Supplementary Information

Reduction of Oxygen Catalyzed by Nickel Diphosphine Complexes with Positioned Pendant Amines

Jenny Y. Yang,[a] R. Morris Bullock,[a] William G. Dougherty,[a] W. Scott Kassel,[b] Brendan Twamley,[c] Daniel L. DuBois,[a] and M. Rakowski DuBois[a]

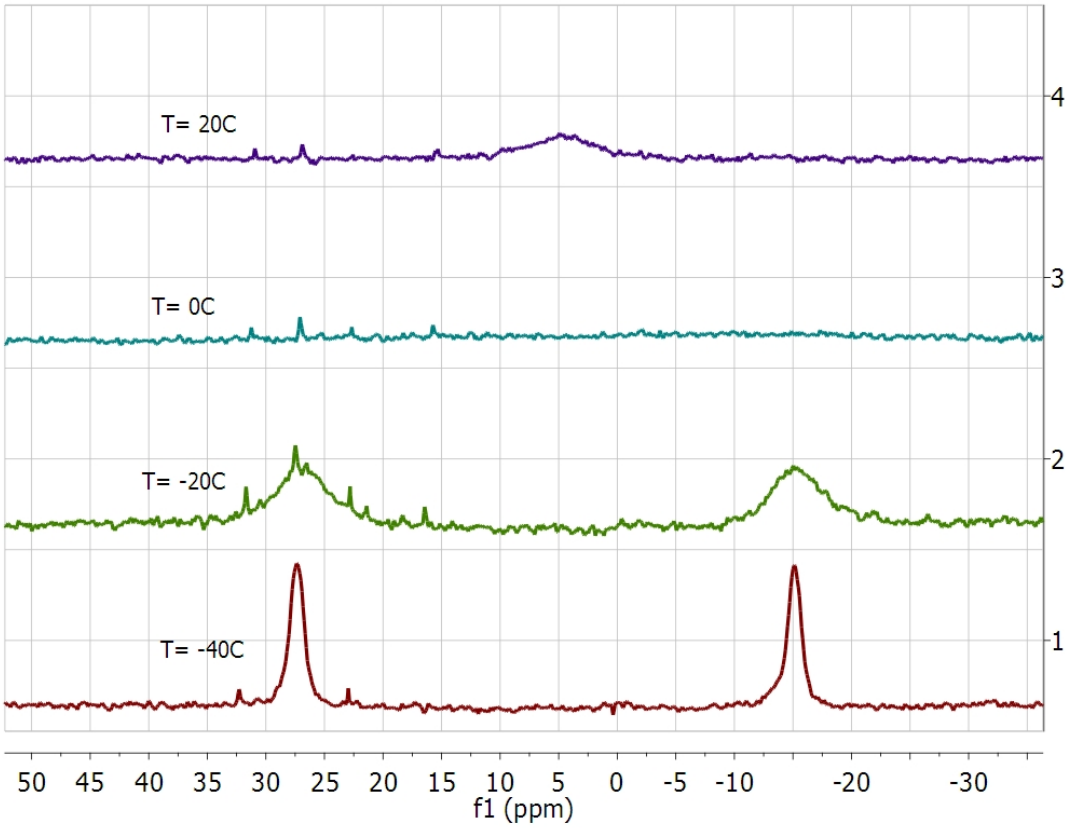
[a]*Chemical and Materials Sciences Division, Pacific Northwest National Laboratory, Richland, WA 99352*

[b]*Department of Chemistry, Villanova University, Villanova, Pennsylvania 19085*

[c]*Department of Chemistry, University of Idaho, Moscow, Idaho 83844*

mary.rakowskidubois@pnl.gov

Table of Contents for Supporting Information



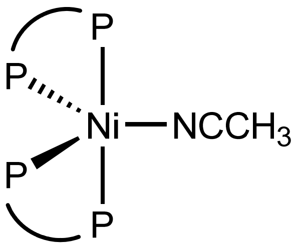


Figure S1. Variable temperature ^{31}P NMR spectra of $[Ni(P^{Ph}{}_2N^{Me}{}_2)_2](BF_4)_2$ in acetonitrile.

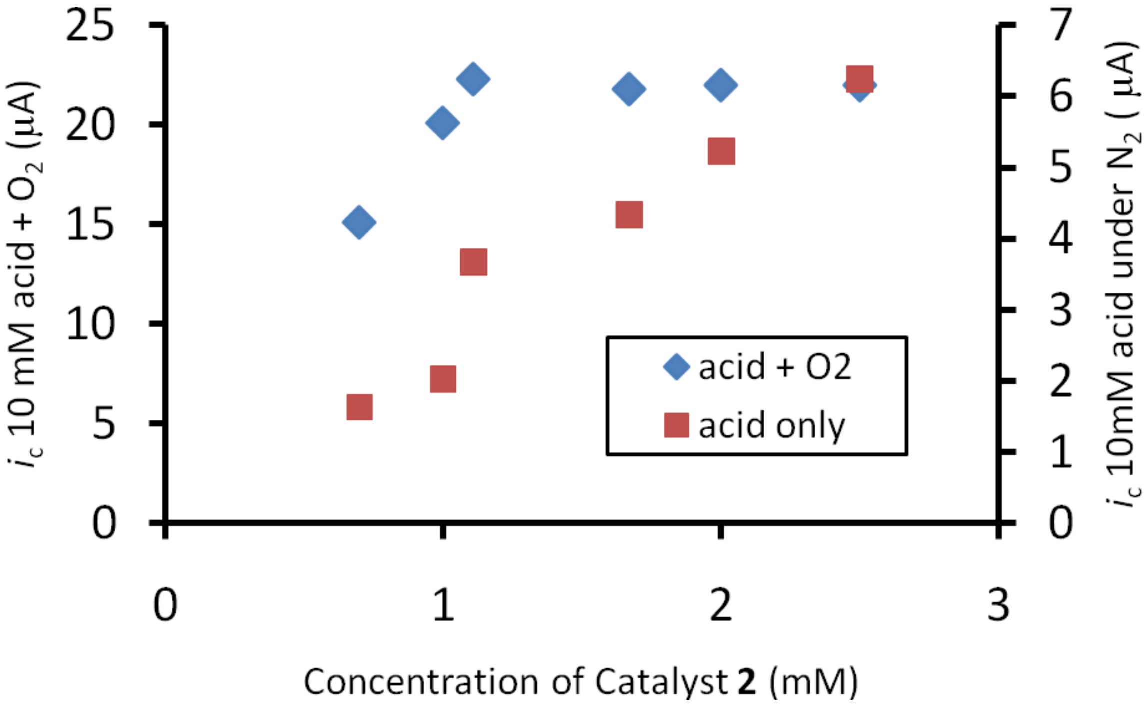


Figure S2. Catalyst (**2**) concentration dependent studies. At 10 mM of 4-bromoanilinium tetrafluoroborate, catalytic current observed as a function of catalyst concentration under: oxygen (blue diamonds), corresponding to the current magnitudes on the left axis, and under nitrogen (red squares), corresponding to the current magnitudes on the right axis. The current under nitrogen is associated with proton reduction by catalyst **2**.

