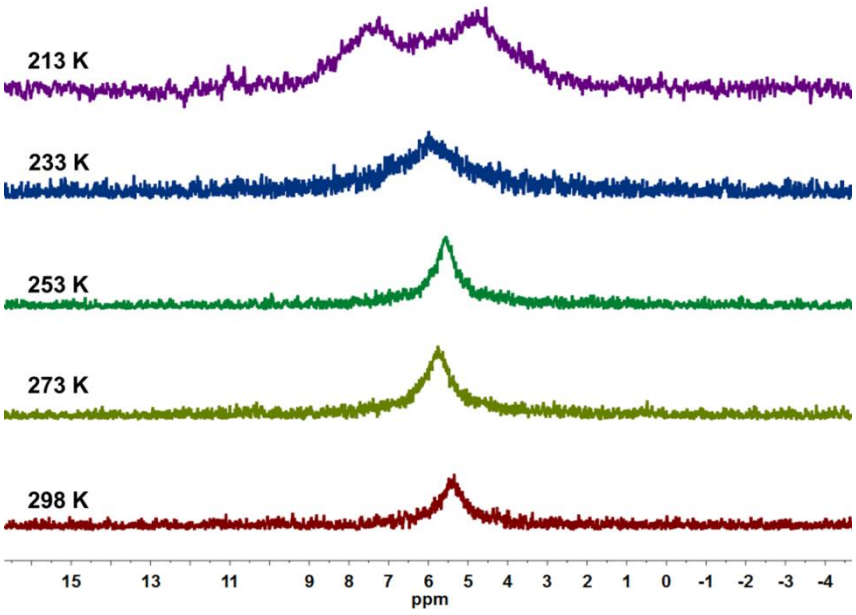

Figure S11 ^{31}P NMR spectra recorded for complex **3** in CD_2Cl_2 at various temperatures from 298 K to 213 K.

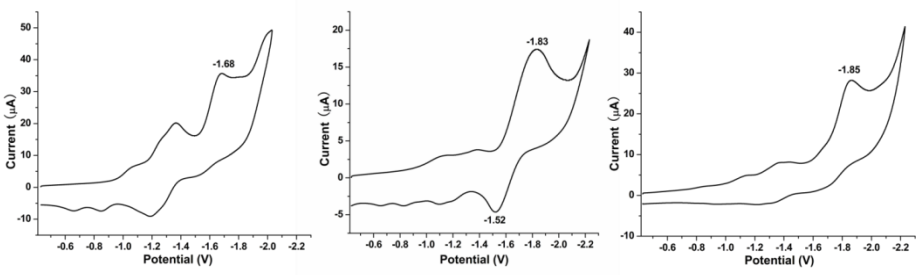

Figure S12. Cyclic voltammograms of (a) complex **1**, (b) **2**, and (c) **3** (1 mM) in 0.1 M *n*-Bu_4NPF_6 in DCM. Conditions: 1 mM sample in CH_2Cl_2, 0.1 M Bu_4NPF_6; Scan rate: 200 mV s^{-1}. Potentials vs. $Fc^{+/0}$.

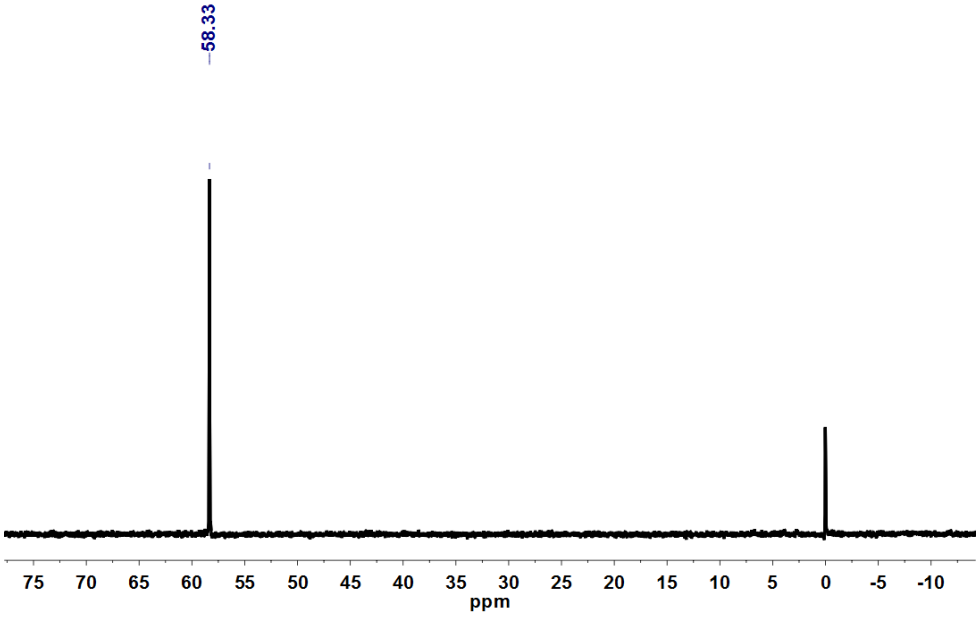

Figure S13. $^{31}P\{^{1}H\}$ NMR spectrum of complex [Ni(dppe)(μ-pdt)Ag]$_2$(BF$_4$)$_2$ (a capillary with 8% H_3PO_4 added as the internal standard).

