Supporting Information

Electronic and Steric Tolman Parameters for Proazaphosphatranes, the Superbase Core of the Tri(pyridylmethyl)azaphosphatrane (TPAP) Ligand

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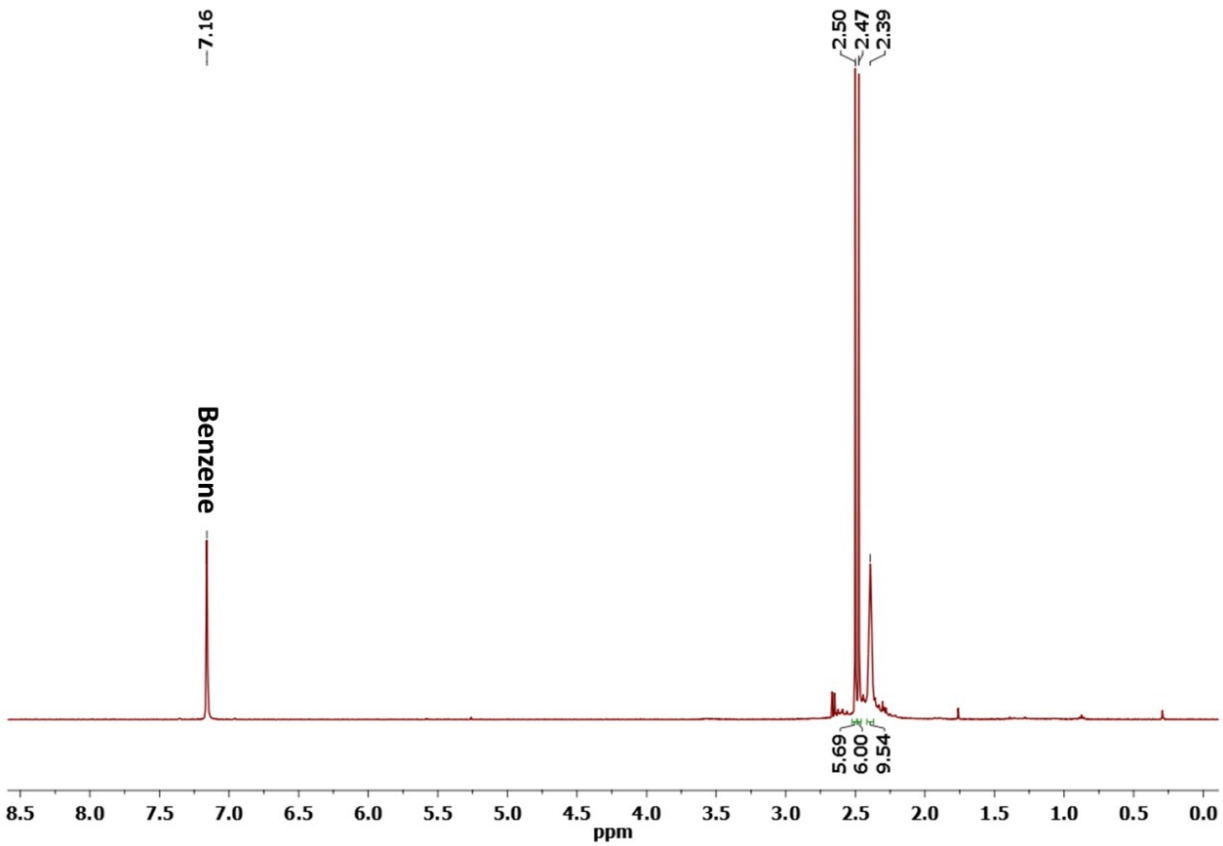

Figure S1. ^{1}H NMR spectrum of $Ni(L^{Me})(CO)_3$ (**1**) in C_6D_6.

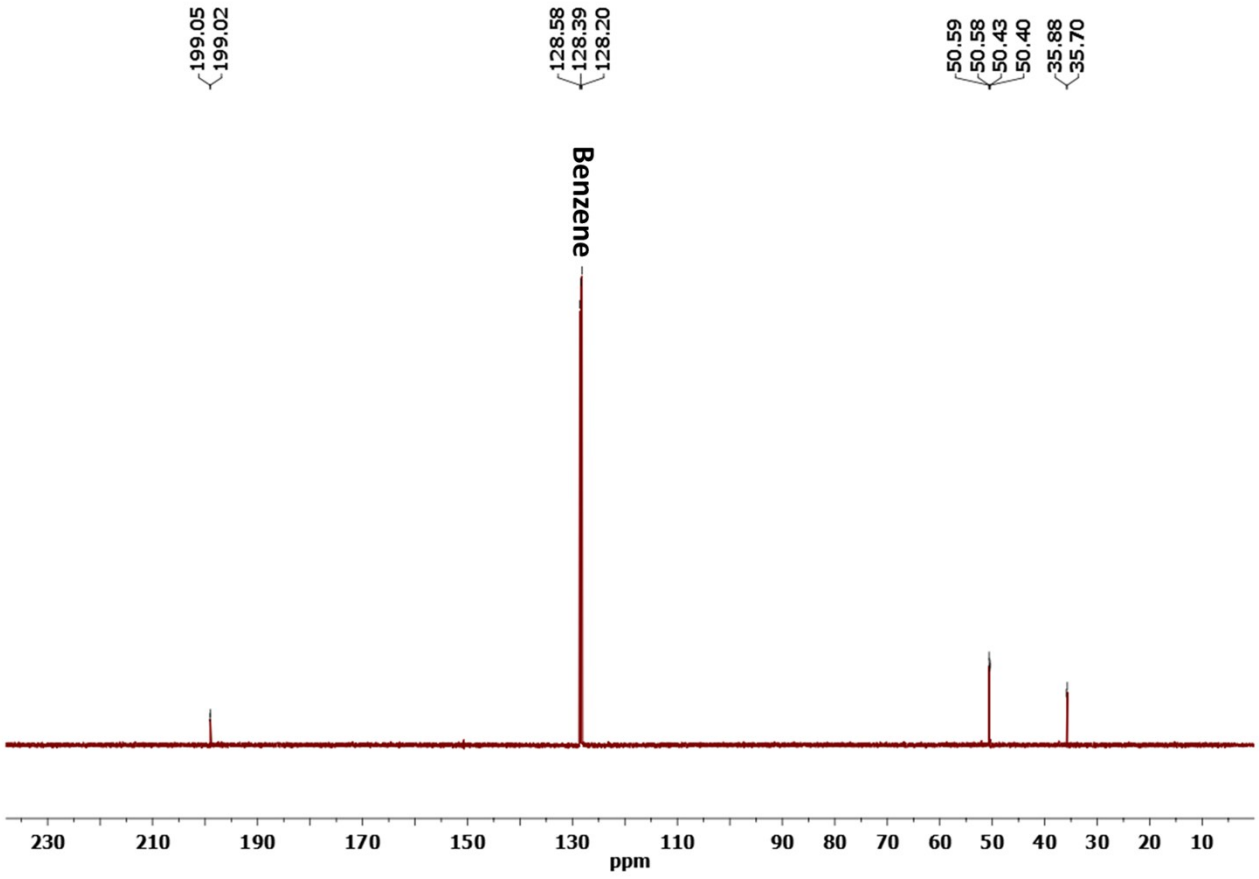

Figure S2. ^{13}C NMR spectrum of $Ni(L^{Me})(CO)_3$ (**1**) in C_6D_6.

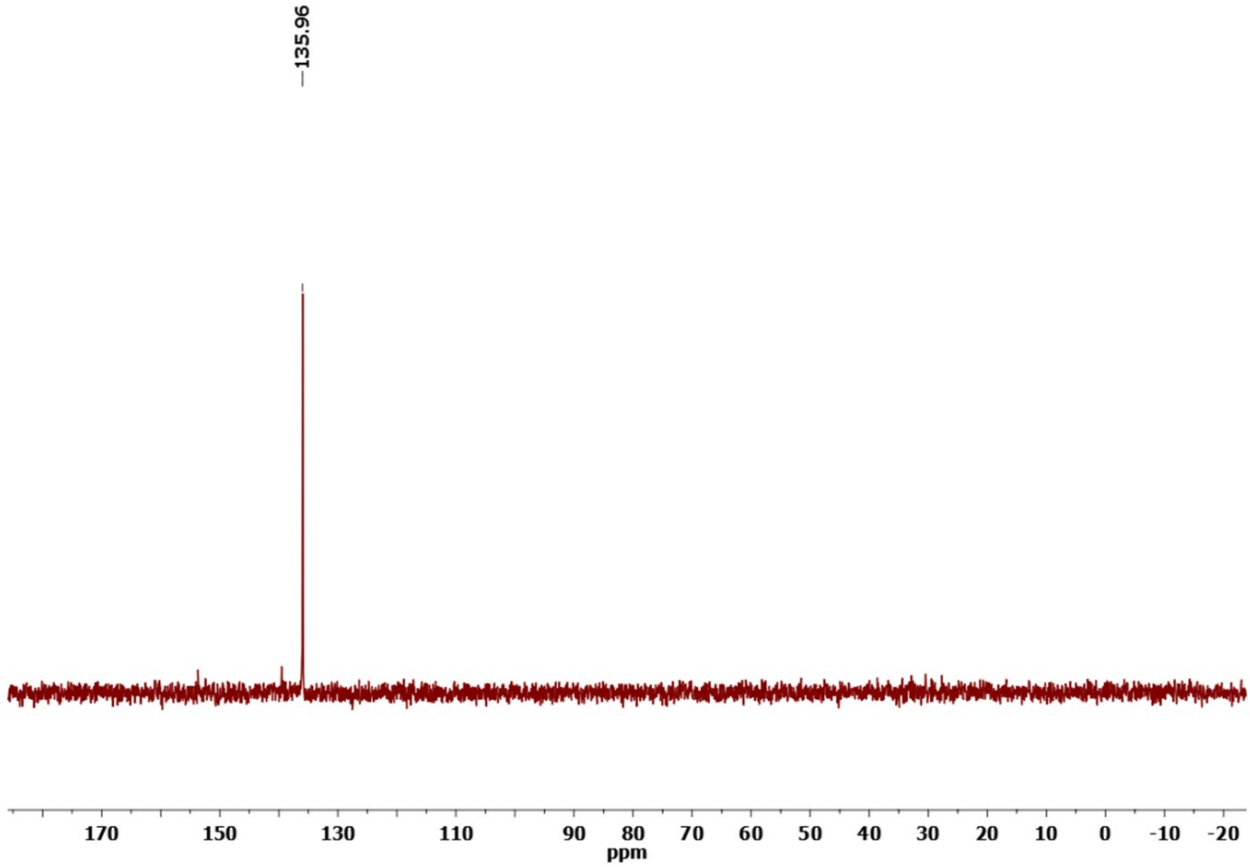

Figure S3. ^{31}P NMR spectrum of $Ni(L^{Me})(CO)_3$ (**1**) in C_6D_6.

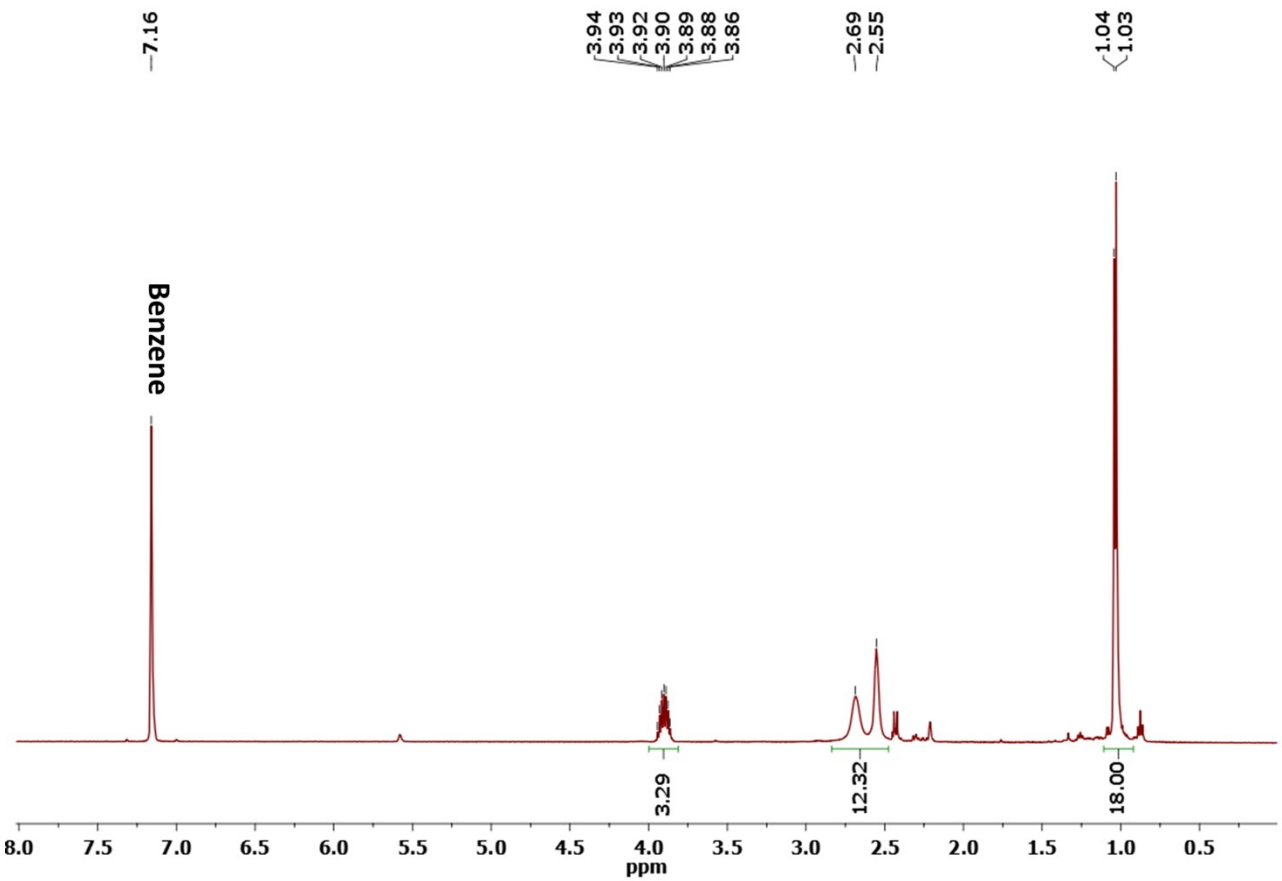

Figure S4. ^{1}H NMR spectrum of Ni(L^{iPr})$(CO)_3$ (**2**) in C_6D_6.

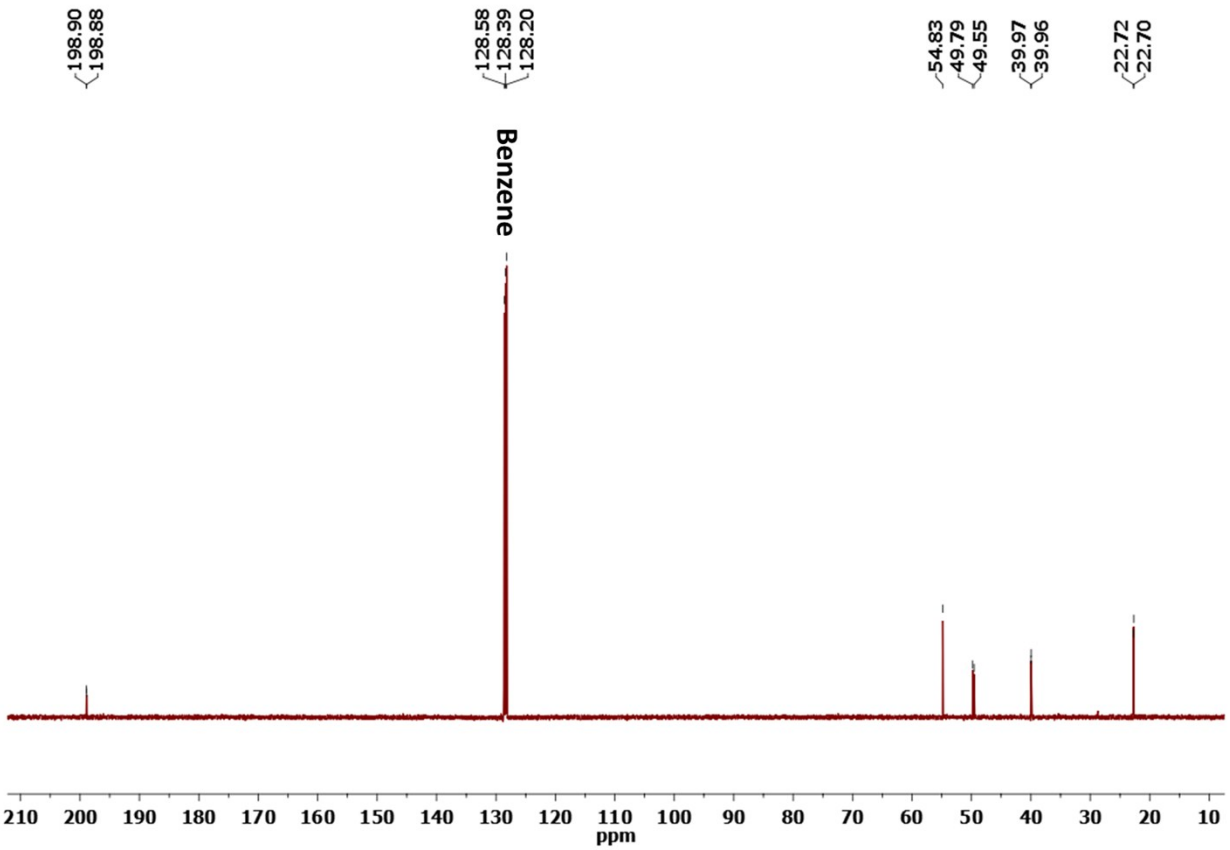

Figure S5. ^{13}C NMR spectrum of Ni(L^{iPr})$(CO)_3$ (**2**) in C_6D_6.