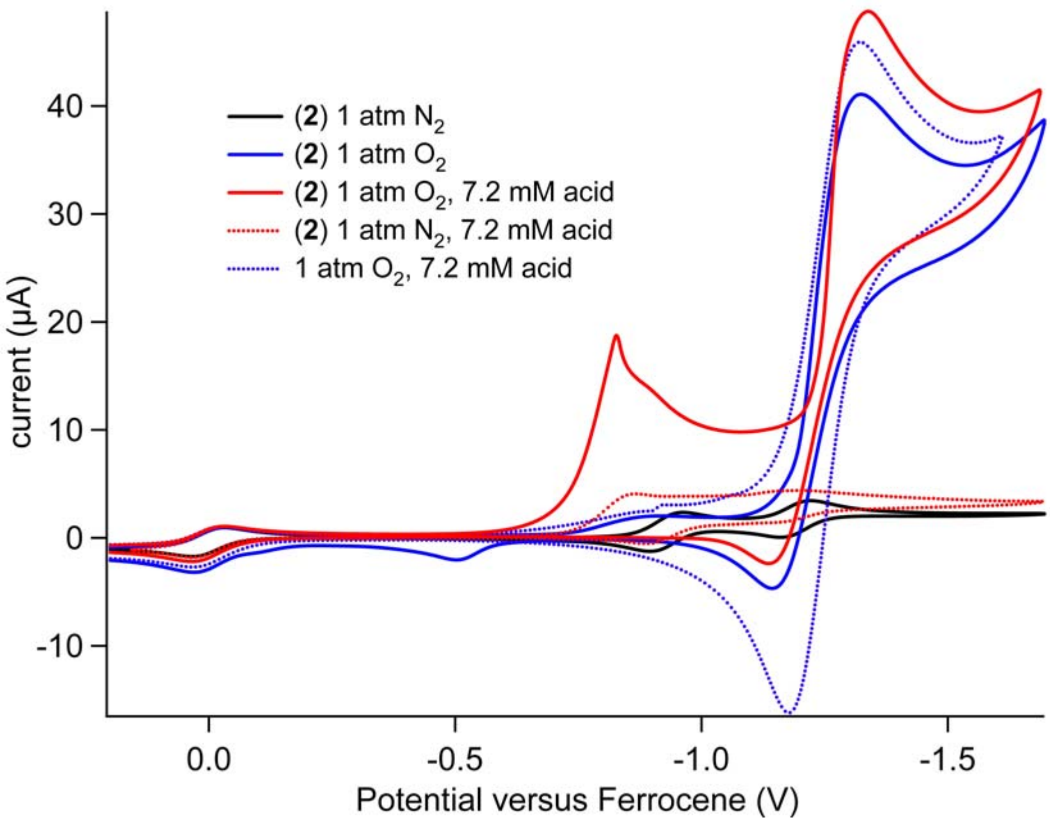


Figure S3. Cyclic voltammograms of 1.7 mM solutions of $Ni(P^{Ph}{}_2N^{Bz}{}_2)_2(BF_4)_2$ (**2**) under 1 atmosphere of nitrogen (black), and oxygen (blue). The same catalyst solution with 7.2 mM of 4-bromoanilinium tetrafluoroborate is also shown under oxygen (red), and nitrogen (dotted red). A solution of 7.2 mM of 4-bromoanilinium tetrafluoroborate with no catalyst under oxygen is shown as the dotted blue trace. Conditions: scan rate = 50 mV/s, acetonitrile solvent, 0.2 M Et_4NBF_4 as supporting electrolyte, glassy carbon working electrode. Potentials are referenced to the ferrocene/ferocenium couple (wave shown at 0.0 V).

Supplementary Information

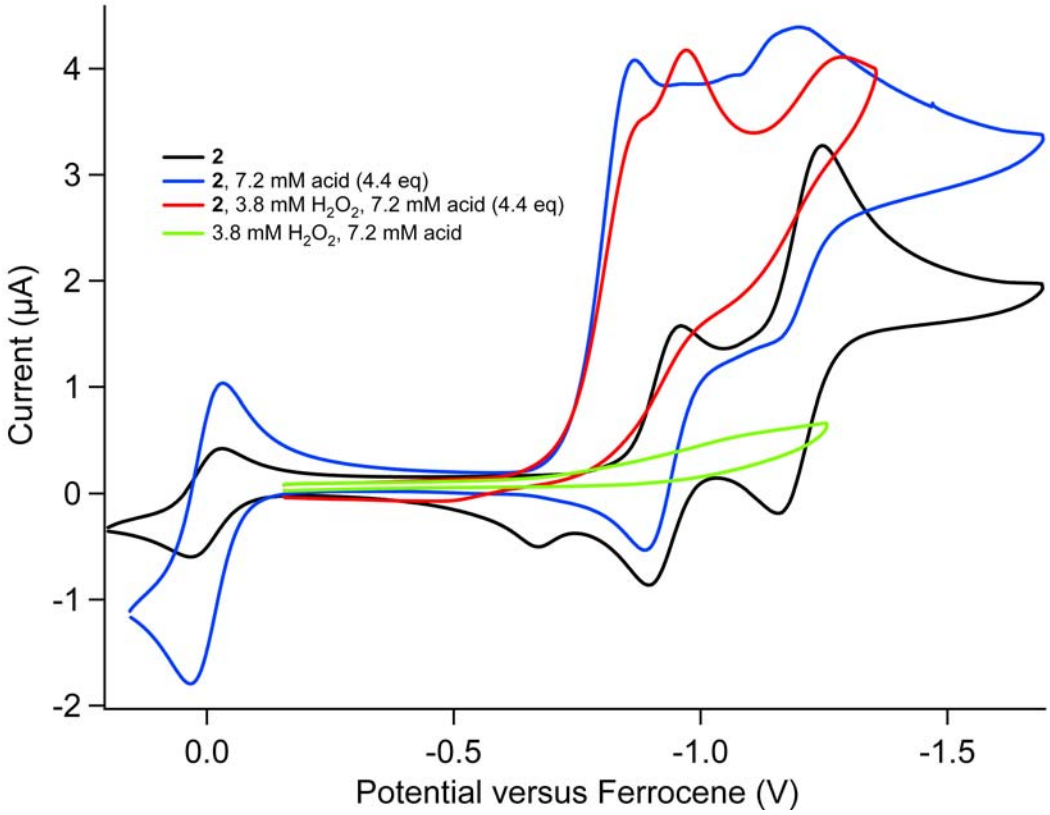


Figure S4. Cyclic voltammagrams of a 1.7 mM solution of $Ni(P^{Ph}{}_2N^{Bz}{}_2)_2(BF_4)_2$ (**2**) under nitrogen (black), and in 7.2 mM of 4-bromoanilinium tetrafluoroborate (4.4 equivalents with respect to catalyst) with 1 μL of 30% w/w aqueous H_2O_2 solution (red) and without added H_2O_2 (blue). The green trace was recorded in a solution with the same concentration of H_2O_2 and acid as red, but in the absence of catalyst. Conditions: scan rate = 50 mV/s, acetonitrile solvent, 0.2 M Et_4NBF_4 as supporting electrolyte, glassy carbon working electrode. Potentials are referenced to the ferrocene/ferocenium couple (wave shown at 0.0 V).