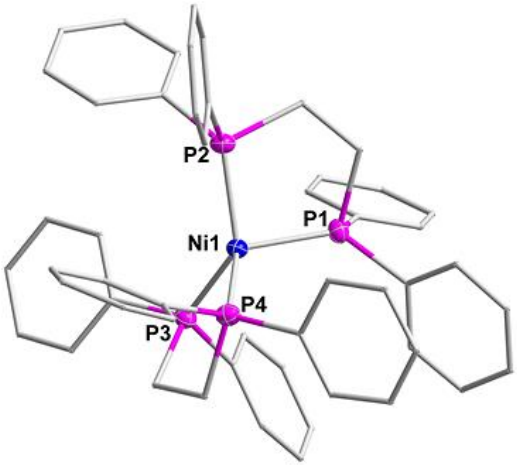

Figure S14. Structures (50% probability thermal ellipsoids) of $Ni(dppe)_2$. For clarity, the four cyclohexyl groups bonded to phosphorus are drawn as lines and hydrogen atoms are omitted.

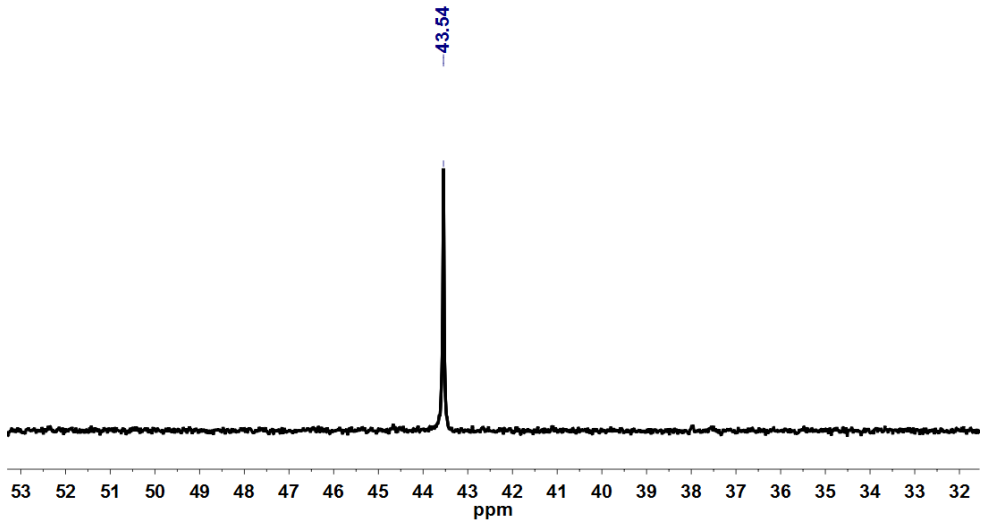

Figure S15. $^{1}P\{^{1}H\}$ NMR spectrum of $Ni(dppe)_2$ in THF.

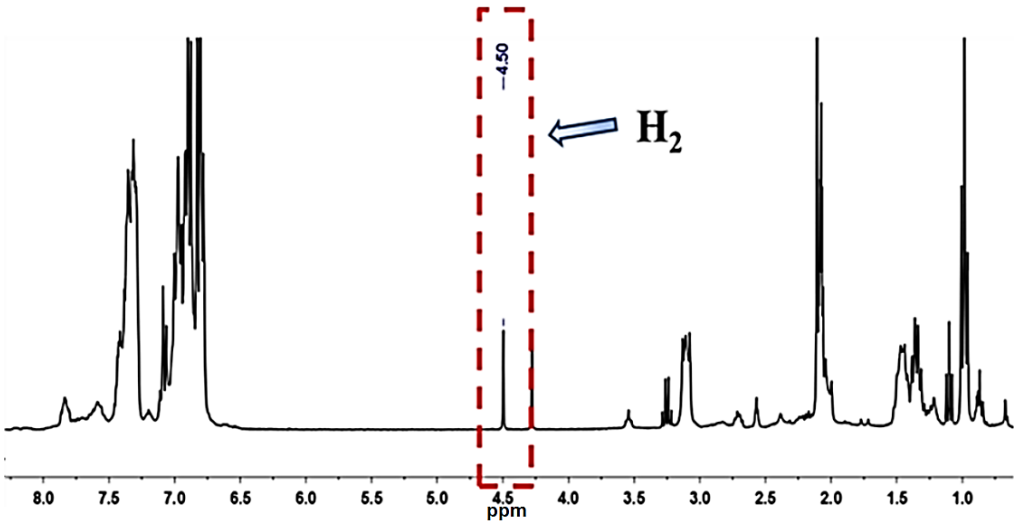

Figure S16. ^{1}H NMR spectrum (300 MHz) of **1** with *n*-Bu_4NBH_4 in toluene-d_8 solution.