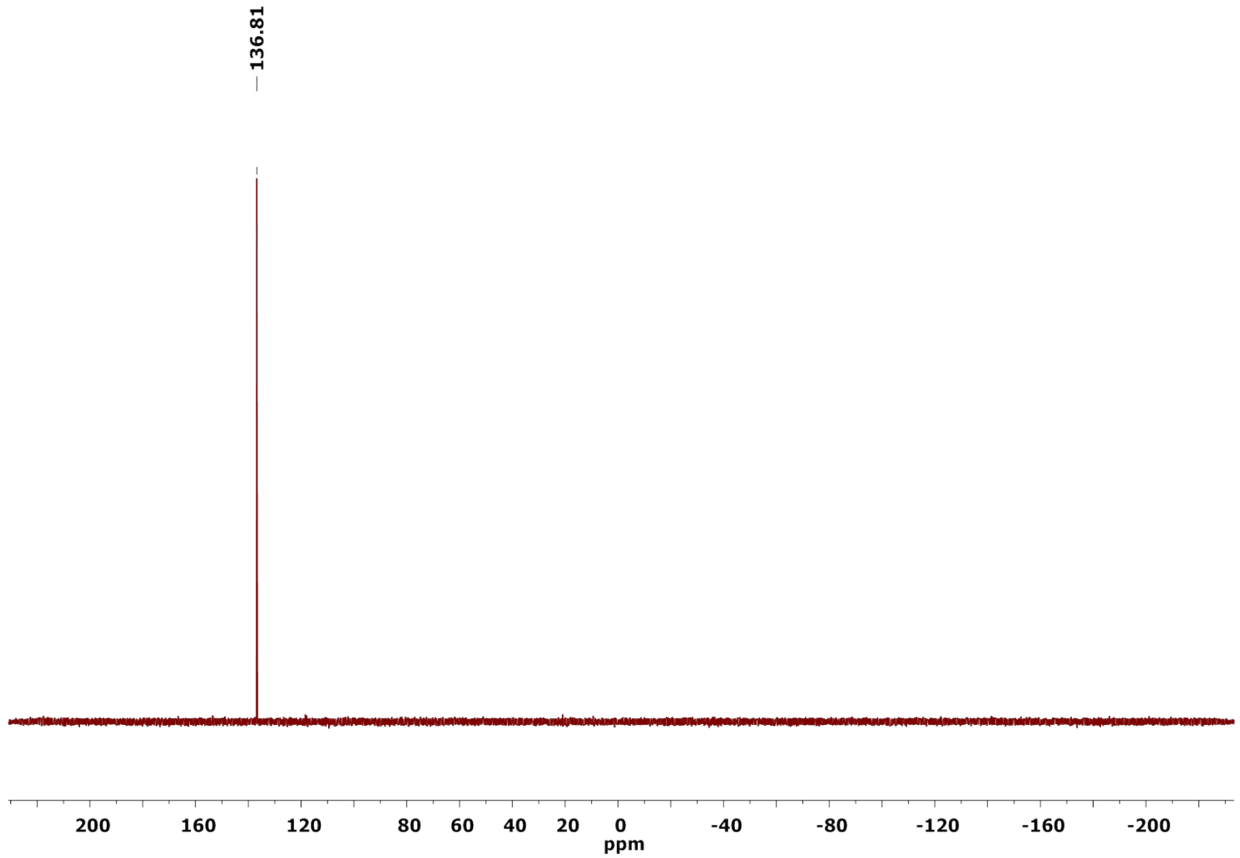

Figure S6. ^{31}P NMR spectrum of Ni(L^{iPr})$(CO)_3$ (**2**) in C_6D_6.

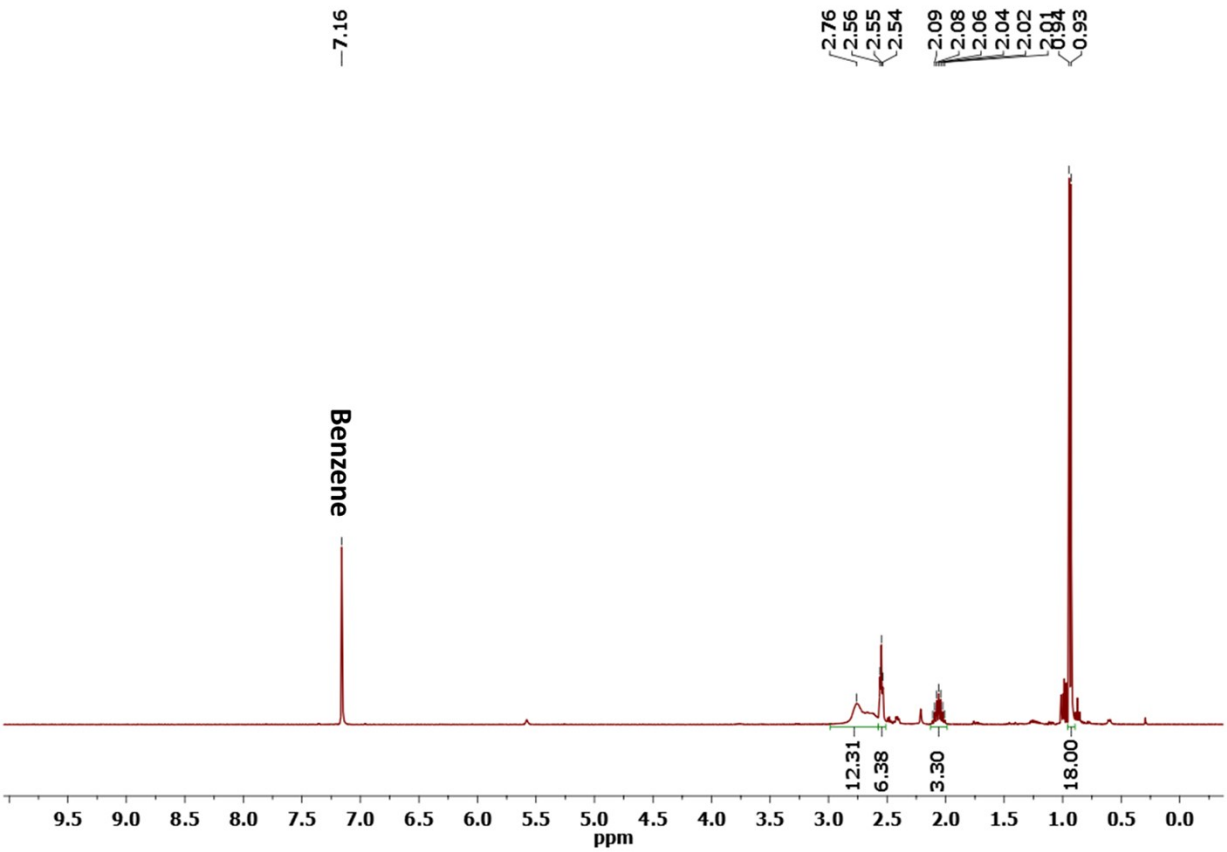

Figure S7. ^{1}H NMR spectrum of Ni(L^{tBu})$(CO)_3$ (**3**) in C_6D_6.

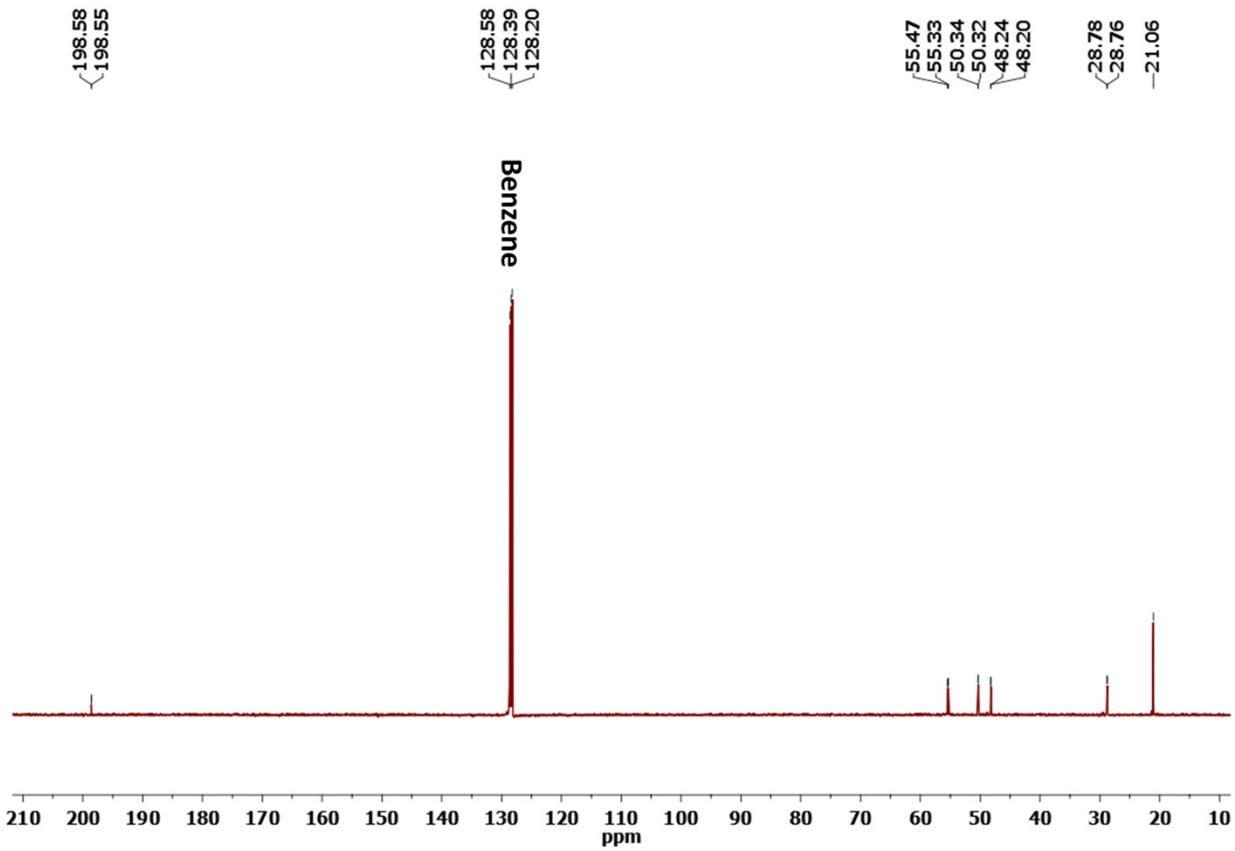

Figure S8. ^{13}C NMR spectrum of Ni(L^{iBu})$(CO)_3$ (**3**) in C_6D_6.

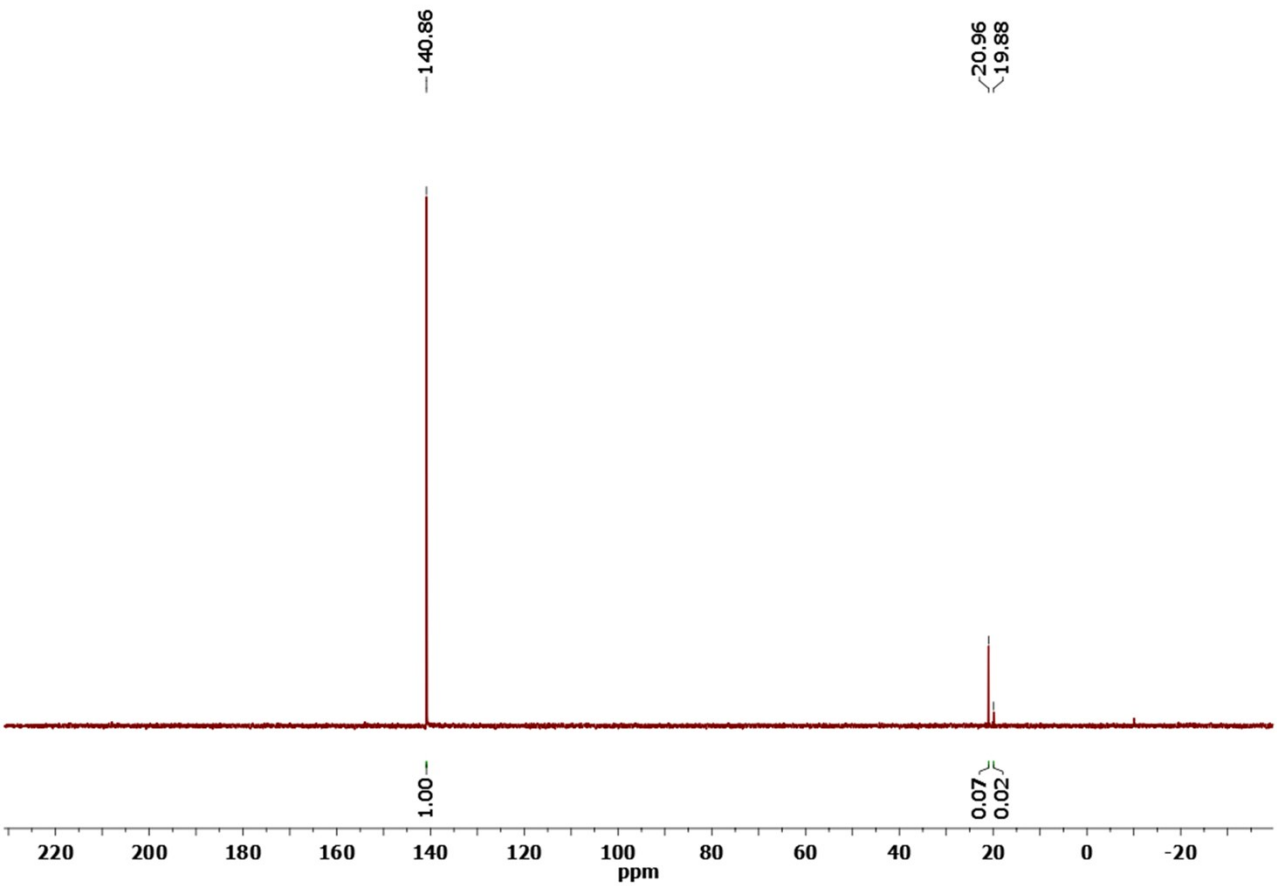

Figure S9. ^{31}P NMR spectrum of Ni(L$^{i\text{Bu}}$)(CO)$_3$ (**3**) in C_6D_6. Resonances around 20 ppm are due to oxidized L$^{i\text{Bu}}$.[1]