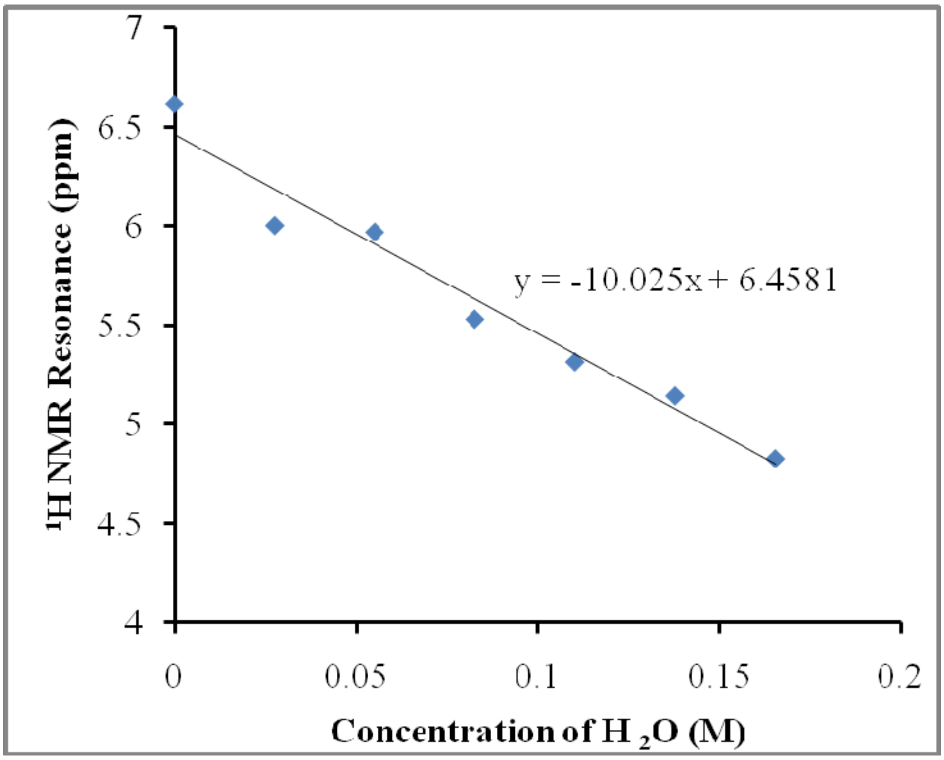


Figure S5. The relative concentration of 4-bromoanilinium tetrafluoroborate and the conjugate base were determined by the ^{1}H NMR spectra of the solution taken after the controlled-potential coulometry experiment. A solution with the same acid-base concentration was prepared and water was titrated into the solution. Because of the fast proton exchange between the acid and the water at room temperature, only one resonance is observed in the ^{1}H NMR for the N-H protons and from H_2O. The resonance shift due to the changes in H_2O concentration was plotted, and the best fit line was used to determine the concentration of water in the post-electrolysis solution.

Table S1. Crystal data and structure refinement for $[Ni(P^{Ph_2}{}^{Me}{}_2)_2]$ (**6**).

Identification code	pnl020	
Empirical formula	$C_{18} H_{24} N_2 Ni_{0.50} P_2$	
Formula weight	359.69	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 9.7763(2) Å	α= 90°.
	b = 19.7795(4) Å	β= 101.1210(10)°.
	c = 19.0291(3) Å	γ = 90°.
Volume	3610.57(12) $Å^3$	
Z	8	
Density (calculated)	1.323 Mg/m^3	
Absorption coefficient	2.685 mm^{-1}	
F(000)	1520	
Crystal size	0.12 x 0.11 x 0.06 mm^3	
Theta range for data collection	4.47 to 69.10°.	
Index ranges	-11<=h<=11, -22<=k<=12, -22<=l<=22	
Reflections collected	10592	
Independent reflections	3181 [R(int) = 0.0201]	
Completeness to theta = 67.00°	97.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8642 and 0.7370	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3181 / 0 / 206	
Goodness-of-fit on F^2	1.026	
Final R indices [I>2sigma(I)]	R1 = 0.0297, wR2 = 0.0787	
R indices (all data)	R1 = 0.0317, wR2 = 0.0804	
Largest diff. peak and hole	0.487 and -0.235 $e.Å^{-3}$	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $[Ni(P^{Ph}{}_2{}^{Me}{}_2)_2]$ (**6**). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ni(1)	0	2917(1)	2500	14(1)
N(1)	500(2)	2278(1)	730(1)	20(1)
N(2)	2552(1)	3596(1)	1753(1)	17(1)
P(1)	1622(1)	2349(1)	2179(1)	15(1)
P(2)	-320(1)	3366(1)	1466(1)	14(1)
C(1)	3742(2)	1974(1)	3318(1)	22(1)
C(2)	4649(2)	1533(1)	3747(1)	26(1)
C(3)	4610(2)	848(1)	3598(1)	30(1)
C(4)	3663(2)	604(1)	3019(1)	33(1)
C(5)	2762(2)	1046(1)	2586(1)	27(1)
C(6)	2798(2)	1738(1)	2723(1)	18(1)
C(7)	971(2)	1844(1)	1354(1)	20(1)
C(8)	252(2)	1866(1)	81(1)	31(1)
C(9)	-717(2)	2701(1)	760(1)	19(1)
C(10)	2932(2)	2878(1)	1828(1)	18(1)
C(11)	3702(2)	3987(1)	1573(1)	21(1)
C(12)	1283(2)	3732(1)	1218(1)	16(1)
C(13)	-1623(2)	4287(1)	393(1)	24(1)
C(14)	-2542(2)	4804(1)	138(1)	29(1)
C(15)	-3444(2)	5053(1)	560(1)	30(1)
C(16)	-3432(2)	4779(1)	1229(1)	26(1)
C(17)	-2500(2)	4262(1)	1494(1)	21(1)
C(18)	-1586(2)	4016(1)	1077(1)	18(1)

Supplementary Information

Table S3. Bond lengths [Å] and angles [°] for $[Ni(P^{Ph}{}_{2}{}^{Me}{}_{2})_2]$ (**6**).

Ni(1)-P(2)	2.1262(4)
Ni(1)-P(2)#1	2.1262(4)
Ni(1)-P(1)	2.1266(4)
Ni(1)-P(1)#1	2.1266(4)
N(1)-C(8)	1.460(2)
N(1)-C(9)	1.464(2)
N(1)-C(7)	1.467(2)
N(2)-C(11)	1.460(2)
N(2)-C(10)	1.468(2)
N(2)-C(12)	1.4693(19)
P(1)-C(6)	1.8428(16)
P(1)-C(7)	1.8654(16)
P(1)-C(10)	1.8723(16)
P(2)-C(18)	1.8375(15)
P(2)-C(9)	1.8671(16)
P(2)-C(12)	1.8679(15)
C(1)-C(2)	1.390(2)
C(1)-C(6)	1.397(2)
C(2)-C(3)	1.384(3)
C(3)-C(4)	1.382(3)
C(4)-C(5)	1.391(3)
C(5)-C(6)	1.392(2)
C(13)-C(14)	1.387(2)
C(13)-C(18)	1.402(2)
C(14)-C(15)	1.392(3)
C(15)-C(16)	1.381(3)
C(16)-C(17)	1.398(2)
C(17)-C(18)	1.392(2)
P(2)-Ni(1)-P(2)#1	130.57(3)
P(2)-Ni(1)-P(1)	86.532(14)
P(2)#1-Ni(1)-P(1)	120.121(14)
P(2)-Ni(1)-P(1)#1	120.123(14)
P(2)#1-Ni(1)-P(1)#1	86.532(14)