Table S1. Structural parameters of the [CuNi] complexes

Complex	**1**	**2**	**3**
Elemental formula	$C_{55}H_{54}P_4S_2BF_4CuNi$	$C_{59}H_{54}P_4S_2BF_4CuNi$	$C_{55}H_{78}P_4S_2BF_4CuNi$
Formula weight	1112.1	1160.1	1136.3
Crystal system	Triclinic	Triclinic	Triclinic
Space group (no.)	$P\ \bar{1}$ (no. 2)	$P\ \bar{1}$ (no. 2)	$P\ \bar{1}$ (no. 2)
a/Å	12.202(5)	11.637(4)	11.618(3)
b/Å	12.646(5)	14.059(5)	19.850(4)
c/Å	19.879(8)	19.665(7)	26.753(5)
α/°	87.047(4)	87.551(3)	85.623(12)
β/°	81.675(4)	77.012(3)	88.579(15)
γ/°	66.275(3)	83.794(3)	87.821(13)
V/Å^3	2778.6(19)	3116.0(190)	6145.6(2)
Z	2	2	4
Final ***R*** indices (all data)	R1 = 0.0542, wR2 = 0.1472	R1 = 0.0616, wR2 = 0.1504	R1 = 0.0672, wR2 = 0.2034

Table S2. Crystal parameters of complex $Ni(dppe)_2$.

Complex	$Ni(dppe)_2$
Elemental formula	$C_{52}H_{48}NiP_4$
Formula weight	855.5
Crystal system	Monoclinic
Space group (no.)	$P\,2_1$ / n
a/Å	9.7754(10)
b/Å	20.995(2)
c/Å	21.283(2)
α/°	90
β/°	91.9332(9)
γ/°	90
V/Å^3	4365.5(7)
Z	4
Final ***R*** indices (all data)	R1 = 0.0521, wR2 = 0.1644

Table S3. Crystal parameters of complex [Ni(dppe)(μ-pdt)Ag]$_2$(BF$_4$)$_2$.

Complex	[Ni(dppe)(pdt)AgBF$_4$]$_2$
Elemental formula	$C_{58}H_{60}Ni_2Ag_2P_4S_4B_2F_8$
Formula weight	1515.9
Crystal system	Monoclinic
Space group (no.)	*C2* / c
a/Å	33.906(2)
b/Å	11.5072(6)
c/Å	19.2841(10)
α/°	90
β/°	116.577(3)
γ/°	90
V/Å^3	6728.9(7)
Z	4
Final ***R*** indices (all data)	R1 = 0.0613, wR2 = 0.1346

Table S4. Selected bond distances (Å) and angles (deg) of Complex **1**.

Cu1- Ni1	2.7983(14)	C21- C22	1.379(7)
Cu1- S1	2.3373(15)	C22 -C23	1.372(8)
Cu1- S2	2.3580(15)	C23 -C24	1.392(7)
Cu1 -P1	2.3034(16)	C24 -C25	1.392(6)
Cu1 -P2	2.2544(16)	C26 -C27	1.391(7)
Ni1 -S1	2.2337(14)	C26 -C31	1.396(8)
Ni1 -S2	2.2246(14)	C27 -C28	1.381(7)
Ni1 -P3	2.1642(14)	C28 -C29	1.387(8)
Ni1 -P4	2.1736(15)	C29 -C30	1.375(10)
S1 -C3	1.825(5)	C30 -C31	1.363(10)
S2 -C1	1.835(5)	C32 -C33	1.390(7)
P1- C6	1.841(5)	C32 -C37	1.382(7)
P1 -C49	1.826(5)	C33 -C34	1.387(7)
P1 -C50	1.830(5)	C34 -C35	1.384(8)
P2 -C7	1.833(5)	C35 -C36	1.367(8)