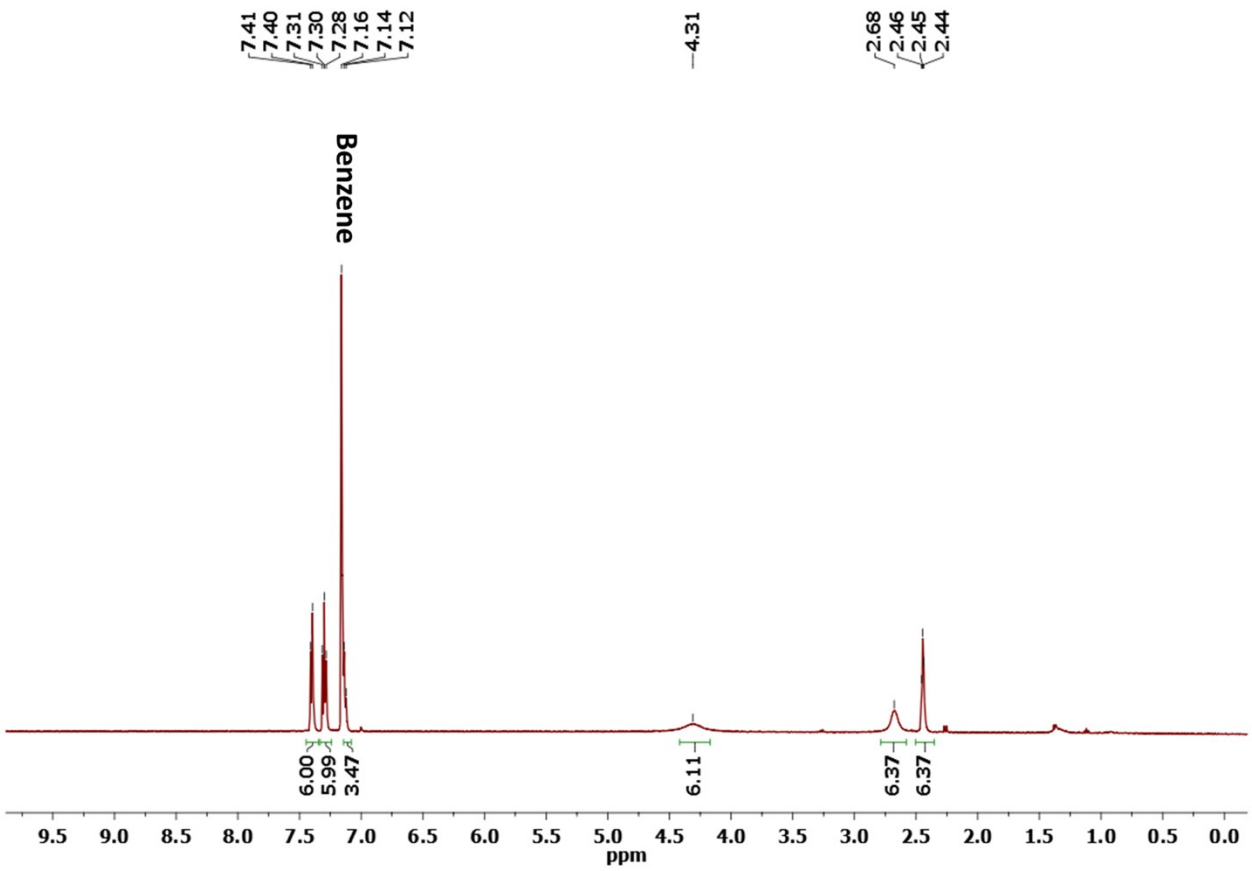

Figure S10. ^{1}H NMR spectrum of $Ni(L^{Bz})(CO)_3$ (**4**) in C_6D_6.

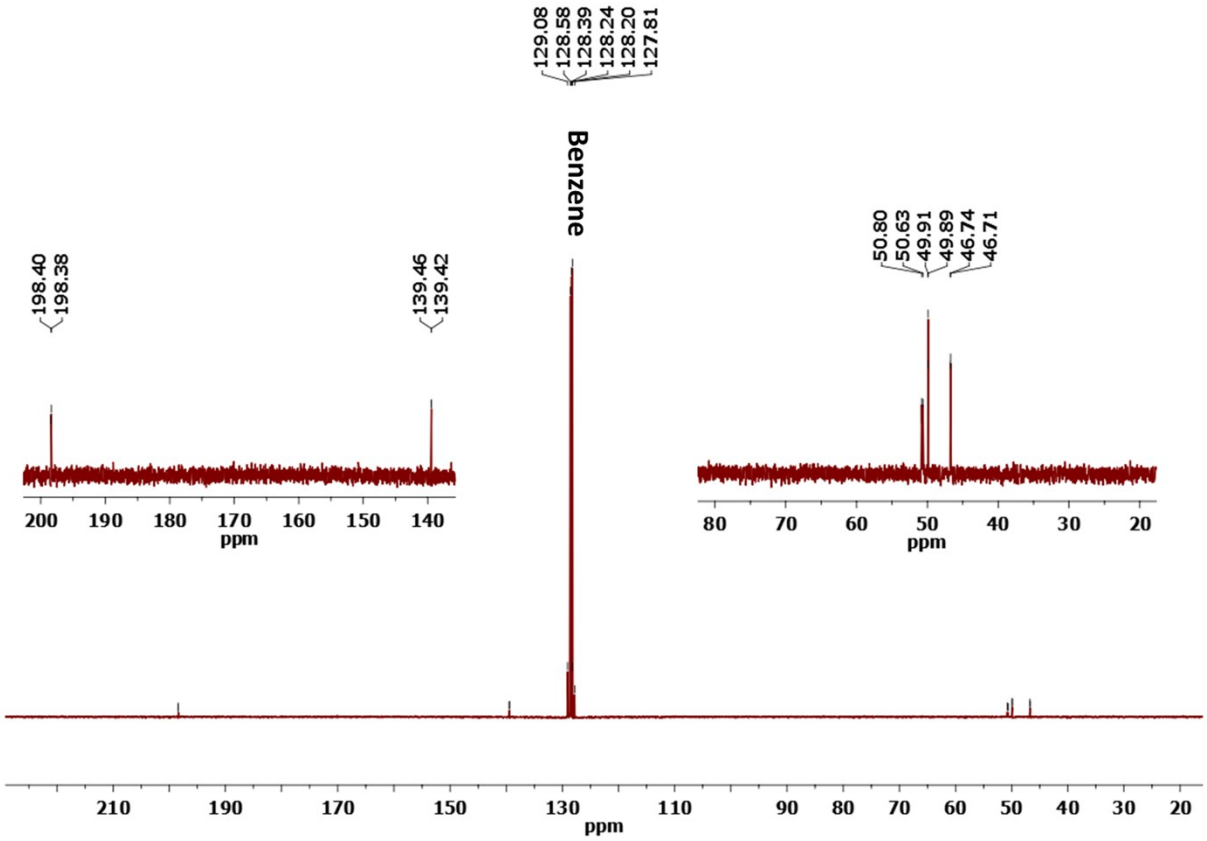

Figure S11. ^{13}C NMR spectrum of Ni(L^{Bz})$(CO)_3$ (**4**) in C_6D_6.

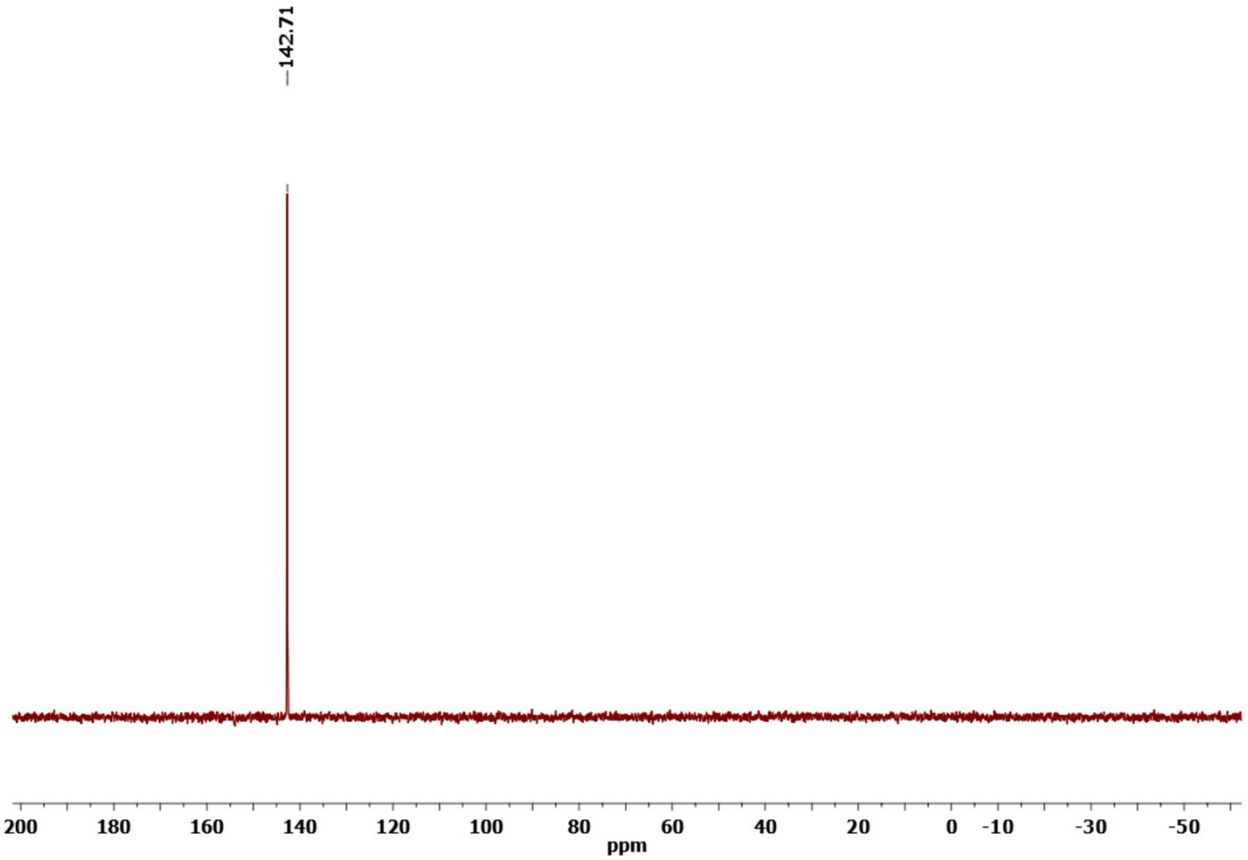

Figure S12. ^{31}P NMR spectrum of Ni(L^{Bz})$(CO)_3$ (**4**) in C_6D_6.

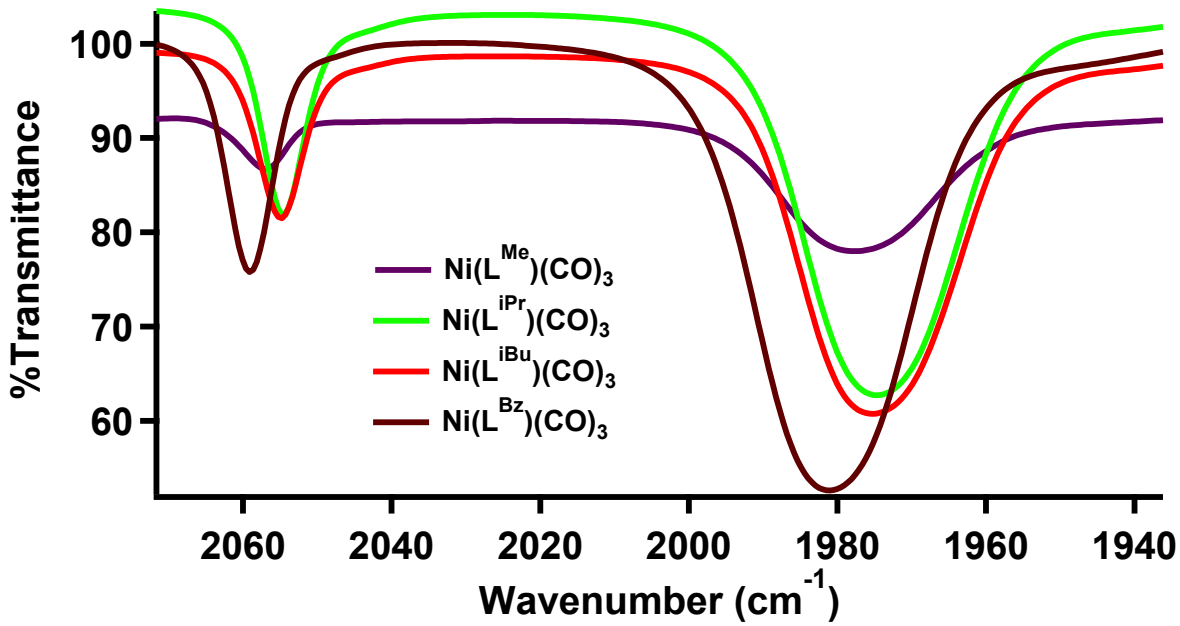

Figure S13. IR spectra of (purple) $Ni(L^{Me})(CO)_3$ (**1**), (green) $Ni(L^{iPr})(CO)_3$ (**2**), (red) $Ni(L^{iBu})(CO)_3$ (**3**) and (dark red) $Ni(L^{Bz})(CO)_3$ (**4**) in CH_2Cl_2.

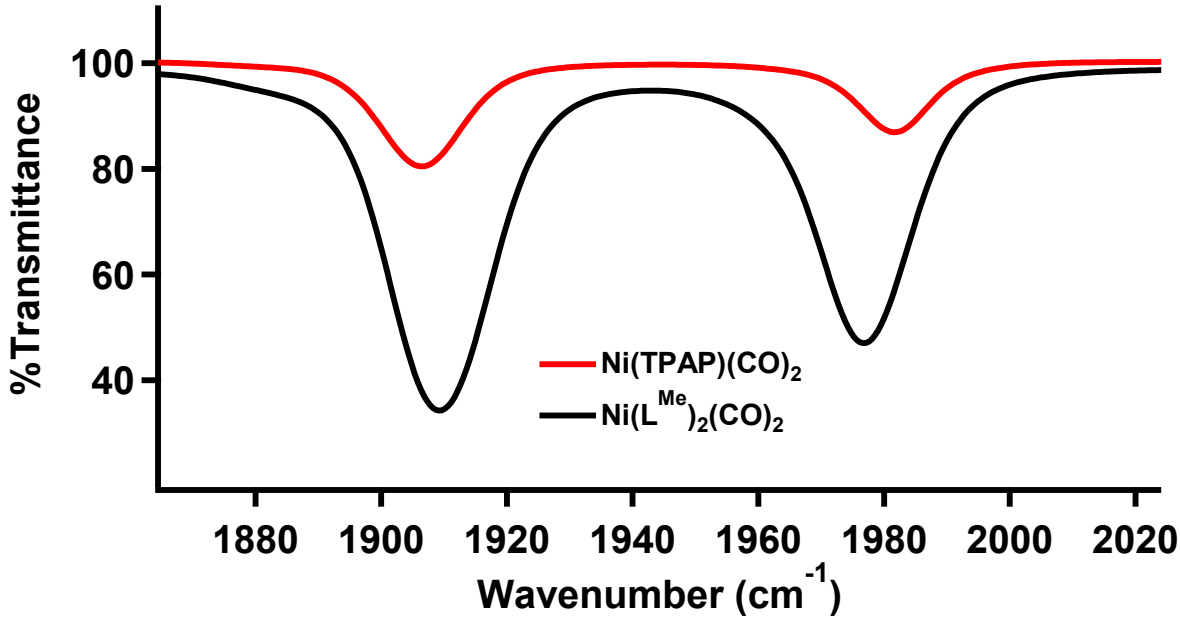

Figure S14. IR spectra of (red) $Ni(TPAP)(CO)_2$ (**5**) and (black) $Ni(L^{Me})_2(CO)_2$ (**6**) in CH_2Cl_2.