P(1)-Ni(1)-P(1)#1	116.29(3)
C(8)-N(1)-C(9)	110.38(13)
C(8)-N(1)-C(7)	109.49(12)
C(9)-N(1)-C(7)	115.69(13)
C(11)-N(2)-C(10)	110.08(12)
C(11)-N(2)-C(12)	108.98(12)
C(10)-N(2)-C(12)	114.15(12)
C(6)-P(1)-C(7)	101.25(7)
C(6)-P(1)-C(10)	99.85(7)
C(7)-P(1)-C(10)	98.40(7)
C(6)-P(1)-Ni(1)	127.13(5)
C(7)-P(1)-Ni(1)	111.84(5)
C(10)-P(1)-Ni(1)	114.01(5)
C(18)-P(2)-C(9)	99.93(7)
C(18)-P(2)-C(12)	99.24(7)
C(9)-P(2)-C(12)	99.16(7)
C(18)-P(2)-Ni(1)	129.24(5)
C(9)-P(2)-Ni(1)	110.13(5)
C(12)-P(2)-Ni(1)	114.49(5)
C(2)-C(1)-C(6)	120.91(16)
C(3)-C(2)-C(1)	120.33(16)
C(2)-C(3)-C(4)	119.48(16)
C(3)-C(4)-C(5)	120.22(17)
C(6)-C(5)-C(4)	121.13(17)
C(5)-C(6)-C(1)	117.90(15)
C(5)-C(6)-P(1)	123.39(13)
C(1)-C(6)-P(1)	118.67(12)
N(1)-C(7)-P(1)	111.72(11)
N(1)-C(9)-P(2)	111.93(10)
N(2)-C(10)-P(1)	113.38(10)
N(2)-C(12)-P(2)	113.02(10)
C(14)-C(13)-C(18)	120.42(16)
C(13)-C(14)-C(15)	119.87(17)
C(16)-C(15)-C(14)	120.05(15)
C(15)-C(16)-C(17)	120.49(16)
C(18)-C(17)-C(16)	119.76(16)

C(17)-C(18)-C(13)	119.39(15)
C(17)-C(18)-P(2)	118.14(12)
C(13)-C(18)-P(2)	122.42(12)

Symmetry transformations used to generate equivalent atoms:

#1 -x,y,-z+1/2

Table S4. Anisotropic displacement parameters ($Å^2$x 10^3) for [Ni($P^{Ph}{}_2N^{Me}{}_2$)$_2$] (**6**). The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ni(1)	14(1)	15(1)	12(1)	0	3(1)	0
N(1)	27(1)	17(1)	15(1)	-2(1)	3(1)	3(1)
N(2)	15(1)	20(1)	16(1)	1(1)	3(1)	-2(1)
P(1)	15(1)	15(1)	13(1)	0(1)	2(1)	2(1)
P(2)	15(1)	14(1)	13(1)	1(1)	2(1)	1(1)
C(1)	22(1)	22(1)	22(1)	2(1)	4(1)	1(1)
C(2)	20(1)	33(1)	24(1)	7(1)	0(1)	0(1)
C(3)	30(1)	32(1)	28(1)	11(1)	6(1)	12(1)
C(4)	49(1)	21(1)	28(1)	4(1)	6(1)	9(1)
C(5)	35(1)	22(1)	22(1)	1(1)	0(1)	3(1)
C(6)	17(1)	21(1)	18(1)	3(1)	6(1)	4(1)
C(7)	24(1)	17(1)	17(1)	-1(1)	2(1)	2(1)
C(8)	50(1)	22(1)	17(1)	-3(1)	0(1)	9(1)
C(9)	21(1)	18(1)	17(1)	-2(1)	-1(1)	0(1)
C(10)	16(1)	21(1)	18(1)	3(1)	5(1)	1(1)
C(11)	19(1)	25(1)	20(1)	2(1)	4(1)	-4(1)
C(12)	18(1)	16(1)	16(1)	2(1)	4(1)	0(1)
C(13)	26(1)	23(1)	20(1)	2(1)	0(1)	0(1)
C(14)	33(1)	22(1)	27(1)	7(1)	-9(1)	-2(1)
C(15)	20(1)	16(1)	45(1)	1(1)	-11(1)	0(1)
C(16)	17(1)	18(1)	42(1)	-6(1)	2(1)	0(1)
C(17)	17(1)	19(1)	26(1)	-2(1)	2(1)	-2(1)
C(18)	16(1)	16(1)	20(1)	1(1)	-1(1)	-1(1)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3)for [Ni($P^{Ph}{}_2{}^{Me}{}_2$)$_2$] (**6**).

	x	y	z	U(eq)
H(1A)	3764	2442	3432	26
H(2A)	5300	1703	4144	31
H(3A)	5230	547	3891	36
H(4A)	3626	134	2916	40
H(5A)	2112	872	2191	33
H(7A)	1725	1544	1259	23
H(7B)	187	1555	1434	23
H(8A)	1101	1615	47	46
H(8B)	-4	2160	-339	46
H(8C)	-508	1548	98	46
H(9A)	-1485	2412	859	23
H(9B)	-1034	2920	289	23
H(10A)	3845	2836	2157	22
H(10B)	3037	2700	1355	22
H(11A)	4559	3887	1918	32
H(11B)	3492	4470	1589	32
H(11C)	3828	3866	1090	32
H(12A)	1398	3542	752	20
H(12B)	1164	4227	1160	20
H(13A)	-1015	4115	102	28
H(14A)	-2557	4989	-324	35
H(15A)	-4068	5410	388	35
H(16A)	-4062	4944	1512	31
H(17A)	-2491	4079	1956	25

Table S6. Crystal data and structure refinement for $[Ni(OP^{Ph}{}_2N^{Bz}{}_2)2](BF_4)_2 \bullet (CH_3CN)$ **8**.

Empirical formula	$C_{62}H_{67}B_2F_8N_5NiO_4P_4$	
Formula weight	1302.42	
Temperature	90(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	*a* = 24.8972(8) Å	α = 90°.
	b = 11.2331(3) Å	β = 113.371(1)°.
	c = 25.3567(8) Å	γ = 90°.
Volume	6509.8(3) $Å^3$	
Z	4	
Density (calculated)	1.329 Mg/m^3	
Absorption coefficient	0.468 mm^{-1}	
F(000)	2704	
Crystal size	0.30 x 0.28 x 0.17 mm^3	
Crystal color and habit	pale green fragment	
Diffractometer	Bruker/Siemens SMART APEX	
Theta range for data collection	1.94 to 25.25°.	
Index ranges	-29<=h<=29, -13<=k<=13, -30<=l<=30	
Reflections collected	95676	
Independent reflections	11797 [R(int) = 0.0409]	
Completeness to theta = 25.25°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9247 and 0.8723	
Solution method	XS, SHELXTL v. 6.14 (Bruker, 2003)	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11797 / 15 / 764	
Goodness-of-fit on F^2	1.075	
Final R indices [I>2sigma(I)]	R1 = 0.0503, wR2 = 0.1319	
R indices (all data)	R1 = 0.0598, wR2 = 0.1383	
Largest diff. peak and hole	1.509 and -0.758 e.$Å^{-3}$	