P2 -C32	1.820(5)	C36 -C37	1.373(7)
P2 -C42	1.840(5)	C38 -C39	1.370(7)
P3 -C4	1.827(5)	C38 -C43	1.376(7)
P3 -C13	1.819(5)	C39 -C40	1.385(7)
P3 -C15	1.812(5)	C40 -C41	1.388(7)
P4 -C5	1.829(5)	C41 -C42	1.386(6)
P4 -C25	1.809(5)	C42 -C43	1.387(7)
P4 -C27	1.821(5)	C44 -C45	1.379(7)
C1 -C2	1.487(7)	C44 -C49	1.390(7)
C2 -C3	1.490(7)	C45 -C46	1.365(8)
C4 -C5	1.527(7)	C46 -C47	1.384(8)
C6 -C7	1.538(6)	C47 -C48	1.395(7)
C8 -C9	1.376(7)	C48 -C49	1.401(7)
C8 -C13	1.375(6)	C50 -C51	1.382(7)
C9 -C10	1.387(7)	C50 -C55	1.393(7)
C10- C11	1.373(7)	C51 -C52	1.391(7)
C11 -C12	1.375(7)	C52 -C53	1.363(7)
C12 -C13	1.401(6)	C53 -C54	1.370(7)
C14 -C15	1.396(7)	C54 -C55	1.380(7)
C14 -C19	1.377(7)	N1 -C57	1.241(10)
C15 -C16	1.382(7)	C56 -C57	1.463(11)
C16 -C17	1.377(7)	N2 -C59	1.128(7)
C17 -C18	1.376(8)	C58 -C59	1.448(8)
C18 -C19	1.381(7)	F1 -B1	1.356(8)
C20 -C21	1.380(7)	F2 -B1	1.295(8)
C20 -C25	1.389(7)	F3 -B1	1.315(8)
		F4 -B1	1.300(8)
S1 -Cu1- Ni1	50.59(4)		
S1- Cu1- S2	85.99(5)	Ni1- S2 -Cu1	75.21(5)
S2- Cu1- Ni1	50.23(4)	C1 -S2- Cu1	102.91(17)
P1- Cu1- Ni1	160.46(4)	C1 -S2 -Ni1	103.62(18)
P1- Cu1- S1	123.59(5)	C6- P1 -Cu1	102.18(16)
P1- Cu1- S2	114.80(5)	C49- P1 -Cu1	115.99(16)
P2- Cu1- Ni1	109.52(4)	C49- P1- C6	104.9(2)
P2- Cu1- S1	117.26(5)	C49 -P1- C50	104.2(2)
P2- Cu1 -S2	129.60(5)	C50- P1- Cu1	123.58(16)
P2 -Cu1- P1	89.76(5)	C50- P1- C6	103.8(2)
S1 -Ni1- Cu1	53.95(4)	C7- P2 -Cu1	103.74(16)
S2- Ni1- Cu1	54.56(4)	C7 -P2- C42	100.3(2)
S2- Ni1- S1	91.81(6)	C32- P2- Cu1	126.15(16)
P3- Ni1- Cu1	126.61(5)	C32- P2- C7	105.3(2)
P3- Ni1 -S1	179.28(5)	C32 -P2- C42	101.7(2)
P3- Ni1 -S2	88.91(6)	C42 -P2 -Cu1	116.39(16)
P3- Ni1- P4	87.24(6)	C4 -P3 -Ni1	109.91(17)
P4 -Ni1 -Cu1	131.08(5)	C13 -P3- Ni1	110.66(16)
P4 -Ni1- S1	92.04(6)	C13- P3- C4	103.9(2)
P4 -Ni1- S2	174.34(6)	C15- P3- Ni1	121.31(16)
Ni1- S1- Cu	175.46(5)	C15 -P3- C4	105.2(2)
C3 -S1- Cu1	104.25(18)	C15 -P3- C13	104.4(2)
C3 -S1- Ni1	104.75(18)	C5 -P4 -Ni1	108.68(16)
C27 -P4 -Ni1	114.30(16)	C25 -P4- Ni1	116.93(16)
C27- P4 -C5	106.5(2)	C25 -P4- C5	103.1(2)
		C25 -P4 -C27	106.3(2)