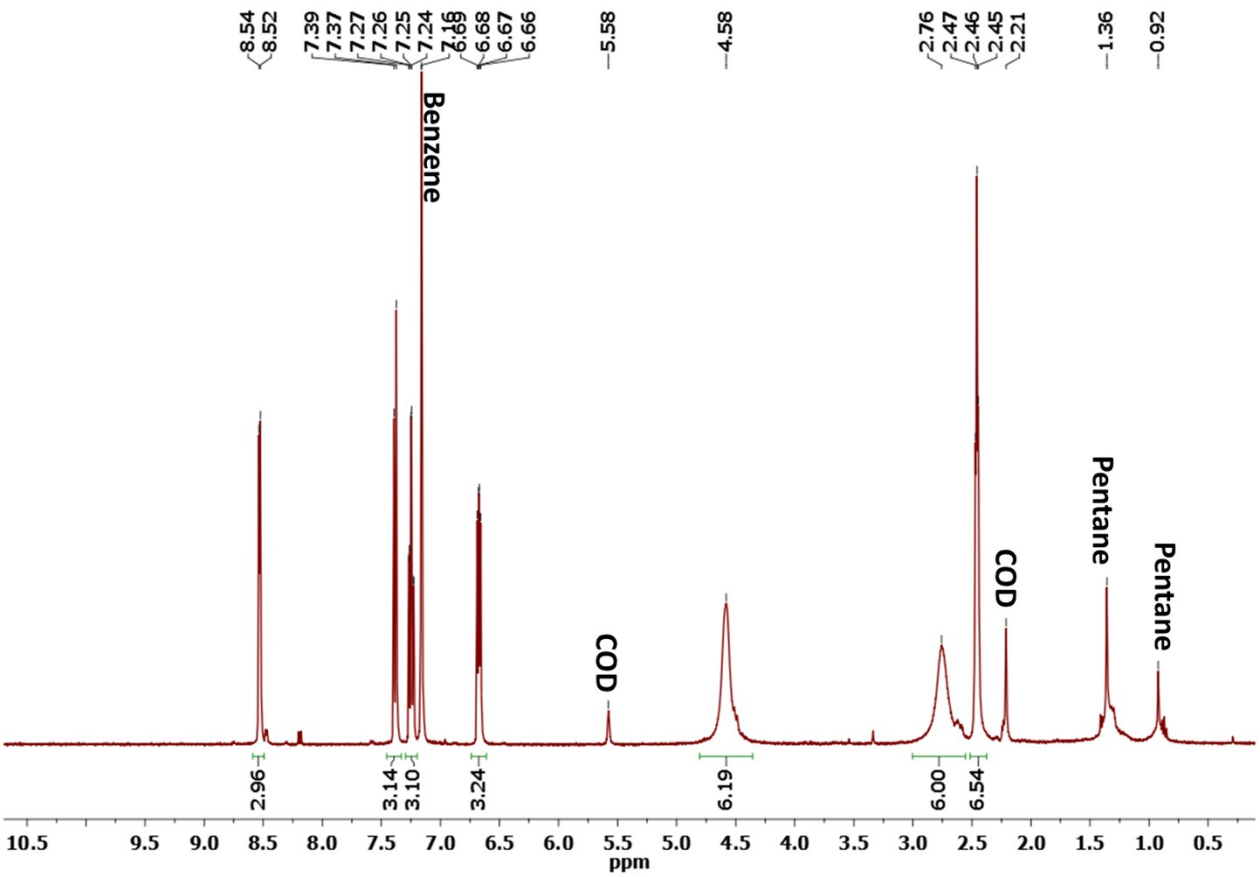

Figure S15. ^{1}H NMR spectrum of Ni(TPAP)$(CO)_2$ (**5**) in C_6D_6. Resonances due to free COD are also shown.

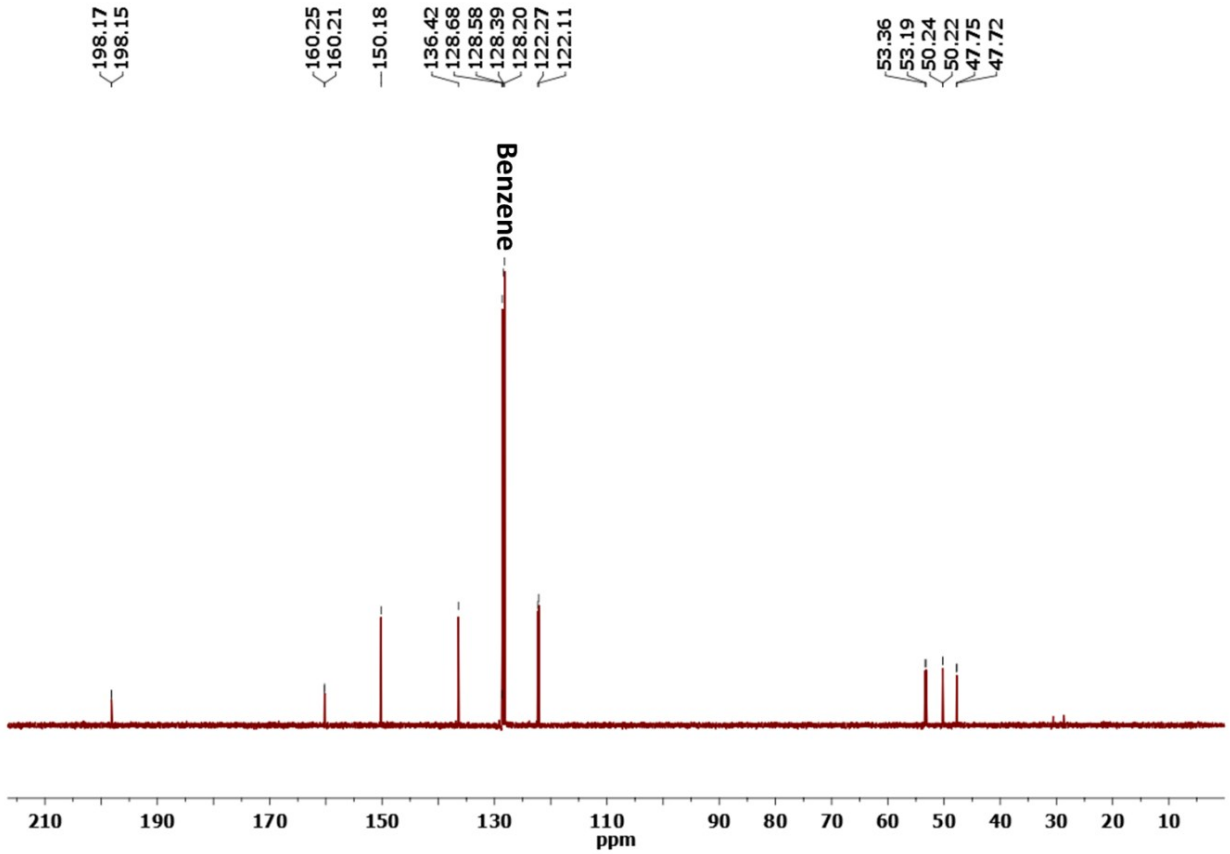

Figure S16. ^{13}C NMR spectrum of Ni(TPAP)$(CO)_2$ (**5**) in C_6D_6.

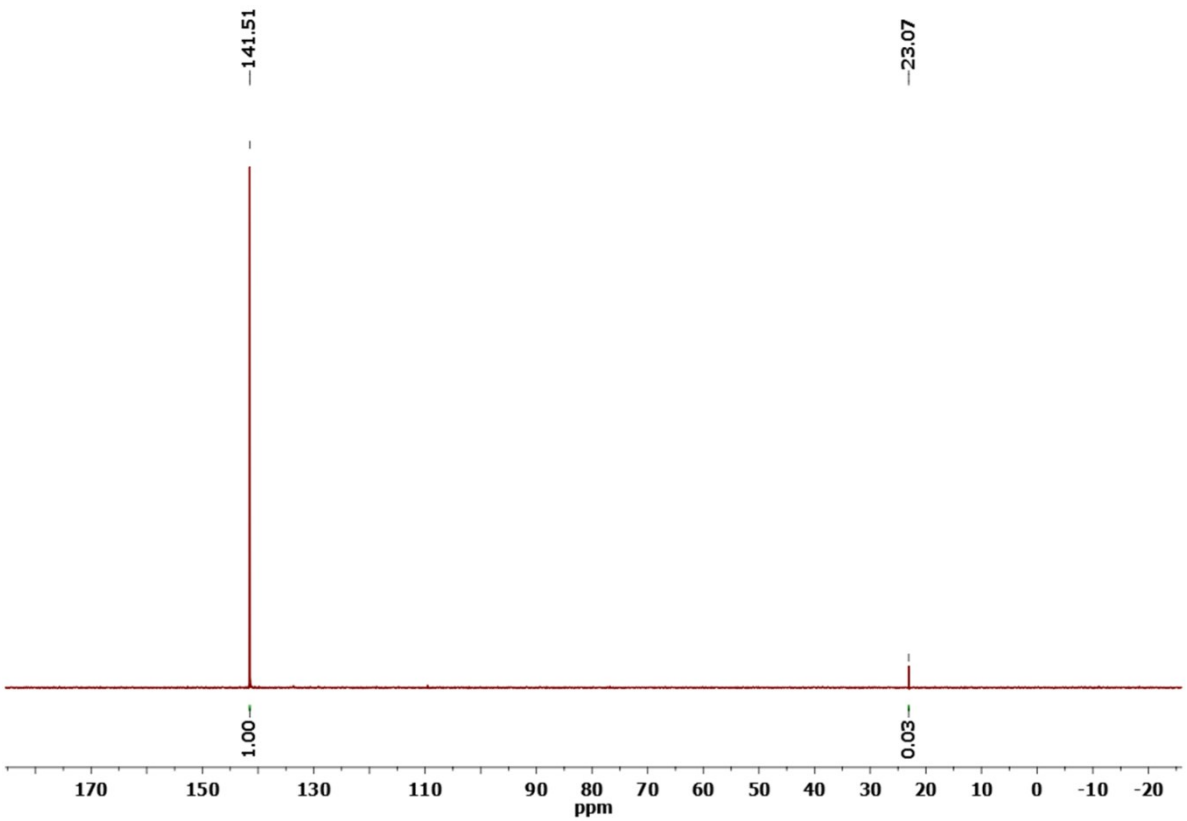

Figure S17. ^{31}P NMR spectrum of Ni(TPAP)$(CO)_2$ (**5**) in C_6D_6. Resonance at 23 ppm is due to oxidized TPAP.

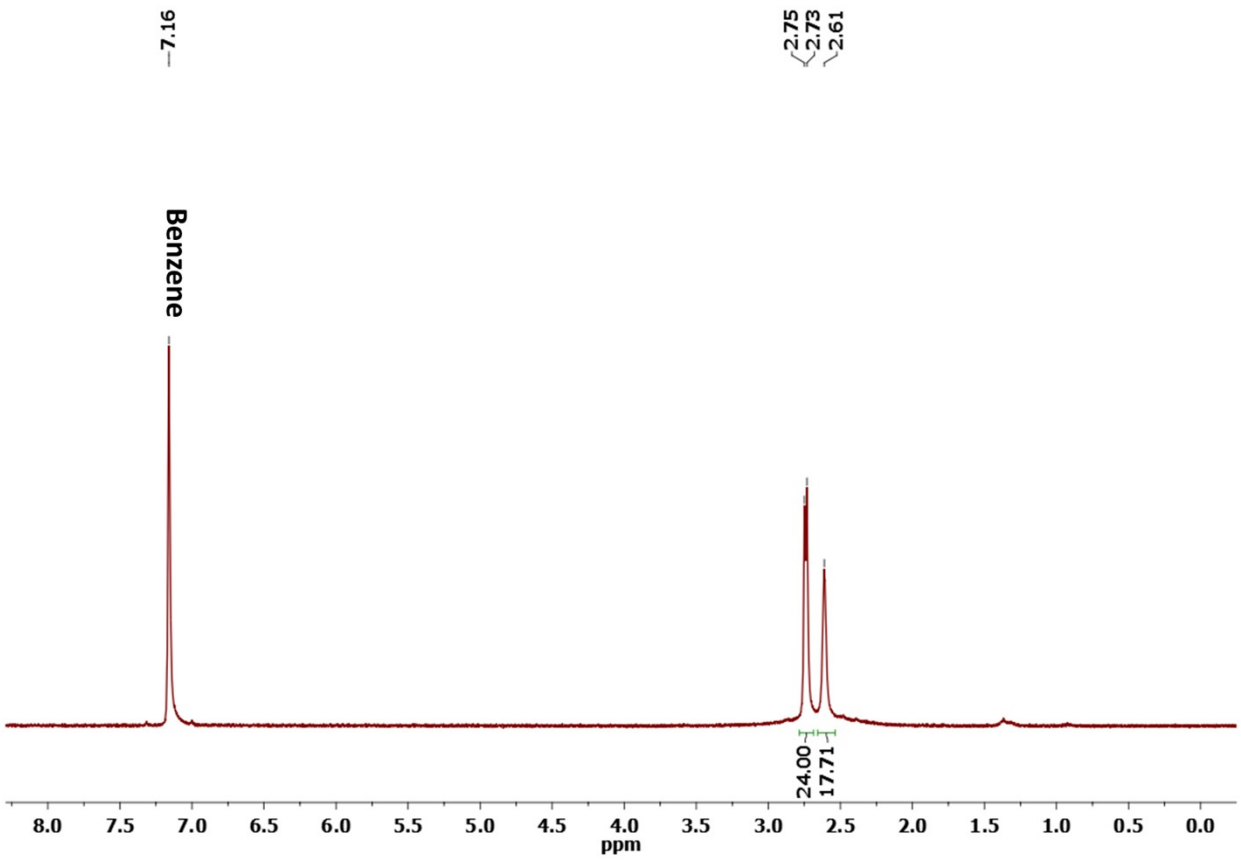

Figure S18. ^{1}H NMR spectrum of $Ni(L^{Me})_2(CO)_2$ (**6**) in C_6D_6.

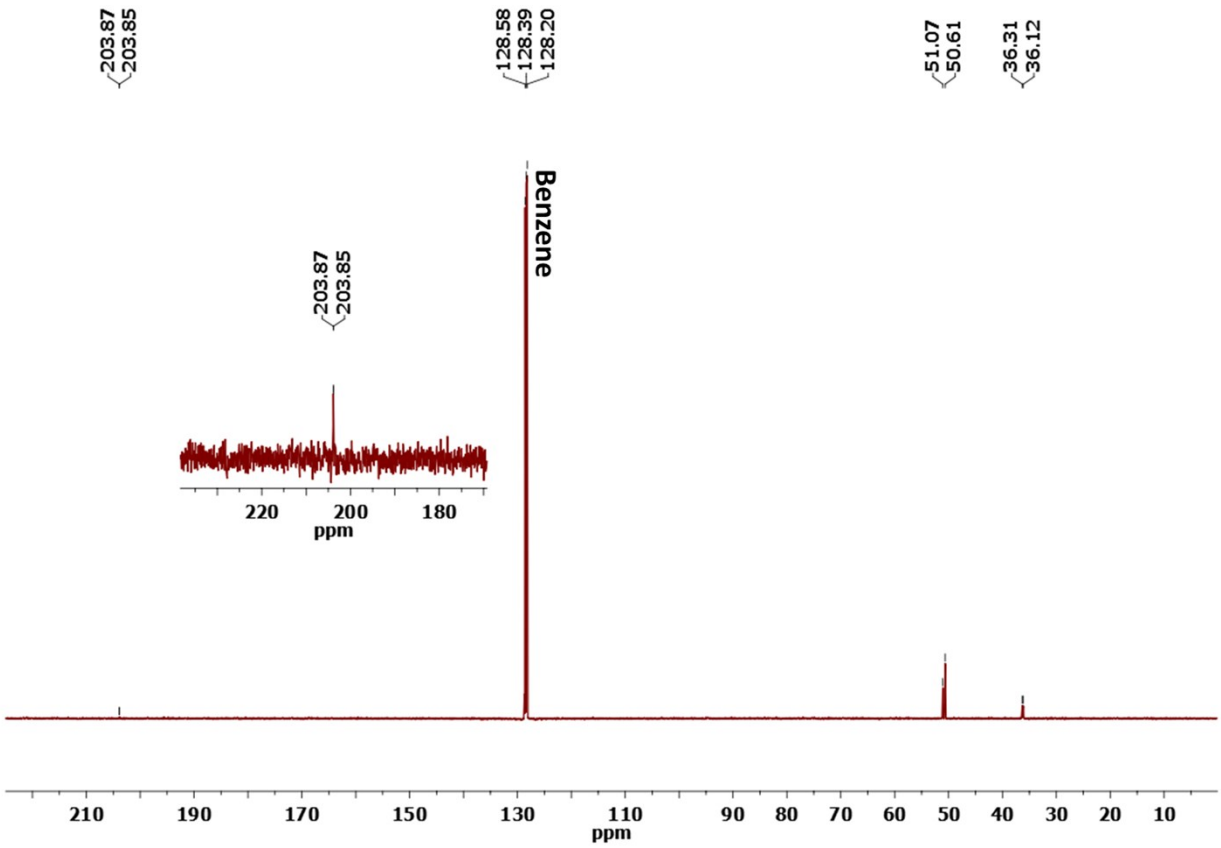

Figure S19. ^{13}C NMR spectrum of $Ni(L^{Me})_2(CO)_2$ (**6**) in C_6D_6.