Table S7. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)for $[Ni(OP^{Ph}{}_2N^{Bz}{}_2)2](BF_4)_2$•$(CH_3CN)$ (**8**). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ni(1)	7694(1)	324(1)	5057(1)	22(1)
B(1)	8483(2)	7250(3)	2899(1)	38(1)
B(2)	6312(2)	2974(3)	6924(2)	48(1)
F(1)	8714(2)	6145(2)	2960(1)	123(1)
F(2)	8054(1)	7344(2)	3113(1)	74(1)
F(3)	8243(1)	7511(2)	2324(1)	60(1)
F(4)	8914(1)	8076(2)	3184(1)	57(1)
F(5)	6754(1)	3145(3)	6730(1)	121(1)
F(6)	5833(2)	3746(3)	6656(1)	123(1)
F(7)	6517(1)	3161(3)	7497(1)	88(1)
F(8)	6093(1)	1876(2)	6770(1)	51(1)
N(1)	7572(1)	1856(2)	4498(1)	24(1)
N(2)	7849(1)	367(2)	3371(1)	22(1)
N(3)	7793(1)	-1243(2)	5594(1)	23(1)
N(4)	7353(1)	53(2)	6639(1)	22(1)
N(5)	9229(2)	4041(4)	5369(2)	93(1)
O(1)	8490(1)	28(2)	5024(1)	24(1)
O(2)	7337(1)	-704(2)	4332(1)	24(1)
O(3)	8022(1)	1309(2)	5799(1)	26(1)
O(4)	6878(1)	635(2)	5045(1)	26(1)
P(1)	8556(1)	686(1)	4533(1)	22(1)
P(2)	7007(1)	-9(1)	3791(1)	23(1)
P(3)	8267(1)	605(1)	6349(1)	23(1)
P(4)	6744(1)	-162(1)	5458(1)	22(1)
C(1)	9502(1)	1711(2)	4360(1)	32(1)
C(2)	10068(1)	2121(3)	4553(1)	39(1)
C(3)	10437(1)	2039(3)	5128(1)	39(1)
C(4)	10234(1)	1543(3)	5516(1)	37(1)
C(5)	9668(1)	1113(2)	5326(1)	31(1)

C(6)	9298(1)	1190(2)	4746(1)	26(1)
C(7)	8117(1)	2039(2)	4399(1)	24(1)
C(8)	7446(1)	2971(2)	4766(1)	27(1)
C(9)	6780(1)	4357(3)	3999(1)	40(1)
C(10)	6684(2)	5328(3)	3631(1)	49(1)
C(11)	7147(2)	6022(3)	3654(1)	45(1)
C(12)	7702(2)	5763(3)	4044(1)	44(1)
C(13)	7798(1)	4801(2)	4415(1)	35(1)
C(14)	7340(1)	4068(2)	4390(1)	29(1)
C(15)	7051(1)	1579(2)	3960(1)	24(1)
C(16)	6071(1)	-1500(2)	3591(1)	32(1)
C(17)	5484(1)	-1817(3)	3343(1)	40(1)
C(18)	5076(1)	-1032(3)	2980(1)	39(1)
C(19)	5249(1)	61(3)	2859(1)	38(1)
C(20)	5832(1)	388(3)	3095(1)	34(1)
C(21)	6247(1)	-400(2)	3465(1)	28(1)
C(22)	7291(1)	-239(2)	3245(1)	24(1)
C(23)	7961(1)	434(2)	2838(1)	26(1)
C(24)	8350(2)	2510(3)	2960(1)	45(1)
C(25)	8785(2)	3334(3)	3009(1)	62(1)
C(26)	9304(2)	2953(4)	2994(1)	72(1)
C(27)	9393(2)	1774(4)	2929(2)	68(1)
C(28)	8965(1)	941(3)	2881(1)	47(1)
C(29)	8437(1)	1315(3)	2896(1)	32(1)
C(30)	8341(1)	-158(2)	3857(1)	23(1)
C(31)	9284(1)	1879(2)	6586(1)	33(1)
C(32)	9865(1)	2150(3)	6904(1)	40(1)
C(33)	10179(1)	1540(3)	7404(1)	38(1)
C(34)	9918(1)	651(3)	7594(1)	37(1)
C(35)	9333(1)	362(3)	7279(1)	32(1)
C(36)	9015(1)	978(2)	6774(1)	26(1)
C(37)	8248(1)	-971(2)	6173(1)	23(1)
C(38)	7987(1)	-2321(2)	5355(1)	27(1)
C(39)	8661(2)	-3687(3)	6113(2)	61(1)
C(40)	8767(3)	-4676(4)	6477(2)	91(2)
C(41)	8318(3)	-5396(4)	6455(2)	83(2)

C(42)	7759(2)	-5161(3)	6065(2)	70(1)
C(43)	7652(2)	-4188(3)	5702(2)	47(1)
C(44)	8102(1)	-3417(2)	5731(1)	32(1)
C(45)	7205(1)	-1492(2)	5595(1)	23(1)
C(46)	5824(1)	-1600(3)	5418(1)	35(1)
C(47)	5264(1)	-2045(3)	5162(1)	43(1)
C(48)	4885(1)	-1610(3)	4634(1)	42(1)
C(49)	5063(1)	-722(3)	4365(1)	39(1)
C(50)	5625(1)	-269(3)	4614(1)	32(1)
C(51)	6010(1)	-710(2)	5145(1)	26(1)
C(52)	6855(1)	538(2)	6147(1)	24(1)
C(53)	7194(1)	-257(2)	7130(1)	27(1)
C(54)	6975(1)	-2425(2)	6887(1)	32(1)
C(55)	6595(1)	-3388(3)	6735(1)	37(1)
C(56)	6025(1)	-3259(3)	6692(1)	42(1)
C(57)	5834(1)	-2165(3)	6802(1)	42(1)
C(58)	6212(1)	-1189(3)	6944(1)	35(1)
C(59)	6782(1)	-1307(2)	6983(1)	29(1)
C(60)	7878(1)	781(2)	6817(1)	26(1)
C(61)	10320(2)	4685(4)	5841(2)	83(2)
C(62)	9707(2)	4337(3)	5582(2)	67(1)

Table S8. Bond lengths [Å] and angles [°] for [Ni(OP$^{Ph}{}_2$N$^{Bz}{}_2$)2](BF$_4$)$_2$•(CH$_3$CN) (**8**).

Ni(1)-O(1)	2.0423(17)
Ni(1)-O(4)	2.0504(17)
Ni(1)-O(2)	2.0512(17)
Ni(1)-O(3)	2.0523(17)
Ni(1)-N(1)	2.172(2)
Ni(1)-N(3)	2.180(2)
B(1)-F(1)	1.351(4)
B(1)-F(3)	1.370(4)
B(1)-F(2)	1.380(4)
B(1)-F(4)	1.385(4)
B(2)-F(8)	1.341(4)
B(2)-F(7)	1.352(4)
B(2)-F(5)	1.385(4)
B(2)-F(6)	1.411(5)
N(1)-C(7)	1.491(3)
N(1)-C(15)	1.493(3)
N(1)-C(8)	1.517(3)
N(2)-C(22)	1.464(3)
N(2)-C(30)	1.472(3)
N(2)-C(23)	1.488(3)
N(3)-C(37)	1.488(3)
N(3)-C(45)	1.490(3)
N(3)-C(38)	1.516(3)
N(4)-C(60)	1.454(3)
N(4)-C(52)	1.471(3)
N(4)-C(53)	1.491(3)
N(5)-C(62)	1.144(5)
O(1)-P(1)	1.5136(18)
O(2)-P(2)	1.5062(18)
O(3)-P(3)	1.5056(18)
O(4)-P(4)	1.5111(18)
P(1)-C(6)	1.798(3)
P(1)-C(7)	1.823(2)
P(1)-C(30)	1.841(2)