Table S5. Selected bond distances (Å) and angles (deg) of Complex

C1 -C2	1.519(9)	C35 -C36	1.380(10)
C1 -S2	1.831(7)	C36 –C7	1.350(10)
C2 -C3	1.498(9)	C37 -C38	1.400(11)
C3 -S1	1.832(7)	C38 -C39	1.364(10)
C4 -C5	1.359(12)	C40 -C41	1.394(9)
C4 -C9	1.419(11)	C40 -C45	1.390(9)
C5 -C6	1.353(13)	C40 -P4	1.819(7)
C6 -C7	1.378(11)	C41 -C42	1.399(9)
C7 -C8	1.394(10)	C42 -C43	1.368(9)
C8 -C9	1.395(9)	C43 -C44	1.392(10)
C8 -P1	1.810(7)	C44 -C45	1.377(9)
C10 -C11	1.372(10)	C46 -C47	1.532(9)
C10 -C15	1.384(9)	C46 -P4	1.817(6)
C11 -C12	1.397(11)	C47 -P3	1.831(6)
C12 -C13	1.365(11)	C48 -C49	1.378(9)
C13 -C14	1.398(10)	C48 -C53	1.399(9)
C14 -C15	1.392(9)	C48 -P3	1.809(7)
C15 -P1	1.810(6)	C49 -C50	1.380(9)
C16 -C17	1.358(9)	C50 -C51	1.414(10)
C16 -C21	1.409(8)	C51 -C52	1.387(11)
C17 -C18	1.386(10)	C52 -C53	1.363(10)
C18 -C19	1.393(9)	C54 -C55	1.379(9)
C19 -C20	1.406(9)	C54 -C59	1.382(9)
C20 -C21	1.415(9)	C55 -C56	1.378(9)
C20 -P2	1.822(7)	C55 -P3	1.822(6)
C21 -P1	1.808(6)	C56 -C57	1.386(9)
C22 -C23	1.374(9)	C57 -C58	1.376(10)
C22 -C27	1.379(9)	C58- C59	1.367(10)
C22 -P2	1.838(6)	Cu1 -Ni1	2.7588(13)
C23 -C24	1.391(10)	Cu1 -P1	2.2952(19)
C24 -C25	1.355(10)	Cu1 -P2	2.2406(19)
C25 -C26	1.380(10)	Cu1 -S1	2.3470(18)
C26 -C27	1.356(10)	Cu1 -S2	2.3406(18)
C28 -C29	1.382(9)	Ni1 -P3	2.1850(18)
C28 -C33	1.399(8)	Ni1 -P4	2.1621(19)
C29 -C30	1.395(10)	Ni1 -S1	2.2480(18)
C30 -C31	1.347(9)	Ni1 -S2	2.2215(18)
C31 -C32	1.403(9)	B1 -F1	1.337(9)
C32 -C33	1.375(9)	B1 -F2	1.336(8)
C33 -P2	1.809(6)	B1 -F3	1.384(9)
C34 -C35	1.386(9)	B1 -F4	1.328(9)
C34 -C39	1.381(9)		
C34 -P4	1.797(6)	C15 -P1 -Cu1	122.1(2)
		C21 -P1 -C8	105.0(3)
P1 -Cu1- Ni1	160.71(6)	C21 -P1 -C15	102.1(3)
P1 -Cu1 -S1	127.04(7)	C21 -P1 -Cu1	101.3(2)
P1 -Cu1 -S2	112.17(7)	C20 -P2 -C22	105.1(3)
P2 -Cu1 -Ni1	112.08(6)	C20-P2- Cu1	102.4(2)
P2 -Cu1 -P1	85.66(7)	C22 -P2 -Cu1	131.4(2)
P2 -Cu1 -S1	119.59(7)	C33 -P2- C20	105.4(3)
P2 -Cu1- S2	130.03(7)	C33- P2- C22	101.8(3)
S1 -Cu1- Ni1	51.47(5)	C33- P2- Cu1	108.4(2)
S2- Cu1- Ni1	50.85(4)	C47 -P3 -Ni1	106.8(2)
S2 -Cu1- S1	87.21(7)	C48 -P3 -C47	103.1(3)
P3 -Ni1 -Cu1	133.29(6)	C48 -P3 -C55	105.8(3)
P3 -Ni1 -S1	171.67(7)	C48 -P3 -Ni1	115.3(2)
P3 -Ni1- S2	91.98(7)	C55 -P3 -C47	105.1(3)
P4 -Ni1 -Cu1	123.74(6)	C55 -P3 -Ni1	119.2(2)
P4 -Ni1- P3	87.31(7)	C34- P4 -C40	106.6(3)
P4 -Ni1- S1	88.46(7)	C34- P4- C46	106.4(3)
P4 -Ni1- S2	176.48(7)	C34- P4- Ni1	118.7(2)
S1 -Ni1 -Cu1	54.77(5)	C40 -P4 -Ni1	112.9(2)
S2 -Ni1- Cu1	54.79(5)	C46- P4- C40	102.3(3)
S2 -Ni1- S1	92.66(7)	C46- P4- Ni1	108.4(2)
C8 -P1 -Cu1	118.9(2)	C3 -S1 -Cu1	103.0(2)
C15- P1 -C8	104.7(3) 102.6(2)	C3 -S1- Ni1	104.2(2)
C1 -S2 -Cu1	105.5(2)	Ni1- S1- Cu1	73.76(6)
C1 -S2- Ni1		Ni1 -S2- Cu1	74.37(6)