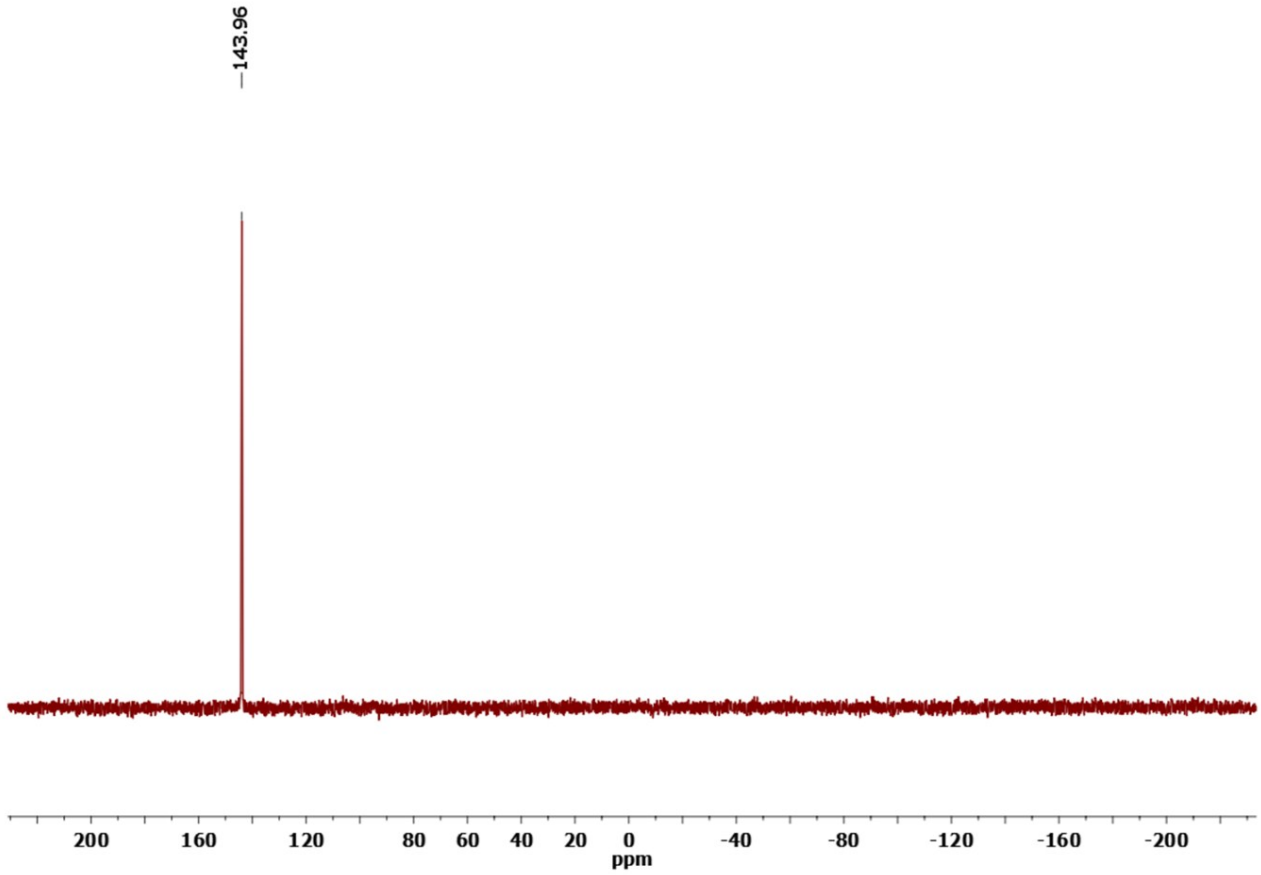

Figure S20. ^{31}P NMR spectrum of $Ni(L^{Me})_2(CO)_2$ (**6**) in C_6D_6.

Table S1. Crystal data and structure refinement for **2**.

Empirical formula	C18 H33 N4 Ni O3 P	
Formula weight	443.16	
Temperature	133(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 9.4521(6) Å	α= 90°.
	b = 16.0515(11) Å	β= 93.8772(8)°.
	c = 14.5677(10) Å	γ= 90°.
Volume	2205.2(3) $Å^3$	
Z	4	
Density (calculated)	1.335 Mg/m^3	
Absorption coefficient	0.977 mm^{-1}	
F(000)	944	
Crystal color	colorless	
Crystal size	0.43 x 0.32 x 0.06 mm^3	
Theta range for data collection	1.89 to 28.29°	
Index ranges	-12 <= h <= 12, -21 <= k <= 21, -19 <= l <= 19	
Reflections collected	24569	
Independent reflections	5360 [R(int) = 0.0353]	
Completeness to theta = 25.00°	100.0 %	
Absorption correction	Numerical	
Max. and min. transmission	0.9455 and 0.6800	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5360 / 0 / 250	
Goodness-of-fit on F^2	1.220	
Final R indices [I>2sigma(I) = 4297 data]	R1 = 0.0359, wR2 = 0.0749	
R indices (all data, ? Å)	R1 = 0.0544, wR2 = 0.0810	
Largest diff. peak and hole	0.548 and -0.499 $e.Å^{-3}$	

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

	x	y	z	U(eq)
Ni(1)	8488(1)	8445(1)	9128(1)	17(1)
P(1)	8146(1)	8593(1)	7581(1)	13(1)
O(1)	11532(2)	8678(1)	9596(1)	31(1)
O(2)	7621(2)	6800(1)	9756(1)	32(1)
O(3)	6783(2)	9662(1)	10082(1)	41(1)
N(2)	6445(2)	8472(1)	7160(1)	16(1)
N(1)	7611(2)	8870(1)	5319(1)	23(1)
N(3)	8612(1)	9538(1)	7189(1)	15(1)
N(4)	9078(2)	7925(1)	6958(1)	16(1)
C(16)	10348(2)	8599(1)	9415(1)	21(1)
C(3)	5283(2)	8683(1)	7746(1)	24(1)
C(5)	4660(2)	7911(2)	8176(2)	42(1)
C(4)	4100(2)	9192(1)	7239(1)	31(1)
C(2)	6063(2)	8031(1)	6299(1)	21(1)
C(1)	6200(2)	8555(1)	5430(1)	23(1)
C(6)	7908(2)	9739(1)	5510(1)	23(1)
C(7)	7731(2)	10008(1)	6506(1)	18(1)
C(8)	9906(2)	9950(1)	7603(1)	19(1)
C(9)	9556(2)	10609(1)	8304(1)	28(1)
C(10)	10825(2)	10340(1)	6893(1)	25(1)
C(11)	8765(2)	8287(1)	5264(1)	25(1)
C(12)	9760(2)	8189(1)	6131(1)	22(1)
C(13)	9405(2)	7078(1)	7306(1)	20(1)
C(15)	10925(2)	7004(1)	7724(2)	34(1)
C(14)	9118(2)	6403(1)	6573(1)	27(1)
C(17)	7951(2)	7435(1)	9487(1)	21(1)
C(18)	7437(2)	9208(1)	9692(1)	24(1)

Table S3. Bond lengths [Å] and angles [°] for **2**.

Ni(1)-C(17)	1.7882(19)	N(4)-P(1)-N(2)	104.46(7)
Ni(1)-C(16)	1.796(2)	N(3)-P(1)-N(2)	104.07(7)
Ni(1)-C(18)	1.8086(19)	N(4)-P(1)-Ni(1)	115.05(5)
Ni(1)-P(1)	2.2680(5)	N(3)-P(1)-Ni(1)	113.96(5)
P(1)-N(4)	1.6894(14)	N(2)-P(1)-Ni(1)	114.59(5)
P(1)-N(3)	1.6900(14)	C(2)-N(2)-C(3)	117.17(14)
P(1)-N(2)	1.6927(14)	C(2)-N(2)-P(1)	122.61(12)
O(1)-C(16)	1.140(2)	C(3)-N(2)-P(1)	119.34(11)
O(2)-C(17)	1.143(2)	C(11)-N(1)-C(1)	119.06(15)
O(3)-C(18)	1.133(2)	C(11)-N(1)-C(6)	119.91(16)
N(2)-C(2)	1.464(2)	C(1)-N(1)-C(6)	118.95(15)
N(2)-C(3)	1.476(2)	C(7)-N(3)-C(8)	117.55(13)
N(1)-C(11)	1.443(2)	C(7)-N(3)-P(1)	122.87(11)
N(1)-C(1)	1.446(2)	C(8)-N(3)-P(1)	119.37(11)
N(1)-C(6)	1.446(2)	C(12)-N(4)-C(13)	117.02(13)
N(3)-C(7)	1.463(2)	C(12)-N(4)-P(1)	122.17(11)
N(3)-C(8)	1.482(2)	C(13)-N(4)-P(1)	120.26(11)
N(4)-C(12)	1.467(2)	O(1)-C(16)-Ni(1)	178.56(16)
N(4)-C(13)	1.477(2)	N(2)-C(3)-C(5)	111.96(16)
C(3)-C(5)	1.525(3)	N(2)-C(3)-C(4)	112.99(15)
C(3)-C(4)	1.534(3)	C(5)-C(3)-C(4)	110.00(16)
C(2)-C(1)	1.533(2)	N(2)-C(2)-C(1)	114.37(14)
C(6)-C(7)	1.535(2)	N(1)-C(1)-C(2)	114.48(14)
C(8)-C(9)	1.521(2)	N(1)-C(6)-C(7)	114.92(14)
C(8)-C(10)	1.530(2)	N(3)-C(7)-C(6)	113.84(14)
C(11)-C(12)	1.530(3)	N(3)-C(8)-C(9)	111.90(15)
C(13)-C(15)	1.527(3)	N(3)-C(8)-C(10)	113.46(14)
C(13)-C(14)	1.532(2)	C(9)-C(8)-C(10)	109.20(15)
		N(1)-C(11)-C(12)	116.47(15)
C(17)-Ni(1)-C(16)	110.42(8)	N(4)-C(12)-C(11)	115.29(15)
C(17)-Ni(1)-C(18)	107.84(8)	N(4)-C(13)-C(15)	112.23(15)
C(16)-Ni(1)-C(18)	111.12(8)	N(4)-C(13)-C(14)	112.86(14)
C(17)-Ni(1)-P(1)	111.15(6)	C(15)-C(13)-C(14)	109.88(15)
C(16)-Ni(1)-P(1)	106.75(6)	O(2)-C(17)-Ni(1)	176.91(16)
C(18)-Ni(1)-P(1)	109.59(6)	O(3)-C(18)-Ni(1)	176.71(17)
N(4)-P(1)-N(3)	103.34(7)		

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **2**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ni(1)	21(1)	18(1)	12(1)	1(1)	1(1)	0(1)
P(1)	14(1)	15(1)	12(1)	0(1)	1(1)	0(1)
O(1)	26(1)	37(1)	28(1)	0(1)	-6(1)	-3(1)
O(2)	41(1)	23(1)	33(1)	4(1)	6(1)	-4(1)
O(3)	46(1)	36(1)	42(1)	-11(1)	19(1)	3(1)
N(2)	14(1)	21(1)	14(1)	-1(1)	0(1)	0(1)
N(1)	29(1)	21(1)	18(1)	0(1)	0(1)	0(1)
N(3)	17(1)	15(1)	14(1)	2(1)	0(1)	-2(1)
N(4)	18(1)	15(1)	15(1)	0(1)	6(1)	3(1)
C(16)	31(1)	20(1)	13(1)	1(1)	0(1)	-1(1)
C(3)	16(1)	35(1)	22(1)	0(1)	3(1)	3(1)
C(5)	22(1)	62(2)	43(1)	25(1)	8(1)	0(1)
C(4)	20(1)	34(1)	38(1)	0(1)	1(1)	7(1)
C(2)	21(1)	22(1)	20(1)	-1(1)	-3(1)	-2(1)
C(1)	29(1)	25(1)	15(1)	-3(1)	-7(1)	-1(1)
C(6)	31(1)	21(1)	16(1)	5(1)	-1(1)	-2(1)
C(7)	23(1)	15(1)	16(1)	3(1)	0(1)	1(1)
C(8)	19(1)	19(1)	18(1)	2(1)	-2(1)	-3(1)
C(9)	36(1)	27(1)	22(1)	-5(1)	2(1)	-11(1)
C(10)	24(1)	23(1)	27(1)	4(1)	3(1)	-4(1)
C(11)	37(1)	23(1)	16(1)	0(1)	8(1)	2(1)
C(12)	24(1)	22(1)	20(1)	0(1)	9(1)	2(1)
C(13)	24(1)	18(1)	18(1)	1(1)	5(1)	5(1)
C(15)	35(1)	31(1)	35(1)	-7(1)	-9(1)	14(1)
C(14)	31(1)	19(1)	31(1)	-3(1)	3(1)	3(1)
C(17)	22(1)	26(1)	15(1)	-2(1)	1(1)	2(1)
C(18)	29(1)	25(1)	19(1)	-1(1)	5(1)	-2(1)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **2**.

	x	y	z	U(eq)
H(3)	5698	9037	8262	29
H(5A)	4213	7558	7690	63
H(5B)	3950	8080	8599	63
H(5C)	5418	7599	8515	63
H(4A)	4508	9687	6965	46
H(4B)	3410	9365	7675	46
H(4C)	3624	8851	6753	46
H(2A)	5071	7835	6309	25
H(2B)	6676	7534	6266	25
H(1A)	5902	8211	4886	28
H(1B)	5539	9032	5443	28
H(6A)	7272	10082	5096	27
H(6B)	8894	9858	5360	27
H(7A)	7969	10607	6569	22
H(7B)	6724	9941	6639	22
H(8)	10489	9513	7939	23
H(9A)	9012	11059	7993	42
H(9B)	10437	10834	8598	42
H(9C)	8993	10357	8772	42
H(10A)	11089	9912	6456	37
H(10B)	11685	10575	7207	37
H(10C)	10292	10783	6562	37
H(11A)	9338	8461	4753	30
H(11B)	8358	7733	5102	30
H(12A)	10500	7776	6003	26
H(12B)	10240	8728	6261	26
H(13)	8762	6965	7809	24
H(15A)	11586	7073	7240	51
H(15B)	11062	6454	8009	51
H(15C)	11101	7437	8191	51
H(14A)	8149	6463	6297	41
H(14B)	9229	5852	6859	41
H(14C)	9792	6463	6095	41

Table S6. Crystal data and structure refinement for **3**.

Empirical formula	C_{21} H_{39} N_4 Ni O_3 P	
Formula weight	485.24	
Temperature	88(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 10.4524(5) Å	α= 90°.
	b = 17.9047(8) Å	β= 97.2348(6)°.
	c = 13.5993(6) Å	γ= 90°.
Volume	2524.8(2) $Å^3$	
Z	4	
Density (calculated)	1.277 Mg/m^3	
Absorption coefficient	0.859 mm^{-1}	
F(000)	1040	
Crystal color	colorless	
Crystal size	0.287 x 0.235 x 0.139 mm^3	
Theta range for data collection	1.890 to 29.204°	
Index ranges	$-14 \le h \le 13$, $-23 \le k \le 23$, $-18 \le l \le 18$	
Reflections collected	31264	
Independent reflections	6479 [R(int) = 0.0258]	
Completeness to theta = 25.500°	99.9 %	
Absorption correction	Numerical	
Max. and min. transmission	0.9423 and 0.8177	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6479 / 0 / 431	
Goodness-of-fit on F^2	1.029	
Final R indices [I>2sigma(I) = 5607 data]	R1 = 0.0272, wR2 = 0.0665	
R indices (all data, 0.73Å)	R1 = 0.0341, wR2 = 0.0701	
Largest diff. peak and hole	0.581 and -0.234 $e.Å^{-3}$	

Table S7. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **3**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ni(1)	3300(1)	8386(1)	3671(1)	14(1)
P(1)	2921(1)	8676(1)	2049(1)	11(1)
O(1)	1819(1)	9458(1)	4717(1)	32(1)
O(2)	2323(1)	6911(1)	4135(1)	43(1)
O(3)	6095(1)	8397(1)	4288(1)	33(1)
N(1)	2282(1)	9143(1)	-414(1)	24(1)
N(2)	1349(1)	8629(1)	1575(1)	14(1)
N(3)	3365(1)	9553(1)	1785(1)	13(1)
N(4)	3688(1)	8133(1)	1295(1)	16(1)
C(1)	993(1)	8900(1)	-273(1)	24(1)
C(2)	913(1)	8348(1)	578(1)	19(1)
C(3)	386(1)	9039(1)	2057(1)	16(1)
C(4)	-795(1)	8588(1)	2274(1)	26(1)
C(5)	-414(2)	7897(1)	2890(2)	40(1)
C(6)	-1670(2)	9106(1)	2784(2)	38(1)
C(7)	2719(1)	9870(1)	-43(1)	24(1)
C(8)	2609(1)	10030(1)	1051(1)	17(1)
C(9)	4666(1)	9810(1)	2163(1)	16(1)
C(10)	4754(1)	10576(1)	2670(1)	22(1)
C(11)	3885(2)	10632(1)	3482(2)	40(1)
C(12)	6153(2)	10725(1)	3094(1)	28(1)
C(13)	3242(2)	8569(1)	-505(1)	26(1)
C(14)	4208(1)	8426(1)	421(1)	21(1)
C(15)	3664(1)	7317(1)	1402(1)	18(1)
C(16)	4977(2)	6926(1)	1358(2)	21(1)
C(17)	6039(4)	7279(2)	2081(3)	31(1)
C(18)	4822(3)	6094(2)	1580(3)	28(1)
C(16B)	4857(4)	6975(2)	2026(3)	23(1)
C(17B)	6100(6)	7189(4)	1648(5)	33(1)
C(18B)	4706(6)	6117(3)	2056(5)	30(1)
C(19)	2416(1)	9055(1)	4314(1)	21(1)
C(20)	2701(1)	7479(1)	3916(1)	24(1)
C(21)	5011(1)	8409(1)	4044(1)	21(1)

Table S8. Bond lengths [Å] and angles [°] for **3**.