P(2)-C(21)	1.795(3)
P(2)-C(22)	1.804(2)
P(2)-C(15)	1.827(3)
P(3)-C(36)	1.792(3)
P(3)-C(60)	1.817(2)
P(3)-C(37)	1.821(3)
P(4)-C(51)	1.788(3)
P(4)-C(45)	1.831(2)
P(4)-C(52)	1.833(2)
C(1)-C(2)	1.376(4)
C(1)-C(6)	1.397(4)
C(2)-C(3)	1.384(4)
C(3)-C(4)	1.386(4)
C(4)-C(5)	1.384(4)
C(5)-C(6)	1.394(4)
C(8)-C(14)	1.516(4)
C(9)-C(14)	1.393(4)
C(9)-C(10)	1.393(4)
C(10)-C(11)	1.372(5)
C(11)-C(12)	1.375(5)
C(12)-C(13)	1.390(4)
C(13)-C(14)	1.387(4)
C(16)-C(21)	1.390(4)
C(16)-C(17)	1.390(4)
C(17)-C(18)	1.384(4)
C(18)-C(19)	1.375(5)
C(19)-C(20)	1.384(4)
C(20)-C(21)	1.400(4)
C(23)-C(29)	1.504(4)
C(24)-C(29)	1.380(4)
C(24)-C(25)	1.392(5)
C(25)-C(26)	1.374(6)
C(26)-C(27)	1.364(6)
C(27)-C(28)	1.387(5)
C(28)-C(29)	1.395(4)
C(31)-C(32)	1.383(4)

C(31)-C(36)	1.396(4)
C(32)-C(33)	1.380(4)
C(33)-C(34)	1.378(4)
C(34)-C(35)	1.395(4)
C(35)-C(36)	1.393(4)
C(38)-C(44)	1.514(4)
C(39)-C(44)	1.378(4)
C(39)-C(40)	1.400(6)
C(40)-C(41)	1.364(7)
C(41)-C(42)	1.376(7)
C(42)-C(43)	1.386(5)
C(43)-C(44)	1.394(4)
C(46)-C(47)	1.378(4)
C(46)-C(51)	1.397(4)
C(47)-C(48)	1.386(4)
C(48)-C(49)	1.377(5)
C(49)-C(50)	1.383(4)
C(50)-C(51)	1.396(4)
C(53)-C(59)	1.509(4)
C(54)-C(55)	1.387(4)
C(54)-C(59)	1.400(4)
C(55)-C(56)	1.387(4)
C(56)-C(57)	1.386(5)
C(57)-C(58)	1.397(4)
C(58)-C(59)	1.389(4)
C(61)-C(62)	1.455(6)
O(1)-Ni(1)-O(4)	177.12(7)
O(1)-Ni(1)-O(2)	87.42(7)
O(4)-Ni(1)-O(2)	90.48(7)
O(1)-Ni(1)-O(3)	94.88(7)
O(4)-Ni(1)-O(3)	87.30(7)
O(2)-Ni(1)-O(3)	176.93(7)
O(1)-Ni(1)-N(1)	89.45(7)
O(4)-Ni(1)-N(1)	88.51(7)
O(2)-Ni(1)-N(1)	87.85(7)

O(3)-Ni(1)-N(1)	94.20(7)
O(1)-Ni(1)-N(3)	91.32(7)
O(4)-Ni(1)-N(3)	90.66(7)
O(2)-Ni(1)-N(3)	90.39(7)
O(3)-Ni(1)-N(3)	87.52(7)
N(1)-Ni(1)-N(3)	178.05(8)
F(1)-B(1)-F(3)	107.6(3)
F(1)-B(1)-F(2)	112.7(3)
F(3)-B(1)-F(2)	108.9(3)
F(1)-B(1)-F(4)	110.5(3)
F(3)-B(1)-F(4)	109.4(3)
F(2)-B(1)-F(4)	107.7(2)
F(8)-B(2)-F(7)	113.0(3)
F(8)-B(2)-F(5)	108.3(3)
F(7)-B(2)-F(5)	110.1(3)
F(8)-B(2)-F(6)	104.9(3)
F(7)-B(2)-F(6)	108.0(3)
F(5)-B(2)-F(6)	112.5(4)
C(7)-N(1)-C(15)	113.17(18)
C(7)-N(1)-C(8)	108.99(19)
C(15)-N(1)-C(8)	108.86(19)
C(7)-N(1)-Ni(1)	108.51(14)
C(15)-N(1)-Ni(1)	106.07(15)
C(8)-N(1)-Ni(1)	111.23(14)
C(22)-N(2)-C(30)	113.53(19)
C(22)-N(2)-C(23)	109.25(19)
C(30)-N(2)-C(23)	112.80(19)
C(37)-N(3)-C(45)	113.69(18)
C(37)-N(3)-C(38)	108.61(18)
C(45)-N(3)-C(38)	108.65(19)
C(37)-N(3)-Ni(1)	107.65(15)
C(45)-N(3)-Ni(1)	106.58(14)
C(38)-N(3)-Ni(1)	111.70(14)
C(60)-N(4)-C(52)	114.0(2)
C(60)-N(4)-C(53)	112.10(19)
C(52)-N(4)-C(53)	112.45(19)

P(1)-O(1)-Ni(1)	112.19(10)
P(2)-O(2)-Ni(1)	114.17(10)
P(3)-O(3)-Ni(1)	115.73(10)
P(4)-O(4)-Ni(1)	112.22(9)
O(1)-P(1)-C(6)	109.88(11)
O(1)-P(1)-C(7)	107.92(10)
C(6)-P(1)-C(7)	105.17(12)
O(1)-P(1)-C(30)	115.34(11)
C(6)-P(1)-C(30)	109.11(12)
C(7)-P(1)-C(30)	108.92(11)
O(2)-P(2)-C(21)	112.73(12)
O(2)-P(2)-C(22)	112.73(11)
C(21)-P(2)-C(22)	105.84(12)
O(2)-P(2)-C(15)	109.39(11)
C(21)-P(2)-C(15)	107.54(12)
C(22)-P(2)-C(15)	108.36(12)
O(3)-P(3)-C(36)	112.19(11)
O(3)-P(3)-C(60)	115.02(11)
C(36)-P(3)-C(60)	106.07(12)
O(3)-P(3)-C(37)	108.79(10)
C(36)-P(3)-C(37)	107.11(12)
C(60)-P(3)-C(37)	107.26(12)
O(4)-P(4)-C(51)	111.29(11)
O(4)-P(4)-C(45)	108.78(11)
C(51)-P(4)-C(45)	104.86(12)
O(4)-P(4)-C(52)	114.45(11)
C(51)-P(4)-C(52)	108.19(12)
C(45)-P(4)-C(52)	108.81(11)
C(2)-C(1)-C(6)	119.8(3)
C(1)-C(2)-C(3)	120.6(3)
C(2)-C(3)-C(4)	119.9(3)
C(5)-C(4)-C(3)	120.0(3)
C(4)-C(5)-C(6)	120.1(3)
C(5)-C(6)-C(1)	119.5(2)
C(5)-C(6)-P(1)	118.0(2)
C(1)-C(6)-P(1)	122.4(2)