Table S6. Selected bond distances (Å) and angles (deg) of Complex **3**.

Cu1 -Ni1	2.7662(10)	S4 -C105	1.829(6)
Cu1 -S1	2.3907(16)	P5 -C58	1.824(6)
Cu1 -S2	2.3903(16)	P5 -C65	1.852(6)
Cu1 -P3	2.2695(17)	P5 -C68	1.815(6)
Cu1 -P4	2.3001(16)	P6 -C64	1.824(6)
Ni1 -S1	2.2071(16)	P6 -C66	1.850(6)
Ni1 -S2	2.2329(16)	P6 -C78	1.829(6)
Ni1 -P1	2.1625(17)	P7 -C83	1.854(6)
Ni1 -P2	2.1724(17)	P7 -C85	1.852(6)
S1 -C110	1.837(6)	P7 -C103	1.867(6)
S2 -C108	1.837(6)	P8 -C93	1.861(6)
P1 -C14	1.853(6)	P8 -C102	1.854(6)
P1 -C20	1.821(6)	P8 -C104	1.844(6)
P1 -C21	1.816(6)	P4 -C39	1.851(6)
P2 -C1	1.834(6)	Cu2 -Ni2	2.7500(10)
P2 -C7	1.811(6)	Cu2 -S3	2.3709(16)
P2 -C13	1.835(6)	Cu2 -S4	2.3983(16)
P3 -C40	1.867(6)	Cu2 -P7	2.2633(16)
P3 -C41	1.852(6)	Cu2 -P8	2.2964(17)
P3 -C52	1.861(6)	Ni2 -S3	2.2075(16)
P4 -C32	1.858(6)	Ni2 -S4	2.2353(16)
P4 -C33	1.849(6)	Ni2 -P5	2.1716(17)
S3 -C107	1.840(6)	Ni2 -P6	2.1991(17)
S1 -Cu1 -Ni1	50.03(4)	C6 -C1 -P2	120.2(5)
S2 -Cu1 -Ni1	50.68(4)	S3 -Cu2 -Ni2	50.41(4)
S2 -Cu1 -S1	84.62(5)	S3 -Cu2 -S4	83.77(5)
P3 -Cu1 -Ni1	111.56(5)	S4 -Cu2 -Ni2	50.91(4)
P3 -Cu1 -S1	138.76(6)	P7 -Cu2 -Ni2	107.50(5)
P3 -Cu1 -S2	112.28(6)	P7 -Cu2 -S3	137.02(6)
P3 -Cu1 -P4	90.96(6)	P7 -Cu2 -S4	111.12(6)
P4 -Cu1 -Ni1	156.14(5)	P7 -Cu2 -P8	90.82(6)
P4 -Cu1 -S1	107.62(6)	P8 -Cu2 -Ni2	159.37(5)
P4 -Cu1 -S2	128.78(6)	P8 -Cu2 -S3	109.47(6)
S1 -Ni1 -Cu1	56.12(4)	P8 -Cu2 -S4	131.38(6)
S1 -Ni1 -S2	92.91(6)	S3 -Ni2 -Cu2	55.86(4)
S2 -Ni1 -Cu1	55.91(4)	S3 -Ni2 -S4	91.56(6)
P1 -Ni1 -Cu1	129.78(5)	S4 -Ni2 -Cu2	56.38(4)
P1 -Ni1 -S1	173.36(7)	P5 -Ni2 -Cu2	130.91(5)
P1 -Ni1 -S2	89.26(6)	P5 -Ni2 -S3	169.86(7)
P1 -Ni1 -P2	86.91(6)	P5 -Ni2 -S4	88.13(6)
P2 -Ni1 -Cu1	125.37(5)	P5 -Ni2 -P6	87.12(6)
P2 -Ni1 -S1	91.19(6)	P6 -Ni2 -Cu2	125.19(5)
P2 -Ni1 -S2	175.38(7)	P6 -Ni2 -S3	93.73(6)
Ni1 -S1 -Cu1	73.85(5)	P6 -Ni2 -S4	174.08(6)
C110 -S1 -Cu1	100.3(2)	Ni2 -S3 -Cu2	73.74(5)
C110 -S1 -Ni1	106.7(2)	C107 -S3 -Cu2	103.7(2)
Ni1 -S2 -Cu1	73.41(5)	C107 -S3 -Ni2	107.6(2)
C108 -S2 -Cu1	106.9(2)	Ni2 -S4 -Cu2	72.71(5)
C108 -S2 -Ni1	105.6(2)	C105 -S4 -Cu2	106.4(2)
C14 -P1 -Ni1	109.9(2)	C105 -S4 -Ni2	107.6(2)
C20 -P1 -Ni1	112.4(2)	C58 -P5 -Ni2	112.5(2)
C20 -P1 -C14	102.2(3)	C58 -P5 -C65	102.0(3)
C21 -P1 -Ni1	118.4(2)	C65 -P5 -Ni2	110.0(2)
C21 -P1 -C14	106.2(3)	C68 -P5 -Ni2	119.5(2)
C21 -P1 -C20	106.3(3)	C68 -P5 -C58	105.8(3)
C1 -P2 -Ni1	111.9(2)	C68 -P5 -C65	105.4(3)
C1 -P2 -C13	105.4(3)	C64 -P6 -Ni2	110.5(2)
C7 -P2 -Ni1	120.7(2)	C64 -P6 -C66	103.4(3)
C7 -P2 -C1	104.1(3)	C64 -P6 -C78	103.0(3)
C7 -P2 -C13	107.0(3)	C66 -P6 -Ni2	107.3(2)
C13 -P2 -Ni1	106.8(2)	C78 -P6 -Ni2	126.0(2)
C40 -P3 -Cu1	105.6(2)	C78 -P6 -C66	104.4(3)
C41 -P3 -Cu1	112.3(2)	C83 -P7 -Cu2	111.05(19)
C41 -P3- C40	104.7(3)	C83 -P7 -C103	104.8(3)
C41 -P3 -C52	102.9(3)	C85 -P7 -Cu2	128.7(2)
C52 -P3 -Cu1	128.9(2)	C85 -P7 -C83	103.1(3)
C52 -P3 -C40	99.6(3)	C85 -P7 -C103	101.1(3)
C32 -P4 -Cu1	113.5(2)	C103 -P7 -Cu2	105.74(19)
C33 -P4 -Cu1	125.1(2)	C93 -P8 -Cu2	111.0(2)
C33 -P4 -C32	103.5(3)	C102 -P8 -Cu2	126.5(2)
C33 -P4 -C39	103.5(3)	C102 -P8 -C93	103.5(3)
C39 -P4 -Cu1	105.0(2)	C104 -P8 -Cu2	105.3(2)
C39 -P4 -C32	104.2(3)	C104 -P8 -C93	104.5(3)
C2 -C1 -P2	119.4(5)	C104 -P8 -C102	104.1(3)
C2 -C1 -C6	120.3(6)		