Ni(1)-C(20)	1.7869(14)	N(4)-P(1)-N(2)	104.64(5)
Ni(1)-C(21)	1.7961(14)	N(3)-P(1)-N(2)	104.18(5)
Ni(1)-C(19)	1.8040(14)	N(4)-P(1)-Ni(1)	115.12(4)
Ni(1)-P(1)	2.2519(3)	N(3)-P(1)-Ni(1)	113.77(4)
P(1)-N(4)	1.6876(11)	N(2)-P(1)-Ni(1)	113.93(4)
P(1)-N(3)	1.6885(11)	C(7)-N(1)-C(1)	118.76(12)
P(1)-N(2)	1.6899(11)	C(7)-N(1)-C(13)	118.28(12)
O(1)-C(19)	1.1385(17)	C(1)-N(1)-C(13)	117.52(13)
O(2)-C(20)	1.1447(18)	C(2)-N(2)-C(3)	115.78(10)
O(3)-C(21)	1.1404(18)	C(2)-N(2)-P(1)	123.02(9)
N(1)-C(7)	1.449(2)	C(3)-N(2)-P(1)	119.63(8)
N(1)-C(1)	1.451(2)	C(9)-N(3)-C(8)	116.88(10)
N(1)-C(13)	1.4532(19)	C(9)-N(3)-P(1)	119.03(8)
N(2)-C(2)	1.4645(16)	C(8)-N(3)-P(1)	123.16(8)
N(2)-C(3)	1.4654(16)	C(14)-N(4)-C(15)	116.66(11)
N(3)-C(9)	1.4654(15)	C(14)-N(4)-P(1)	122.74(9)
N(3)-C(8)	1.4668(15)	C(15)-N(4)-P(1)	119.84(9)
N(4)-C(14)	1.4643(17)	N(1)-C(1)-C(2)	115.66(11)
N(4)-C(15)	1.4691(17)	N(2)-C(2)-C(1)	115.90(11)
C(1)-C(2)	1.532(2)	N(2)-C(3)-C(4)	115.95(11)
C(3)-C(4)	1.5344(18)	C(5)-C(4)-C(6)	112.01(15)
C(4)-C(5)	1.519(2)	C(5)-C(4)-C(3)	111.95(12)
C(4)-C(6)	1.529(2)	C(6)-C(4)-C(3)	108.02(13)
C(7)-C(8)	1.5332(19)	N(1)-C(7)-C(8)	116.54(11)
C(9)-C(10)	1.5330(19)	N(3)-C(8)-C(7)	116.86(11)
C(10)-C(11)	1.518(2)	N(3)-C(9)-C(10)	116.05(11)
C(10)-C(12)	1.5267(19)	C(11)-C(10)-C(12)	110.25(13)
C(13)-C(14)	1.533(2)	C(11)-C(10)-C(9)	112.24(12)
C(15)-C(16B)	1.544(4)	C(12)-C(10)-C(9)	109.05(12)
C(15)-C(16)	1.548(2)	N(1)-C(13)-C(14)	116.05(12)
C(16)-C(17)	1.525(5)	N(4)-C(14)-C(13)	116.93(12)
C(16)-C(18)	1.534(4)	N(4)-C(15)-C(16B)	115.23(17)
C(16B)-C(17B)	1.506(8)	N(4)-C(15)-C(16)	114.78(13)
C(16B)-C(18B)	1.545(6)	C(17)-C(16)-C(18)	111.2(2)
		C(17)-C(16)-C(15)	111.4(2)
C(20)-Ni(1)-C(21)	109.14(6)	C(18)-C(16)-C(15)	108.39(19)
C(20)-Ni(1)-C(19)	107.43(7)	C(17B)-C(16B)-C(15)	112.5(4)
C(21)-Ni(1)-C(19)	113.64(6)	C(17B)-C(16B)-C(18B)	111.0(4)
C(20)-Ni(1)-P(1)	111.64(5)	C(15)-C(16B)-C(18B)	109.3(3)
C(21)-Ni(1)-P(1)	108.50(4)	O(1)-C(19)-Ni(1)	177.39(13)
C(19)-Ni(1)-P(1)	106.52(4)	O(2)-C(20)-Ni(1)	175.61(14)
N(4)-P(1)-N(3)	104.00(5)	O(3)-C(21)-Ni(1)	177.56(13)

Table S9. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **3**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ni(1)	18(1)	13(1)	11(1)	2(1)	1(1)	0(1)
P(1)	12(1)	12(1)	11(1)	0(1)	1(1)	1(1)
O(1)	36(1)	38(1)	22(1)	-6(1)	4(1)	13(1)
O(2)	53(1)	20(1)	55(1)	9(1)	6(1)	-8(1)
O(3)	22(1)	47(1)	28(1)	10(1)	-2(1)	1(1)
N(1)	28(1)	29(1)	15(1)	1(1)	1(1)	7(1)
N(2)	12(1)	16(1)	14(1)	-3(1)	0(1)	1(1)
N(3)	12(1)	13(1)	14(1)	4(1)	0(1)	0(1)
N(4)	18(1)	15(1)	15(1)	-1(1)	4(1)	4(1)
C(1)	25(1)	30(1)	16(1)	-2(1)	-5(1)	7(1)
C(2)	17(1)	21(1)	18(1)	-5(1)	-4(1)	2(1)
C(3)	14(1)	16(1)	20(1)	-2(1)	2(1)	0(1)
C(4)	17(1)	29(1)	31(1)	1(1)	4(1)	-3(1)
C(5)	28(1)	36(1)	57(1)	18(1)	9(1)	-9(1)
C(6)	22(1)	50(1)	45(1)	-5(1)	15(1)	-2(1)
C(7)	27(1)	27(1)	18(1)	10(1)	3(1)	4(1)
C(8)	17(1)	15(1)	18(1)	6(1)	1(1)	2(1)
C(9)	13(1)	18(1)	17(1)	4(1)	2(1)	-1(1)
C(10)	19(1)	20(1)	27(1)	-1(1)	0(1)	-4(1)
C(11)	37(1)	38(1)	47(1)	-23(1)	17(1)	-12(1)
C(12)	24(1)	27(1)	31(1)	3(1)	-5(1)	-8(1)
C(13)	33(1)	33(1)	14(1)	0(1)	6(1)	8(1)
C(14)	23(1)	26(1)	16(1)	1(1)	7(1)	6(1)
C(15)	18(1)	15(1)	20(1)	-4(1)	0(1)	3(1)
C(16)	20(1)	18(1)	26(2)	-3(1)	4(1)	4(1)
C(17)	20(1)	24(2)	44(2)	-4(2)	-7(2)	5(1)
C(18)	30(1)	17(1)	38(2)	-3(1)	5(1)	6(1)
C(16B)	29(2)	15(2)	24(3)	-3(1)	-4(2)	10(1)
C(17B)	24(2)	28(3)	46(4)	1(3)	1(3)	11(2)
C(18B)	40(3)	18(2)	30(3)	-4(2)	-3(2)	11(2)
C(19)	26(1)	22(1)	14(1)	3(1)	0(1)	0(1)
C(20)	28(1)	20(1)	24(1)	2(1)	0(1)	-1(1)
C(21)	25(1)	22(1)	14(1)	3(1)	0(1)	1(1)

Table S10. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x10^3) for **3**.

	x	y	z	U(eq)
H(16)	5213	6978	671	25
H(17A)	6848	7008	2055	46
H(17B)	5800	7254	2754	46
H(17C)	6151	7803	1899	46
H(18A)	4590	6035	2252	43
H(18B)	5636	5834	1530	43
H(18C)	4141	5881	1102	43
H(16B)	4887	7167	2719	28
H(17D)	6210	7732	1688	49
H(17E)	6075	7028	957	49
H(17F)	6824	6945	2053	49
H(18D)	5450	5900	2469	45
H(18E)	4657	5916	1382	45
H(18F)	3914	5991	2337	45
H(1A)	542(16)	8631(10)	-895(13)	26(4)
H(1B)	480(15)	9338(9)	-186(11)	19(4)
H(2A)	49(16)	8196(9)	553(12)	20(4)
H(2B)	1403(15)	7900(9)	460(11)	18(4)
H(3A)	27(15)	9468(9)	1668(12)	19(4)
H(3B)	812(14)	9248(9)	2659(12)	16(4)
H(4A)	-1308(16)	8408(8)	1632(12)	20(4)
H(5A)	130(20)	7536(13)	2532(17)	58(6)
H(5B)	-1180(20)	7602(12)	2957(15)	51(6)
H(5C)	70(20)	8084(13)	3568(18)	61(7)
H(6A)	-1930(20)	9591(14)	2352(18)	65(7)
H(6B)	-1192(17)	9184(10)	3438(14)	29(4)
H(6C)	-2460(20)	8840(12)	2924(15)	49(6)
H(7A)	2202(17)	10255(10)	-409(13)	31(5)
H(7B)	3623(16)	9950(9)	-181(12)	22(4)
H(8A)	2888(15)	10542(9)	1179(11)	19(4)
H(8B)	1699(14)	9997(8)	1160(10)	11(3)
H(9A)	5218(15)	9819(9)	1617(12)	21(4)
H(9B)	5032(15)	9427(9)	2640(12)	22(4)
H(10A)	4503(16)	10961(9)	2162(13)	26(4)
H(11A)	2990(20)	10504(12)	3209(15)	49(6)
H(11B)	3896(19)	11159(12)	3749(15)	43(5)
H(11C)	4170(20)	10287(13)	4027(17)	53(6)
H(12A)	6735(18)	10689(10)	2562(14)	36(5)
H(12B)	6436(17)	10342(10)	3570(14)	32(5)
H(12C)	6262(18)	11231(11)	3407(14)	38(5)

H(13A)	3758(16)	8720(9)	-1029(13)	25(4)
H(13B)	2803(17)	8111(10)	-723(13)	28(4)
H(14A)	4834(16)	8077(9)	232(12)	21(4)
H(14B)	4684(15)	8885(9)	603(11)	16(4)
H(15A)	3199(19)	7095(11)	843(15)	41(5)
H(15B)	3210(20)	7187(12)	1882(16)	50(6)

Table S11. Crystal data and structure refinement for **4**.

Empirical formula	C30 H33 N4 Ni O3 P	
Formula weight	587.28	
Temperature	133(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 9.7263(8) Å	α= 90°.
	b = 23.412(2) Å	β= 99.3160(10)°.
	c = 12.5881(11) Å	γ = 90°.
Volume	2828.6(4) $Å^3$	
Z	4	
Density (calculated)	1.379 Mg/m^3	
Absorption coefficient	0.781 mm^{-1}	
F(000)	1232	
Crystal color	colorless	
Crystal size	0.34 x 0.26 x 0.18 mm^3	
Theta range for data collection	1.74 to 29.23°	
Index ranges	-13 <= h <= 13, -32 <= k <= 31, -16 <= l <= 17	
Reflections collected	70276	
Independent reflections	7270 [R(int) = 0.0433]	
Completeness to theta = 25.00°	100.0 %	
Absorption correction	Numerical	
Max. and min. transmission	0.8748 and 0.7788	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7270 / 0 / 352	
Goodness-of-fit on F^2	1.168	
Final R indices [I>2sigma(I) = 6422 data]	R1 = 0.0400, wR2 = 0.1283	
R indices (all data, ? Å)	R1 = 0.0470, wR2 = 0.1393	
Largest diff. peak and hole	1.370 and -0.630 $e.Å^{-3}$	

Table S12. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **4**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ni(1)	-1800(1)	1743(1)	2556(1)	15(1)
P(1)	476(1)	1706(1)	2446(1)	12(1)
O(1)	-2179(2)	2655(1)	4078(1)	37(1)
N(1)	3848(2)	1599(1)	2327(1)	18(1)
C(1)	3990(2)	1365(1)	3400(1)	18(1)
O(2)	-3570(1)	1895(1)	449(1)	28(1)
N(2)	1464(1)	1498(1)	3610(1)	14(1)
C(2)	2644(2)	1104(1)	3685(1)	16(1)
O(3)	-2685(1)	625(1)	3269(1)	32(1)
N(3)	876(1)	1232(1)	1539(1)	13(1)
C(3)	1301(2)	1791(1)	4603(1)	15(1)
N(4)	1196(1)	2328(1)	2140(1)	14(1)
C(4)	732(2)	1427(1)	5429(1)	15(1)
C(5)	136(2)	894(1)	5183(1)	19(1)
C(6)	-395(2)	577(1)	5959(1)	24(1)
C(7)	-332(2)	788(1)	6994(1)	24(1)
C(8)	267(2)	1320(1)	7255(1)	23(1)
C(9)	793(2)	1637(1)	6480(1)	18(1)
C(10)	3446(2)	1232(1)	1408(1)	18(1)
C(11)	1939(2)	1321(1)	848(1)	15(1)
C(12)	275(2)	659(1)	1530(1)	14(1)
C(13)	-1030(2)	564(1)	704(1)	14(1)
C(14)	-1909(2)	111(1)	858(1)	16(1)
C(15)	-3109(2)	4(1)	125(1)	20(1)
C(16)	-3438(2)	350(1)	-780(1)	21(1)
C(17)	-2572(2)	799(1)	-945(1)	21(1)
C(18)	-1369(2)	906(1)	-200(1)	18(1)
C(19)	3807(2)	2212(1)	2193(1)	17(1)
C(20)	2606(2)	2509(1)	2622(1)	15(1)
C(21)	569(2)	2639(1)	1166(1)	16(1)
C(22)	385(2)	3273(1)	1321(1)	15(1)
C(23)	-640(2)	3476(1)	1883(1)	21(1)
C(24)	-896(2)	4058(1)	1943(1)	25(1)
C(25)	-125(2)	4448(1)	1453(1)	24(1)
C(26)	922(2)	4252(1)	917(1)	23(1)
C(27)	1173(2)	3669(1)	851(1)	19(1)
C(28)	-2030(2)	2301(1)	3480(1)	22(1)
C(29)	-2848(2)	1844(1)	1252(1)	18(1)
C(30)	-2316(2)	1059(1)	3009(1)	22(1)

Table S13. Bond lengths [Å] and angles [°] for **4**.