N(1)-C(7)-P(1)	111.87(16)
C(14)-C(8)-N(1)	113.84(19)
C(14)-C(9)-C(10)	121.0(3)
C(11)-C(10)-C(9)	119.9(3)
C(10)-C(11)-C(12)	119.9(3)
C(11)-C(12)-C(13)	120.3(3)
C(14)-C(13)-C(12)	120.9(3)
C(13)-C(14)-C(9)	117.9(3)
C(13)-C(14)-C(8)	121.3(2)
C(9)-C(14)-C(8)	120.8(3)
N(1)-C(15)-P(2)	111.53(16)
C(21)-C(16)-C(17)	119.6(3)
C(18)-C(17)-C(16)	120.0(3)
C(19)-C(18)-C(17)	120.3(3)
C(18)-C(19)-C(20)	120.6(3)
C(19)-C(20)-C(21)	119.3(3)
C(16)-C(21)-C(20)	120.1(3)
C(16)-C(21)-P(2)	118.9(2)
C(20)-C(21)-P(2)	121.1(2)
N(2)-C(22)-P(2)	113.08(17)
N(2)-C(23)-C(29)	111.6(2)
C(29)-C(24)-C(25)	120.3(4)
C(26)-C(25)-C(24)	119.8(4)
C(27)-C(26)-C(25)	120.4(3)
C(26)-C(27)-C(28)	120.6(4)
C(27)-C(28)-C(29)	119.6(4)
C(24)-C(29)-C(28)	119.3(3)
C(24)-C(29)-C(23)	119.9(3)
C(28)-C(29)-C(23)	120.9(3)
N(2)-C(30)-P(1)	114.27(17)
C(32)-C(31)-C(36)	119.6(3)
C(33)-C(32)-C(31)	120.4(3)
C(34)-C(33)-C(32)	120.6(3)
C(33)-C(34)-C(35)	119.9(3)
C(36)-C(35)-C(34)	119.6(3)
C(35)-C(36)-C(31)	120.0(2)

C(35)-C(36)-P(3)	120.8(2)
C(31)-C(36)-P(3)	119.2(2)
N(3)-C(37)-P(3)	112.13(16)
C(44)-C(38)-N(3)	114.11(19)
C(44)-C(39)-C(40)	120.8(4)
C(41)-C(40)-C(39)	120.4(4)
C(40)-C(41)-C(42)	119.7(4)
C(41)-C(42)-C(43)	120.1(4)
C(42)-C(43)-C(44)	121.0(4)
C(39)-C(44)-C(43)	117.9(3)
C(39)-C(44)-C(38)	120.5(3)
C(43)-C(44)-C(38)	121.6(3)
N(3)-C(45)-P(4)	112.85(17)
C(47)-C(46)-C(51)	119.9(3)
C(46)-C(47)-C(48)	120.1(3)
C(49)-C(48)-C(47)	120.3(3)
C(48)-C(49)-C(50)	120.3(3)
C(49)-C(50)-C(51)	119.6(3)
C(50)-C(51)-C(46)	119.7(2)
C(50)-C(51)-P(4)	119.8(2)
C(46)-C(51)-P(4)	120.5(2)
N(4)-C(52)-P(4)	114.04(16)
N(4)-C(53)-C(59)	110.8(2)
C(55)-C(54)-C(59)	120.3(3)
C(56)-C(55)-C(54)	120.3(3)
C(57)-C(56)-C(55)	120.0(3)
C(56)-C(57)-C(58)	119.9(3)
C(59)-C(58)-C(57)	120.6(3)
C(58)-C(59)-C(54)	119.0(3)
C(58)-C(59)-C(53)	121.2(3)
C(54)-C(59)-C(53)	119.8(2)
N(4)-C(60)-P(3)	112.50(17)
N(5)-C(62)-C(61)	178.1(5)

Symmetry transformations used to generate equivalent atoms:

Table S9. Anisotropic displacement parameters ($Å^2$x 10^3) for $Ni(OP^{Ph}{}_2N^{Bz}{}_2)2](BF_4)_2$•$(CH_3CN)$ (**8**). The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ni(1)	28(1)	24(1)	16(1)	2(1)	10(1)	4(1)
B(1)	44(2)	36(2)	29(2)	-7(1)	9(2)	0(2)
B(2)	57(2)	39(2)	54(2)	-20(2)	29(2)	-10(2)
F(1)	192(3)	59(2)	60(2)	-13(1)	-14(2)	65(2)
F(2)	85(2)	86(2)	74(2)	-27(1)	54(1)	-46(1)
F(3)	75(1)	67(1)	26(1)	-12(1)	9(1)	-2(1)
F(4)	34(1)	84(2)	50(1)	-31(1)	13(1)	-12(1)
F(5)	142(2)	133(3)	144(3)	-100(2)	115(2)	-99(2)
F(6)	199(4)	70(2)	110(2)	17(2)	71(2)	69(2)
F(7)	51(1)	149(3)	62(1)	-62(2)	20(1)	-12(1)
F(8)	58(1)	45(1)	61(1)	-22(1)	34(1)	-20(1)
N(1)	30(1)	25(1)	17(1)	-2(1)	10(1)	3(1)
N(2)	25(1)	27(1)	15(1)	0(1)	8(1)	1(1)
N(3)	26(1)	25(1)	18(1)	-2(1)	9(1)	5(1)
N(4)	23(1)	31(1)	15(1)	1(1)	8(1)	2(1)
N(5)	74(3)	83(3)	94(3)	-27(2)	4(2)	23(2)
O(1)	27(1)	28(1)	18(1)	2(1)	9(1)	4(1)
O(2)	29(1)	26(1)	19(1)	1(1)	10(1)	3(1)
O(3)	34(1)	25(1)	20(1)	0(1)	12(1)	2(1)
O(4)	30(1)	28(1)	20(1)	6(1)	11(1)	6(1)
P(1)	25(1)	24(1)	17(1)	0(1)	8(1)	2(1)
P(2)	25(1)	26(1)	18(1)	0(1)	9(1)	2(1)
P(3)	26(1)	26(1)	18(1)	0(1)	10(1)	2(1)
P(4)	24(1)	25(1)	17(1)	2(1)	8(1)	4(1)
C(1)	31(1)	34(2)	29(1)	4(1)	8(1)	0(1)
C(2)	37(2)	36(2)	45(2)	7(1)	17(1)	-4(1)
C(3)	28(1)	34(2)	49(2)	-5(1)	8(1)	-1(1)
C(4)	32(2)	38(2)	31(2)	-5(1)	2(1)	6(1)
C(5)	33(1)	32(2)	24(1)	-3(1)	9(1)	4(1)
C(6)	29(1)	21(1)	26(1)	-2(1)	9(1)	2(1)