Table S7. Selected bond distances (Å) and angles (deg) of Complex

$[Ni(dppe)(\mu\text{-}pdt)Ag]_2(BF_4)_2$

Ag1- Ag1	3.0642(10)	C7- C8	1.361(11)
Ag1- Ni1	3.1337(9)	C7- C12	1.395(12)
Ag1- Ni1	3.1803(10)	C8- C9	1.378(10)
Ag1- S1	2.3989(18)	C9- C10	1.379(11)
Ag1- S2	2.3913(19)	C10- C11	1.329(12)
Ni1- Ag1	3.1337(9)	C11- C12	1.341(12)
Ni1- S1	2.1918(18)	C13- C14	1.527(9)
Ni1- S2	2.192(2)	C15- C16	1.378(10)
Ni1- P1	2.1859(18)	C15- C20	1.388(10)
Ni1- P2	2.1883(19)	C16- C17	1.359(12)
S1- Ag1	2.3990(18)	C17- C18	1.388(12)
S1- C27	1.814(8)	C18- C19	1.365(11)
S2- C29	1.797(9)	C19- C20	1.398(9)
P1- C6	1.811(6)	C21- C22	1.387(9)
P1- C8	1.812(7)	C21- C26	1.396(10)
P1- C13	1.827(7)	C22- C23	1.394(10)
P2- C14	1.844(6)	C23- C24	1.362(12)
P2- C20	1.809(7)	C24- C25	1.375(12)
P2- C21	1.813(6)	C25- C26	1.388(10)
C1- C2	1.396(9)	C27- C58	1.577(14)
C1- C6	1.364(9)	C29- C58	1.410(14)
C2- C3	1.366(10)	C4- C5	1.374(11)
C3- C4	1.368(12)	C5- C6	1.389(9)
Ag1- Ag1- Ni1	61.73(2)	C1- C6- P1	121.1(5)
Ag1- Ag1- Ni1	60.21(2)	C1- C6- C5	118.5(6)
Ni1- Ag1- Ni1	121.94(2)	C5- C6- P1	120.3(6)
S1- Ag1- Ag1	95.04(5)	C8- C7- C12	120.3(9)
S1- Ag1- Ni1	44.24(4)	C7- C8- P1	119.3(6)
S1- Ag1- Ni1	142.24(5)	C7- C8- C9	118.3(7)
S2- Ag1- Ag1	91.97(5)	C9- C8- P1	121.9(6)
S2- Ag1- Ni1	140.31(5)	C8- C9- C10	119.1(8)
S2- Ag1- Ni1	43.52(5)	C11- C10- C9	122.5(8)
S2- Ag1- S1	172.93(7)	C10- C11- C12	118.9(8)
Ag1- Ni1- Ag1	58.06(2)	C11- C12- C7	120.7(9)
S1- Ni1- Ag1	96.25(5)	C14- C13- P1	105.9(5)
S1- Ni1- Ag1	49.79(5)	C13- C14- P2	110.9(4)
S1- Ni1- S2	99.98(7)	C16- C15- C20	119.5(7)
S2- Ni1- Ag1	48.71(5)	C17- C16- C15	121.1(8)
S2- Ni1- Ag1	94.12(5)	C16- C17- C18	119.5(8)
P1- Ni1- Ag1	130.23(6)	C19- C18- C17	120.9(8)
P1- Ni1- Ag1	89.00(5)	C18- C19- C20	119.3(8)
P1- Ni1- S1	172.09(8)	C15- C20- P2	120.5(5)
P1- Ni1- S2	87.94(7)	C15- C20- C19	119.7(7)
P1- Ni1- P2	86.00(7)	C19- C20- P2	119.7(6)
P2- Ni1- Ag1	134.13(6)	C22- C21- P2	120.5(6)
P2- Ni1- Ag1	92.15(5)	C22- C21- C26	119.4(6)
P2- Ni1- S1	86.09(7)	C26- C21- P2	120.1(5)
P2- Ni1- S2	173.20(7)	C21- C22- C23	119.5(8)
Ni1- S1- Ag1	85.97(6)	C24- C23- C22	120.1(8)
C27- S1- Ag1	110.0(3)	C23- C24- C25	121.4(7)
C27- S1- Ni1	114.1(3)	C24- C25- C26	119.1(8)
Ni1- S2- Ag1	87.77(7)	C25- C26- C21	120.3(7)
C29- S2- Ag1	109.3(3)	C58- C27- S1	114.2(6)
C29- S2- Ni1	114.1(3)	C58 -C29- S2	118.2(7)
C6- P1- Ni1	113.2(2)	C29- C58- C27	114.9(9)
C6 -P1- C8	103.7(3)	C20- P2- C14	105.1(3)
C6- P1 -C13	105.8(3)	C20- P2- C21	106.5(3)
C8- P1- Ni1	117.2(2)	C21- P2- Ni1	115.3(2)
C8 -P1 -C13	107.6(3)	C21- P2- C14	106.4(3)
C13- P1- Ni1	108.7(2)	C6- C1- C2	121.1(6)
C14- P2- Ni1	109.3(2)	C3- C2- C1	119.1(7)
C20- P2- Ni1	113.5(2)	C2- C3- C4	120.6(7)
C4- C5- C6	120.6(8)	C3- C4- C5	119.9(8)

Table S8. Optimized coordinates on DFT calculation of complex **3**

atom	x	y	z
Cu	-1.387052	-0.200069	-0.24397
Ni	1.63572	-0.158972	-0.700593
S	0.272711	-1.96852	-0.835521
S	0.073795	1.127313	-1.774444
P	3.205713	-1.384687	0.42296
P	3.097807	1.596098	-0.565061
P	-3.702462	-0.922222	-0.561821
P	-2.031682	0.897921	1.789488
C	-0.141353	0.299843	-3.415666
H	-0.776536	0.978082	-3.994331
H	0.831439	0.275167	-3.917439
C	-0.775713	-1.088272	-3.386217
H	-0.910631	-1.41641	-4.427837
H	-1.773597	-1.015619	-2.94298
C	0.019016	-2.173012	-2.662904
H	1.004197	-2.305659	-3.122817
H	-0.50282	-3.130108	-2.762916
C	-3.762599	0.235114	2.086826
H	-3.615336	-0.695155	2.642195
H	-4.310196	0.907501	2.756335
C	-4.610395	-0.046451	0.82875
H	-4.970349	0.897521	0.408643
H	-5.502296	-0.616858	1.113184
C	4.365746	-0.161018	1.221806
H	3.853359	0.247697	2.098567
H	5.280798	-0.653952	1.565359
C	4.672895	0.951716	0.211857
H	5.268231	0.554683	-0.616455
H	5.25099	1.765074	0.660934
C	-4.728959	-0.479018	-2.078596
H	-4.321447	-1.131765	-2.864178
C	-6.243138	-0.756973	-1.973931
H	-6.430211	-1.801062	-1.70054
H	-6.673813	-0.140419	-1.173379
C	-6.963535	-0.435684	-3.295835
H	-6.618946	-1.134075	-4.071411
H	-8.039855	-0.607535	-3.180082
C	-6.697159	1.004834	-3.754082
H	-7.180482	1.191149	-4.719757
H	-7.15323	1.703127	-3.038003
C	-5.191334	1.289881	-3.848765
H	-5.016861	2.336071	-4.126003