Ni(1)-C(28)	1.7859(18)	C(26)-C(27)	1.392(2)
Ni(1)-C(30)	1.7987(17)		
Ni(1)-C(29)	1.8023(17)	C(28)-Ni(1)-C(30)	111.96(8)
Ni(1)-P(1)	2.2424(5)	C(28)-Ni(1)-C(29)	112.66(8)
P(1)-N(3)	1.6824(13)	C(30)-Ni(1)-C(29)	105.09(8)
P(1)-N(2)	1.6879(13)	C(28)-Ni(1)-P(1)	107.31(6)
P(1)-N(4)	1.6890(13)	C(30)-Ni(1)-P(1)	108.27(5)
O(1)-C(28)	1.146(2)	C(29)-Ni(1)-P(1)	111.53(5)
N(1)-C(10)	1.444(2)	N(3)-P(1)-N(2)	103.78(6)
N(1)-C(19)	1.444(2)	N(3)-P(1)-N(4)	105.32(6)
N(1)-C(1)	1.443(2)	N(2)-P(1)-N(4)	104.32(6)
C(1)-C(2)	1.538(2)	N(3)-P(1)-Ni(1)	114.01(5)
O(2)-C(29)	1.140(2)	N(2)-P(1)-Ni(1)	112.74(5)
N(2)-C(3)	1.4570(19)	N(4)-P(1)-Ni(1)	115.49(5)
N(2)-C(2)	1.4635(19)	C(10)-N(1)-C(19)	119.93(13)
O(3)-C(30)	1.142(2)	C(10)-N(1)-C(1)	119.75(14)
N(3)-C(12)	1.4627(19)	C(19)-N(1)-C(1)	118.90(13)
N(3)-C(11)	1.4690(19)	N(1)-C(1)-C(2)	114.39(13)
C(3)-C(4)	1.517(2)	C(3)-N(2)-C(2)	115.76(12)
N(4)-C(20)	1.4688(19)	C(3)-N(2)-P(1)	118.95(10)
N(4)-C(21)	1.4698(19)	C(2)-N(2)-P(1)	124.55(10)
C(4)-C(5)	1.389(2)	N(2)-C(2)-C(1)	115.07(13)
C(4)-C(9)	1.404(2)	C(12)-N(3)-C(11)	116.37(12)
C(5)-C(6)	1.392(2)	C(12)-N(3)-P(1)	118.25(10)
C(6)-C(7)	1.386(3)	C(11)-N(3)-P(1)	124.81(10)
C(7)-C(8)	1.390(3)	N(2)-C(3)-C(4)	115.20(13)
C(8)-C(9)	1.388(2)	C(20)-N(4)-C(21)	115.85(12)
C(10)-C(11)	1.534(2)	C(20)-N(4)-P(1)	123.24(10)
C(12)-C(13)	1.521(2)	C(21)-N(4)-P(1)	119.04(10)
C(13)-C(18)	1.389(2)	C(5)-C(4)-C(9)	118.51(15)
C(13)-C(14)	1.395(2)	C(5)-C(4)-C(3)	122.52(14)
C(14)-C(15)	1.388(2)	C(9)-C(4)-C(3)	118.97(14)
C(15)-C(16)	1.392(2)	C(4)-C(5)-C(6)	120.78(15)
C(16)-C(17)	1.384(2)	C(7)-C(6)-C(5)	120.26(16)
C(17)-C(18)	1.398(2)	C(6)-C(7)-C(8)	119.69(16)
C(19)-C(20)	1.532(2)	C(9)-C(8)-C(7)	120.04(16)
C(21)-C(22)	1.513(2)	C(8)-C(9)-C(4)	120.72(16)
C(22)-C(27)	1.393(2)	N(1)-C(10)-C(11)	113.74(13)
C(22)-C(23)	1.396(2)	N(3)-C(11)-C(10)	114.86(12)
C(23)-C(24)	1.389(2)	N(3)-C(12)-C(13)	115.34(12)
C(24)-C(25)	1.387(3)	C(18)-C(13)-C(14)	118.89(14)
C(25)-C(26)	1.387(3)	C(18)-C(13)-C(12)	122.48(14)

C(14)-C(13)-C(12)	118.63(13)	C(27)-C(22)-C(21)	120.88(15)
C(15)-C(14)-C(13)	120.83(15)	C(23)-C(22)-C(21)	120.59(14)
C(14)-C(15)-C(16)	119.80(15)	C(24)-C(23)-C(22)	120.65(15)
C(17)-C(16)-C(15)	119.97(15)	C(25)-C(24)-C(23)	120.44(16)
C(16)-C(17)-C(18)	119.95(16)	C(24)-C(25)-C(26)	119.44(16)
C(13)-C(18)-C(17)	120.57(15)	C(27)-C(26)-C(25)	120.13(16)
N(1)-C(19)-C(20)	114.77(13)	C(26)-C(27)-C(22)	120.87(16)
N(4)-C(20)-C(19)	115.92(13)	O(1)-C(28)-Ni(1)	179.42(17)
N(4)-C(21)-C(22)	114.80(12)	O(2)-C(29)-Ni(1)	176.22(15)
C(27)-C(22)-C(23)	118.42(15)	O(3)-C(30)-Ni(1)	177.53(17)

Symmetry transformations used to generate equivalent atoms:

Table S14. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **4**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ni(1)	10(1)	18(1)	18(1)	0(1)	6(1)	0(1)
P(1)	9(1)	14(1)	12(1)	0(1)	4(1)	-1(1)
O(1)	44(1)	38(1)	33(1)	-12(1)	19(1)	5(1)
N(1)	16(1)	20(1)	19(1)	-1(1)	4(1)	-2(1)
C(1)	12(1)	23(1)	20(1)	0(1)	2(1)	2(1)
O(2)	25(1)	27(1)	29(1)	0(1)	-2(1)	5(1)
N(2)	13(1)	18(1)	12(1)	1(1)	3(1)	3(1)
C(2)	12(1)	19(1)	16(1)	3(1)	3(1)	3(1)
O(3)	27(1)	27(1)	44(1)	8(1)	16(1)	-5(1)
N(3)	11(1)	14(1)	14(1)	-1(1)	6(1)	-2(1)
C(3)	16(1)	17(1)	14(1)	-1(1)	4(1)	0(1)
N(4)	11(1)	15(1)	15(1)	2(1)	1(1)	-2(1)
C(4)	13(1)	18(1)	14(1)	2(1)	4(1)	4(1)
C(5)	20(1)	19(1)	20(1)	0(1)	7(1)	3(1)
C(6)	25(1)	18(1)	32(1)	4(1)	13(1)	3(1)
C(7)	24(1)	25(1)	26(1)	9(1)	14(1)	9(1)
C(8)	23(1)	29(1)	18(1)	5(1)	9(1)	10(1)
C(9)	16(1)	21(1)	17(1)	1(1)	5(1)	4(1)
C(10)	12(1)	22(1)	20(1)	-2(1)	7(1)	0(1)
C(11)	13(1)	18(1)	16(1)	-1(1)	7(1)	-1(1)
C(12)	10(1)	16(1)	16(1)	0(1)	3(1)	0(1)
C(13)	12(1)	16(1)	16(1)	-2(1)	5(1)	1(1)
C(14)	15(1)	18(1)	17(1)	-1(1)	4(1)	-1(1)
C(15)	14(1)	21(1)	26(1)	-4(1)	6(1)	-4(1)
C(16)	12(1)	29(1)	21(1)	-7(1)	2(1)	1(1)
C(17)	18(1)	27(1)	17(1)	0(1)	4(1)	3(1)
C(18)	15(1)	20(1)	18(1)	0(1)	5(1)	-2(1)
C(19)	12(1)	20(1)	20(1)	0(1)	4(1)	-4(1)
C(20)	11(1)	17(1)	18(1)	-1(1)	2(1)	-4(1)
C(21)	17(1)	17(1)	14(1)	1(1)	1(1)	0(1)
C(22)	13(1)	17(1)	14(1)	2(1)	-1(1)	-2(1)
C(23)	16(1)	24(1)	24(1)	1(1)	5(1)	-3(1)
C(24)	17(1)	27(1)	31(1)	-6(1)	4(1)	4(1)
C(25)	24(1)	17(1)	28(1)	-2(1)	-5(1)	3(1)
C(26)	23(1)	19(1)	25(1)	4(1)	0(1)	-4(1)
C(27)	18(1)	20(1)	18(1)	3(1)	3(1)	-2(1)
C(28)	18(1)	28(1)	23(1)	2(1)	10(1)	1(1)
C(29)	15(1)	17(1)	24(1)	-1(1)	7(1)	0(1)
C(30)	15(1)	25(1)	27(1)	1(1)	9(1)	0(1)

Table S15. Hydrogen coordinates ($x10^4$) and isotropic displacement parameters ($Å^2x10^3$) for **4**.

	x	y	z	U(eq)
H(1A)	4311	1671	3924	22
H(1B)	4719	1066	3478	22
H(2A)	2369	777	3199	19
H(2B)	2844	954	4429	19
H(3A)	670	2121	4420	18
H(3B)	2220	1944	4936	18
H(5)	91	744	4477	23
H(6)	-803	214	5779	29
H(7)	-696	571	7523	29
H(8)	316	1466	7964	27
H(9)	1198	2000	6663	22
H(10A)	3564	829	1644	21
H(10B)	4080	1302	880	21
H(11A)	1846	1714	559	18
H(11B)	1750	1055	229	18
H(12A)	49	578	2255	17
H(12B)	990	379	1394	17
H(14)	-1683	-128	1472	20
H(15)	-3704	-303	241	24
H(16)	-4257	278	-1285	25
H(17)	-2794	1035	-1564	25
H(18)	-779	1216	-315	21
H(19A)	3737	2300	1417	21
H(19B)	4697	2373	2565	21
H(20A)	2719	2444	3409	18
H(20B)	2686	2926	2508	18
H(21A)	-354	2469	897	19
H(21B)	1161	2582	604	19
H(23)	-1169	3214	2228	25
H(24)	-1602	4191	2322	30
H(25)	-313	4845	1483	29
H(26)	1470	4517	594	28
H(27)	1891	3539	482	22

Table S16. Crystal data and structure refinement for **5**.

Empirical formula	C26 H30 N7 Ni O2 P	
Formula weight	562.25	
Temperature	88(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 12.8799(6) Å	α= 90°.
	b = 14.0169(7) Å	β= 109.6630(10)°.
	c = 15.4714(7) Å	γ = 90°.
Volume	2630.3(2) $Å^3$	
Z	4	
Density (calculated)	1.420 Mg/m^3	
Absorption coefficient	0.836 mm^{-1}	
F(000)	1176	
Crystal color	yellow	
Crystal size	0.41 x 0.22 x 0.11 mm^3	
Theta range for data collection	1.79 to 29.27°	
Index ranges	-17 <= h <= 16, -18 <= k <= 19, -20 <= l <= 21	
Reflections collected	32415	
Independent reflections	6760 [R(int) = 0.0553]	
Completeness to theta = 25.00°	100.0 %	
Absorption correction	Numerical	
Max. and min. transmission	0.9151 and 0.7276	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6760 / 0 / 334	
Goodness-of-fit on F^2	1.045	
Final R indices [I>2sigma(I) = 5554 data]	R1 = 0.0291, wR2 = 0.0753	
R indices (all data, ? Å)	R1 = 0.0380, wR2 = 0.0776	
Largest diff. peak and hole	0.521 and -0.418 $e.Å^{-3}$	

Table S17. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **5**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ni(1)	3033(1)	6319(1)	1036(1)	12(1)
P(1)	2376(1)	7652(1)	286(1)	10(1)
O(1)	3004(1)	6329(1)	2914(1)	23(1)
N(1)	1891(1)	9716(1)	-764(1)	16(1)
C(1)	1225(1)	9214(1)	-1572(1)	19(1)
O(2)	1894(1)	4597(1)	151(1)	22(1)
N(2)	1603(1)	8374(1)	693(1)	12(1)
C(2)	793(1)	8257(1)	-1357(1)	16(1)
N(3)	1644(1)	7579(1)	-845(1)	12(1)
C(3)	1414(1)	9997(1)	-82(1)	17(1)
N(4)	3482(1)	8340(1)	360(1)	12(1)
C(4)	1772(1)	9406(1)	803(1)	15(1)
N(5)	-585(1)	8036(1)	1690(1)	22(1)
C(5)	3061(1)	9810(1)	-584(1)	17(1)
N(6)	1390(1)	5376(1)	-2214(1)	15(1)
C(6)	3652(1)	8846(1)	-406(1)	15(1)
N(7)	4623(1)	6483(1)	1032(1)	13(1)
C(7)	596(1)	7963(1)	775(1)	14(1)
C(8)	463(1)	8079(1)	1704(1)	15(1)
C(9)	1352(1)	8175(1)	2510(1)	18(1)
C(10)	1160(2)	8197(1)	3341(1)	24(1)
C(11)	86(2)	8145(1)	3335(1)	28(1)
C(12)	-748(2)	8075(1)	2501(1)	29(1)
C(13)	1936(1)	6840(1)	-1380(1)	13(1)
C(14)	1115(1)	6030(1)	-1693(1)	13(1)
C(15)	166(1)	5959(1)	-1459(1)	17(1)
C(16)	-532(1)	5190(1)	-1780(1)	22(1)
C(17)	-255(1)	4506(1)	-2309(1)	21(1)
C(18)	713(1)	4627(1)	-2498(1)	19(1)
C(19)	4452(1)	8200(1)	1178(1)	13(1)
C(20)	5126(1)	7342(1)	1102(1)	13(1)
C(21)	6199(1)	7434(1)	1096(1)	16(1)
C(22)	6794(1)	6627(1)	1029(1)	19(1)
C(23)	6285(1)	5748(1)	971(1)	18(1)
C(24)	5211(1)	5708(1)	972(1)	15(1)
C(25)	3051(1)	6345(1)	2183(1)	16(1)
C(26)	2391(1)	5266(1)	469(1)	15(1)

Table S18. Bond lengths [Å] and angles [°] for **5**.

Ni(1)-C(25)	1.7665(16)		
Ni(1)-C(26)	1.7731(15)	C(25)-Ni(1)-C(26)	111.14(7)
Ni(1)-N(7)	2.0619(12)	C(25)-Ni(1)-N(7)	108.89(6)
Ni(1)-P(1)	2.2121(4)	C(26)-Ni(1)-N(7)	112.94(6)
P(1)-N(2)	1.6837(12)	C(25)-Ni(1)-P(1)	112.51(5)
P(1)-N(3)	1.6880(12)	C(26)-Ni(1)-P(1)	114.23(5)
P(1)-N(4)	1.6919(12)	N(7)-Ni(1)-P(1)	96.25(3)
O(1)-C(25)	1.1541(18)	N(2)-P(1)-N(3)	103.28(6)
N(1)-C(1)	1.4380(19)	N(2)-P(1)-N(4)	102.83(6)
N(1)-C(5)	1.4428(18)	N(3)-P(1)-N(4)	105.56(6)
N(1)-C(3)	1.4445(18)	N(2)-P(1)-Ni(1)	118.80(4)
C(1)-C(2)	1.531(2)	N(3)-P(1)-Ni(1)	118.35(5)
O(2)-C(26)	1.1482(17)	N(4)-P(1)-Ni(1)	106.32(4)
N(2)-C(7)	1.4633(17)	C(1)-N(1)-C(5)	119.45(12)
N(2)-C(4)	1.4637(18)	C(1)-N(1)-C(3)	119.45(12)
C(2)-N(3)	1.4662(18)	C(5)-N(1)-C(3)	120.50(13)
N(3)-C(13)	1.4524(18)	N(1)-C(1)-C(2)	113.22(12)
C(3)-C(4)	1.534(2)	C(7)-N(2)-C(4)	118.71(11)
N(4)-C(6)	1.4595(18)	C(7)-N(2)-P(1)	116.62(9)
N(4)-C(19)	1.4619(18)	C(4)-N(2)-P(1)	123.69(9)
N(5)-C(12)	1.342(2)	N(3)-C(2)-C(1)	115.15(12)
N(5)-C(8)	1.3440(19)	C(13)-N(3)-C(2)	116.37(12)
C(5)-C(6)	1.5288(19)	C(13)-N(3)-P(1)	118.20(9)
N(6)-C(18)	1.3401(19)	C(2)-N(3)-P(1)	125.20(10)
N(6)-C(14)	1.3452(18)	N(1)-C(3)-C(4)	115.51(12)
N(7)-C(24)	1.3463(18)	C(6)-N(4)-C(19)	116.73(11)
N(7)-C(20)	1.3549(18)	C(6)-N(4)-P(1)	125.13(10)
C(7)-C(8)	1.512(2)	C(19)-N(4)-P(1)	115.92(9)
C(8)-C(9)	1.387(2)	N(2)-C(4)-C(3)	116.20(12)
C(9)-C(10)	1.389(2)	C(12)-N(5)-C(8)	117.16(14)
C(10)-C(11)	1.383(2)	N(1)-C(5)-C(6)	112.26(12)
C(11)-C(12)	1.377(2)	C(18)-N(6)-C(14)	117.24(13)
C(13)-C(14)	1.515(2)	N(4)-C(6)-C(5)	112.01(12)
C(14)-C(15)	1.390(2)	C(24)-N(7)-C(20)	117.25(12)
C(15)-C(16)	1.384(2)	C(24)-N(7)-Ni(1)	119.50(10)
C(16)-C(17)	1.384(2)	C(20)-N(7)-Ni(1)	123.24(9)
C(17)-C(18)	1.383(2)	N(2)-C(7)-C(8)	115.29(12)
C(19)-C(20)	1.5099(19)	N(5)-C(8)-C(9)	122.59(14)
C(20)-C(21)	1.391(2)	N(5)-C(8)-C(7)	114.51(13)
C(21)-C(22)	1.389(2)	C(9)-C(8)-C(7)	122.82(13)
C(22)-C(23)	1.383(2)	C(8)-C(9)-C(10)	119.02(15)
C(23)-C(24)	1.385(2)	C(11)-C(10)-C(9)	118.81(16)

C(12)-C(11)-C(10)	118.27(15)	N(4)-C(19)-C(20)	112.67(11)
N(5)-C(12)-C(11)	124.11(16)	N(7)-C(20)-C(21)	122.08(13)
N(3)-C(13)-C(14)	115.46(12)	N(7)-C(20)-C(19)	116.20(12)
N(6)-C(14)-C(15)	122.58(14)	C(21)-C(20)-C(19)	121.72(13)
N(6)-C(14)-C(13)	113.96(12)	C(22)-C(21)-C(20)	119.97(14)
C(15)-C(14)-C(13)	123.47(13)	C(23)-C(22)-C(21)	117.96(14)
C(16)-C(15)-C(14)	119.00(14)	C(22)-C(23)-C(24)	119.20(14)
C(15)-C(16)-C(17)	119.08(14)	N(7)-C(24)-C(23)	123.54(14)
C(18)-C(17)-C(16)	118.07(14)	O(1)-C(25)-Ni(1)	175.82(13)
N(6)-C(18)-C(17)	124.01(14)	O(2)-C(26)-Ni(1)	172.49(13)