C(7)	29(1)	24(1)	20(1)	-1(1)	10(1)	1(1)
C(8)	36(1)	26(1)	21(1)	-1(1)	13(1)	6(1)
C(9)	45(2)	30(2)	38(2)	1(1)	10(1)	4(1)
C(10)	60(2)	34(2)	38(2)	5(1)	6(2)	10(2)
C(11)	73(2)	29(2)	30(2)	4(1)	17(2)	5(2)
C(12)	66(2)	30(2)	46(2)	-2(1)	31(2)	-1(2)
C(13)	42(2)	29(2)	34(2)	0(1)	16(1)	4(1)
C(14)	42(2)	23(1)	24(1)	-1(1)	15(1)	6(1)
C(15)	25(1)	28(1)	20(1)	1(1)	9(1)	3(1)
C(16)	34(2)	32(2)	29(1)	-4(1)	13(1)	0(1)
C(17)	43(2)	42(2)	43(2)	-12(1)	24(2)	-10(1)
C(18)	28(1)	55(2)	37(2)	-16(1)	14(1)	-8(1)
C(19)	27(2)	49(2)	32(2)	-7(1)	6(1)	7(1)
C(20)	31(2)	36(2)	32(2)	-2(1)	8(1)	4(1)
C(21)	27(1)	33(1)	23(1)	-4(1)	11(1)	2(1)
C(22)	27(1)	29(1)	17(1)	-1(1)	8(1)	0(1)
C(23)	32(1)	30(1)	17(1)	1(1)	11(1)	0(1)
C(24)	55(2)	39(2)	22(1)	8(1)	-4(1)	-9(2)
C(25)	81(3)	44(2)	32(2)	16(2)	-9(2)	-26(2)
C(26)	81(3)	100(4)	27(2)	2(2)	13(2)	-61(3)
C(27)	66(2)	107(4)	48(2)	-23(2)	38(2)	-44(2)
C(28)	48(2)	66(2)	35(2)	-13(2)	26(2)	-15(2)
C(29)	41(2)	40(2)	14(1)	4(1)	9(1)	-8(1)
C(30)	28(1)	24(1)	18(1)	1(1)	8(1)	1(1)
C(31)	34(2)	34(2)	32(2)	0(1)	14(1)	0(1)
C(32)	39(2)	39(2)	48(2)	-4(1)	24(2)	-8(1)
C(33)	25(1)	47(2)	43(2)	-13(1)	12(1)	-4(1)
C(34)	30(2)	47(2)	31(2)	-1(1)	10(1)	3(1)
C(35)	28(1)	41(2)	29(1)	2(1)	11(1)	0(1)
C(36)	27(1)	29(1)	24(1)	-4(1)	11(1)	1(1)
C(37)	24(1)	26(1)	21(1)	3(1)	9(1)	4(1)
C(38)	34(1)	27(1)	21(1)	-1(1)	13(1)	7(1)
C(39)	59(2)	37(2)	60(2)	-1(2)	-5(2)	18(2)
C(40)	124(4)	45(2)	48(2)	2(2)	-26(2)	33(3)
C(41)	171(5)	34(2)	37(2)	11(2)	34(3)	26(3)
C(42)	124(4)	29(2)	84(3)	10(2)	71(3)	12(2)

C(43)	63(2)	27(2)	58(2)	4(1)	31(2)	7(2)
C(44)	46(2)	26(1)	22(1)	-2(1)	13(1)	10(1)
C(45)	27(1)	22(1)	20(1)	0(1)	9(1)	3(1)
C(46)	28(1)	40(2)	32(2)	5(1)	8(1)	1(1)
C(47)	37(2)	43(2)	47(2)	5(1)	14(1)	-2(1)
C(48)	27(2)	54(2)	39(2)	-11(2)	8(1)	0(1)
C(49)	31(2)	61(2)	24(1)	-1(1)	10(1)	10(1)
C(50)	29(1)	45(2)	20(1)	-1(1)	8(1)	7(1)
C(51)	27(1)	30(1)	21(1)	-2(1)	9(1)	6(1)
C(52)	27(1)	27(1)	19(1)	0(1)	9(1)	3(1)
C(53)	30(1)	34(2)	19(1)	3(1)	12(1)	4(1)
C(54)	35(2)	38(2)	22(1)	11(1)	11(1)	4(1)
C(55)	46(2)	37(2)	27(1)	10(1)	12(1)	2(1)
C(56)	50(2)	45(2)	33(2)	8(1)	16(1)	-11(2)
C(57)	38(2)	55(2)	39(2)	7(2)	21(1)	-5(1)
C(58)	40(2)	41(2)	31(2)	3(1)	20(1)	2(1)
C(59)	34(1)	36(2)	18(1)	6(1)	12(1)	2(1)
C(60)	30(1)	32(1)	18(1)	-2(1)	12(1)	0(1)
C(61)	87(3)	46(2)	76(3)	-8(2)	-11(2)	-4(2)
C(62)	74(3)	48(2)	53(2)	-10(2)	-2(2)	14(2)

Table S10. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for [Ni(OP$^{Ph}{}_2$N$^{Bz}{}_2$)2]$(BF_4)_2$•(CH_3CN) (**8**).

	x	y	z	U(eq)
H(1A)	9250	1781	3966	39
H(2A)	10208	2464	4289	47
H(3A)	10827	2323	5257	47
H(4A)	10485	1499	5912	44
H(5A)	9532	764	5591	37
H(7A)	8352	2679	4655	29
H(7B)	8013	2298	3997	29
H(8A)	7097	2830	4853	33
H(8B)	7781	3126	5135	33
H(9A)	6457	3885	3983	48
H(10A)	6300	5509	3364	58
H(11A)	7083	6680	3402	54
H(12A)	8022	6244	4060	53
H(13A)	8182	4644	4690	42
H(15A)	7076	2037	3637	29
H(15B)	6691	1828	4007	29
H(16A)	6351	-2032	3846	38
H(17A)	5362	-2572	3424	48
H(18A)	4674	-1250	2812	47
H(19A)	4965	596	2612	46
H(20A)	5951	1140	3007	41
H(22A)	7344	-1103	3206	29
H(22B)	7000	53	2873	29
H(23A)	7597	671	2512	31
H(23B)	8076	-362	2751	31
H(24A)	7992	2773	2971	54
H(25A)	8724	4156	3052	75
H(26A)	9601	3514	3030	86
H(27A)	9751	1522	2915	82
H(28A)	9031	120	2839	56
H(30A)	8683	-216	3753	28

H(30B)	8233	-976	3923	28
H(31A)	9068	2302	6243	40
H(32A)	10050	2760	6776	48
H(33A)	10578	1735	7619	46
H(34A)	10137	236	7940	44
H(35A)	9152	-252	7408	39
H(37A)	8636	-1213	6186	28
H(37B)	8170	-1440	6465	28
H(38A)	7681	-2512	4973	32
H(38B)	8348	-2116	5301	32
H(39A)	8978	-3197	6129	73
H(40A)	9155	-4846	6740	109
H(41A)	8391	-6058	6707	100
H(42A)	7445	-5666	6046	84
H(43A)	7266	-4044	5428	57
H(45A)	7255	-1829	5973	28
H(45B)	7005	-2096	5298	28
H(46A)	6084	-1897	5781	42
H(47A)	5138	-2651	5348	52
H(48A)	4501	-1925	4456	50
H(49A)	4799	-419	4006	46
H(50A)	5748	338	4426	38
H(52A)	6917	1402	6119	29
H(52B)	6495	438	6218	29
H(53A)	7005	436	7227	32
H(53B)	7553	-451	7471	32
H(54A)	7368	-2524	6926	38
H(55A)	6726	-4138	6660	45
H(56A)	5766	-3921	6587	51
H(57A)	5446	-2080	6780	51
H(58A)	6079	-438	7015	42
H(60A)	8142	560	7214	31
H(60B)	7769	1628	6820	31
H(61A)	10531	4161	6167	125
H(61B)	10351	5510	5975	125

H(61C)	10492	4618	5555	125