H	-4.755224	0.677463	-4.650812
C	-4.471168	0.975759	-2.52643
H	-4.833869	1.668597	-1.755009
H	-3.394114	1.155823	-2.622205
C	-4.102606	-2.74008	-0.277937
H	-5.19427	-2.819889	-0.175444
C	-3.662835	-3.60564	-1.478329
H	-2.584623	-3.469599	-1.636658
H	-4.163097	-3.277811	-2.396206
C	-3.954451	-5.097864	-1.244896
H	-5.041596	-5.249035	-1.19116
H	-3.602567	-5.67959	-2.10485
C	-3.306262	-5.605163	0.049629
H	-3.560552	-6.658272	0.214976
H	-2.212486	-5.557143	-0.048957
C	-3.744529	-4.75626	1.249741
H	-3.239731	-5.092358	2.163074
H	-4.82126	-4.896817	1.419462
C	-3.458322	-3.261171	1.025583
H	-2.373517	-3.096551	0.97814
H	-3.829834	-2.694794	1.886853
C	-2.870068	3.172218	0.306266
H	-2.329434	2.700389	-0.520894
H	-3.903523	2.803063	0.267052
C	-2.89156	4.699906	0.130553
H	-1.857842	5.064727	0.058235
H	-3.378649	4.956322	-0.817617
C	-3.597176	5.397701	1.301692
H	-3.553453	6.486104	1.180085
H	-4.662671	5.127624	1.295338
C	-2.980483	4.987207	2.645984
H	-3.528843	5.448731	3.47535
H	-1.949974	5.365051	2.704979
C	-2.963986	3.457537	2.823516
H	-4.000739	3.098444	2.874046
H	-2.49898	3.205655	3.782729
C	-2.233325	2.7674	1.653042
H	-1.196103	3.131013	1.635706
C	-1.286457	0.651008	3.502652
H	-2.044335	0.9878	4.224987
C	-0.011274	1.490252	3.72067
H	-0.202283	2.552719	3.542963
H	0.74846	1.185291	2.987047
C	0.541124	1.303999	5.144369

H	1.458997	1.892323	5.264057
H	-0.182179	1.711104	5.864463
C	0.80459	-0.172541	5.466669
H	1.626151	-0.5373	4.835591
H	1.134885	-0.281953	6.506243
C	-0.438658	-1.035223	5.208994
H	-1.22021	-0.774748	5.936205
H	-0.204736	-2.09421	5.367651
C	-0.986777	-0.836849	3.78498
H	-1.883911	-1.452122	3.654705
H	-0.252848	-1.200571	3.053331
C	4.282301	-2.298099	-0.75047
C	4.062299	-2.182054	-2.12999
H	3.229974	-1.582935	-2.486422
C	4.895048	-2.840591	-3.037242
H	4.71511	-2.747401	-4.104076
C	5.952642	-3.621846	-2.571005
H	6.599683	-4.136499	-3.274838
C	6.175799	-3.748364	-1.196831
H	6.994512	-4.361527	-0.832609
C	5.344893	-3.093386	-0.289605
H	5.515978	-3.212385	0.776527
C	3.518597	1.628954	-3.330207
H	2.994906	0.67903	-3.319161
C	4.020751	2.13679	-4.528662
H	3.89052	1.577285	-5.450165
C	4.680184	3.367005	-4.542654
H	5.067232	3.765677	-5.475467
C	4.838603	4.087075	-3.356345
H	5.349953	5.044871	-3.364707
C	4.339893	3.580804	-2.15619
H	4.461284	4.152399	-1.241355
C	3.675407	2.344225	-2.134545
C	3.072772	3.218878	1.771181
H	3.796784	2.535057	2.20149
C	2.655949	4.315367	2.52896
H	3.056236	4.46112	3.527788
C	1.744017	5.227807	1.99778
H	1.431698	6.0886	2.581332
C	1.244051	5.035666	0.707075
H	0.545324	5.749967	0.282286
C	1.648826	3.936727	-0.050653
H	1.253005	3.795393	-1.050931
C	2.578235	3.019892	0.472526

C	2.260107	-3.849107	1.357671
H	2.056439	-4.059061	0.314364
C	1.965695	-4.808315	2.325712
H	1.538662	-5.759715	2.023428
C	2.224887	-4.55256	3.673958
H	2.001273	-5.304386	4.424762
C	2.781821	-3.330485	4.051662
H	2.997544	-3.126997	5.096128
C	3.075545	-2.3642	3.087105
H	3.519212	-1.428512	3.408544
C	2.819236	-2.612846	1.729145