Symmetry transformations used to generate equivalent atoms:

Table S19. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **5**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ni(1)	11(1)	11(1)	14(1)	1(1)	4(1)	1(1)
P(1)	9(1)	11(1)	10(1)	0(1)	3(1)	2(1)
O(1)	25(1)	29(1)	17(1)	5(1)	8(1)	0(1)
N(1)	15(1)	19(1)	16(1)	0(1)	6(1)	4(1)
C(1)	19(1)	23(1)	15(1)	6(1)	5(1)	8(1)
O(2)	23(1)	17(1)	26(1)	-3(1)	8(1)	-3(1)
N(2)	12(1)	10(1)	15(1)	-1(1)	7(1)	1(1)
C(2)	13(1)	22(1)	12(1)	1(1)	1(1)	6(1)
N(3)	11(1)	15(1)	10(1)	-1(1)	2(1)	5(1)
C(3)	19(1)	14(1)	21(1)	1(1)	10(1)	4(1)
N(4)	10(1)	13(1)	12(1)	3(1)	2(1)	0(1)
C(4)	18(1)	12(1)	16(1)	-3(1)	8(1)	2(1)
N(5)	18(1)	26(1)	24(1)	-4(1)	12(1)	-2(1)
C(5)	18(1)	15(1)	20(1)	5(1)	9(1)	2(1)
N(6)	15(1)	16(1)	14(1)	0(1)	4(1)	3(1)
C(6)	14(1)	16(1)	17(1)	3(1)	7(1)	1(1)
N(7)	12(1)	14(1)	10(1)	0(1)	2(1)	2(1)
C(7)	11(1)	15(1)	16(1)	-1(1)	6(1)	1(1)
C(8)	18(1)	11(1)	18(1)	-1(1)	9(1)	1(1)
C(9)	20(1)	17(1)	19(1)	-3(1)	8(1)	-3(1)
C(10)	32(1)	22(1)	18(1)	-4(1)	9(1)	-7(1)
C(11)	42(1)	25(1)	25(1)	-8(1)	22(1)	-10(1)
C(12)	26(1)	35(1)	34(1)	-7(1)	21(1)	-6(1)
C(13)	11(1)	17(1)	12(1)	-2(1)	4(1)	1(1)
C(14)	12(1)	16(1)	9(1)	2(1)	2(1)	3(1)
C(15)	16(1)	22(1)	14(1)	-2(1)	6(1)	1(1)
C(16)	17(1)	28(1)	21(1)	2(1)	8(1)	-3(1)
C(17)	23(1)	18(1)	22(1)	0(1)	5(1)	-6(1)
C(18)	22(1)	16(1)	18(1)	-1(1)	6(1)	2(1)
C(19)	11(1)	12(1)	15(1)	-1(1)	2(1)	0(1)
C(20)	12(1)	15(1)	9(1)	0(1)	1(1)	2(1)
C(21)	12(1)	19(1)	16(1)	0(1)	2(1)	-1(1)
C(22)	11(1)	27(1)	17(1)	-1(1)	5(1)	2(1)
C(23)	16(1)	20(1)	18(1)	0(1)	5(1)	8(1)
C(24)	16(1)	14(1)	15(1)	0(1)	3(1)	3(1)
C(25)	11(1)	14(1)	20(1)	4(1)	2(1)	1(1)
C(26)	14(1)	16(1)	17(1)	3(1)	7(1)	4(1)

Table S20. Hydrogen coordinates ($x10^4$) and isotropic displacement parameters ($Å^2x10^3$) for **5**.

	x	y	z	U(eq)
H(1A)	1667	9101	-1975	23
H(1B)	591	9621	-1911	23
H(2A)	298	8381	-1000	19
H(2B)	346	7956	-1943	19
H(3A)	601	9959	-360	21
H(3B)	1606	10673	81	21
H(4A)	2566	9524	1129	18
H(4B)	1366	9641	1202	18
H(5A)	3381	10226	-43	21
H(5B)	3184	10119	-1116	21
H(6A)	3377	8449	-966	18
H(6B)	4452	8950	-270	18
H(7A)	582	7273	633	17
H(7B)	-45	8261	306	17
H(9)	2080	8225	2494	22
H(10)	1757	8247	3903	28
H(11)	-73	8156	3892	33
H(12)	-1486	8054	2500	35
H(13A)	2658	6569	-1009	16
H(13B)	2028	7139	-1929	16
H(15)	-2	6431	-1085	21
H(16)	-1193	5134	-1640	26
H(17)	-716	3969	-2536	26
H(18)	911	4150	-2851	23
H(19A)	4212	8120	1718	16
H(19B)	4921	8777	1280	16
H(21)	6525	8048	1137	19
H(22)	7527	6677	1024	22
H(23)	6668	5180	930	22
H(24)	4872	5100	929	18

Table S21. Crystal data and structure refinement for **6**.

Empirical formula	C20 H42 N8 Ni O2 P2	
Formula weight	547.27	
Temperature	133(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 8.5551(5) Å	α= 90°.
	b = 19.4034(12) Å	β= 104.7970(10)°.
	c = 15.9663(10) Å	γ = 90°.
Volume	2562.5(3) $Å^3$	
Z	4	
Density (calculated)	1.419 Mg/m^3	
Absorption coefficient	0.916 mm^{-1}	
F(000)	1168	
Crystal color	Colorless	
Crystal size	0.66 x 0.29 x 0.26 mm^3	
Theta range for data collection	1.69 to 29.20°	
Index ranges	-11 <= h <= 11, -25 <= k <= 25, -21 <= l <= 21	
Reflections collected	62910	
Independent reflections	6562 [R(int) = 0.0160]	
Completeness to theta = 25.00°	100.0 %	
Absorption correction	Numerical	
Max. and min. transmission	0.7980 and 0.5853	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6562 / 0 / 304	
Goodness-of-fit on F^2	1.056	
Final R indices [I>2sigma(I) = 6327 data]	R1 = 0.0232, wR2 = 0.1097	
R indices (all data, ? Å)	R1 = 0.0242, wR2 = 0.1122	
Largest diff. peak and hole	0.459 and -0.295 $e.Å^{-3}$	

Table S22. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **6**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ni(1)	4198(1)	7157(1)	5251(1)	8(1)
P(1)	6056(1)	6502(1)	6134(1)	8(1)
O(1)	5925(1)	7796(1)	4090(1)	24(1)
N(1)	8892(1)	5367(1)	7348(1)	13(1)
C(1)	7583(1)	4875(1)	7041(1)	14(1)
P(2)	3056(1)	7990(1)	5847(1)	7(1)
O(2)	1584(1)	6188(1)	4526(1)	21(1)
N(2)	5406(1)	5690(1)	6227(1)	11(1)
C(2)	6355(1)	5068(1)	6198(1)	12(1)
N(3)	6840(1)	6741(1)	7174(1)	10(1)
C(3)	3896(1)	5583(1)	6468(1)	15(1)
N(4)	7726(1)	6375(1)	5768(1)	10(1)
C(4)	8783(1)	5837(1)	8040(1)	14(1)
N(5)	1239(1)	9302(1)	6727(1)	16(1)
C(5)	7220(1)	6260(1)	7906(1)	12(1)
N(6)	3387(1)	7989(1)	6934(1)	10(1)
C(6)	7324(1)	7457(1)	7369(1)	12(1)
N(7)	3573(1)	8801(1)	5619(1)	11(1)
C(7)	9809(1)	5595(1)	6750(1)	14(1)
N(8)	1014(1)	8011(1)	5513(1)	10(1)
C(8)	9357(1)	6306(1)	6335(1)	12(1)
C(9)	7575(1)	6201(1)	4863(1)	14(1)
C(10)	2193(1)	9013(1)	7536(1)	16(1)
C(11)	3696(1)	8605(1)	7474(1)	14(1)
C(12)	3160(1)	7352(1)	7373(1)	13(1)
C(13)	2055(1)	9730(1)	6222(1)	17(1)
C(14)	2441(1)	9378(1)	5437(1)	14(1)
C(15)	5268(1)	8974(1)	5719(1)	15(1)
C(16)	-224(1)	8942(1)	6274(1)	16(1)
C(17)	-31(1)	8174(1)	6080(1)	12(1)
C(18)	210(1)	7946(1)	4597(1)	13(1)
C(19)	5224(1)	7551(1)	4541(1)	14(1)
C(20)	2616(1)	6572(1)	4794(1)	13(1)

Table S23. Bond lengths [Å] and angles [°] for **6**.

Ni(1)-C(19)	1.7747(11)	P(2)-Ni(1)-P(1)	117.644(12)
Ni(1)-C(20)	1.7751(11)	N(2)-P(1)-N(3)	103.10(5)
Ni(1)-P(2)	2.2238(3)	N(2)-P(1)-N(4)	102.71(4)
Ni(1)-P(1)	2.2320(3)	N(3)-P(1)-N(4)	102.74(5)
P(1)-N(2)	1.6892(9)	N(2)-P(1)-Ni(1)	112.92(3)
P(1)-N(3)	1.6902(9)	N(3)-P(1)-Ni(1)	120.25(3)
P(1)-N(4)	1.6939(9)	N(4)-P(1)-Ni(1)	113.12(3)
O(1)-C(19)	1.1500(15)	C(7)-N(1)-C(4)	117.32(9)
N(1)-C(7)	1.4507(14)	C(7)-N(1)-C(1)	118.48(9)
N(1)-C(4)	1.4542(14)	C(4)-N(1)-C(1)	118.23(9)
N(1)-C(1)	1.4572(14)	N(1)-C(1)-C(2)	115.65(9)
C(1)-C(2)	1.5270(15)	N(6)-P(2)-N(8)	102.25(5)
P(2)-N(6)	1.6871(9)	N(6)-P(2)-N(7)	103.68(5)
P(2)-N(8)	1.6921(9)	N(8)-P(2)-N(7)	102.37(4)
P(2)-N(7)	1.6975(9)	N(6)-P(2)-Ni(1)	117.57(3)
O(2)-C(20)	1.1506(14)	N(8)-P(2)-Ni(1)	114.47(3)
N(2)-C(3)	1.4544(13)	N(7)-P(2)-Ni(1)	114.55(3)
N(2)-C(2)	1.4618(13)	C(3)-N(2)-C(2)	115.33(8)
N(3)-C(6)	1.4595(13)	C(3)-N(2)-P(1)	119.42(7)
N(3)-C(5)	1.4657(13)	C(2)-N(2)-P(1)	124.71(7)
N(4)-C(9)	1.4565(13)	N(2)-C(2)-C(1)	115.94(9)
N(4)-C(8)	1.4623(12)	C(6)-N(3)-C(5)	116.33(9)
C(4)-C(5)	1.5365(15)	C(6)-N(3)-P(1)	119.38(7)
N(5)-C(13)	1.4529(15)	C(5)-N(3)-P(1)	124.03(7)
N(5)-C(10)	1.4530(15)	C(9)-N(4)-C(8)	114.93(8)
N(5)-C(16)	1.4538(14)	C(9)-N(4)-P(1)	120.44(7)
N(6)-C(11)	1.4571(13)	C(8)-N(4)-P(1)	123.75(7)
N(6)-C(12)	1.4594(13)	N(1)-C(4)-C(5)	116.80(9)
N(7)-C(15)	1.4575(13)	C(13)-N(5)-C(10)	118.23(9)
N(7)-C(14)	1.4602(13)	C(13)-N(5)-C(16)	118.26(10)
C(7)-C(8)	1.5369(15)	C(10)-N(5)-C(16)	118.22(10)
N(8)-C(18)	1.4547(14)	N(3)-C(5)-C(4)	117.37(9)
N(8)-C(17)	1.4613(13)	C(11)-N(6)-C(12)	115.97(9)
C(10)-C(11)	1.5336(15)	C(11)-N(6)-P(2)	124.40(7)
C(13)-C(14)	1.5365(16)	C(12)-N(6)-P(2)	119.17(7)
C(16)-C(17)	1.5395(15)	C(15)-N(7)-C(14)	115.84(8)
		C(15)-N(7)-P(2)	119.74(7)
C(19)-Ni(1)-C(20)	117.55(5)	C(14)-N(7)-P(2)	123.90(7)
C(19)-Ni(1)-P(2)	107.61(4)	N(1)-C(7)-C(8)	116.07(9)
C(20)-Ni(1)-P(2)	105.59(4)	C(18)-N(8)-C(17)	115.82(9)
C(19)-Ni(1)-P(1)	105.09(4)	C(18)-N(8)-P(2)	119.97(7)
C(20)-Ni(1)-P(1)	103.92(4)	C(17)-N(8)-P(2)	123.81(7)

N(4)-C(8)-C(7)	116.37(9)	N(5)-C(16)-C(17)	116.21(9)
N(5)-C(10)-C(11)	115.60(9)	N(8)-C(17)-C(16)	116.63(9)
N(6)-C(11)-C(10)	115.62(9)	O(1)-C(19)-Ni(1)	178.13(10)
N(5)-C(13)-C(14)	115.62(9)	O(2)-C(20)-Ni(1)	177.61(11)
N(7)-C(14)-C(13)	116.59(9)		

Symmetry transformations used to generate equivalent atoms:

Table S24. Anisotropic displacement parameters ($Å^2x10^3$) for **6**. The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [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)	8(1)	9(1)	7(1)	0(1)	2(1)	1(1)
P(1)	7(1)	8(1)	8(1)	0(1)	2(1)	0(1)
O(1)	20(1)	31(1)	23(1)	12(1)	12(1)	5(1)
N(1)	13(1)	13(1)	13(1)	-1(1)	3(1)	1(1)
C(1)	15(1)	10(1)	16(1)	2(1)	2(1)	2(1)
P(2)	7(1)	8(1)	7(1)	0(1)	2(1)	0(1)
O(2)	17(1)	21(1)	24(1)	-8(1)	0(1)	-4(1)
N(2)	9(1)	8(1)	16(1)	0(1)	4(1)	0(1)
C(2)	13(1)	8(1)	15(1)	-1(1)	2(1)	0(1)
N(3)	12(1)	9(1)	8(1)	0(1)	2(1)	0(1)
C(3)	12(1)	14(1)	20(1)	2(1)	7(1)	-3(1)
N(4)	7(1)	13(1)	10(1)	0(1)	3(1)	1(1)
C(4)	15(1)	14(1)	10(1)	2(1)	1(1)	3(1)
N(5)	16(1)	15(1)	16(1)	-2(1)	2(1)	2(1)
C(5)	15(1)	14(1)	9(1)	1(1)	4(1)	1(1)
N(6)	12(1)	10(1)	7(1)	-1(1)	1(1)	0(1)
C(6)	14(1)	10(1)	12(1)	-2(1)	2(1)	-2(1)
N(7)	9(1)	8(1)	16(1)	2(1)	3(1)	-1(1)
C(7)	10(1)	16(1)	16(1)	0(1)	3(1)	4(1)
N(8)	6(1)	13(1)	8(1)	-1(1)	1(1)	0(1)
C(8)	7(1)	14(1)	13(1)	1(1)	3(1)	0(1)
C(9)	15(1)	16(1)	11(1)	-2(1)	5(1)	0(1)
C(10)	18(1)	16(1)	14(1)	-5(1)	3(1)	2(1)
C(11)	14(1)	14(1)	10(1)	-4(1)	0(1)	0(1)
C(12)	16(1)	15(1)	10(1)	2(1)	4(1)	0(1)
C(13)	20(1)	9(1)	22(1)	-2(1)	4(1)	2(1)
C(14)	15(1)	9(1)	17(1)	2(1)	3(1)	1(1)
C(15)	12(1)	14(1)	19(1)	0(1)	4(1)	-4(1)
C(16)	12(1)	18(1)	19(1)	-3(1)	3(1)	3(1)
C(17)	9(1)	16(1)	13(1)	-2(1)	4(1)	0(1)
C(18)	11(1)	16(1)	10(1)	-1(1)	0(1)	1(1)
C(19)	12(1)	16(1)	13(1)	2(1)	2(1)	5(1)
C(20)	12(1)	15(1)	12(1)	-2(1)	2(1)	4(1)

Table S25. Hydrogen coordinates ($x10^4$) and isotropic displacement parameters ($Å^2x10^3$) for **6**.

	x	y	z	U(eq)
H(1A)	7000	4817	7498	17
H(1B)	8062	4424	6959	17
H(2A)	6940	5128	5742	15
H(2B)	5599	4677	6023	15
H(3A)	4128	5415	7067	23
H(3B)	3239	5242	6080	23
H(3C)	3303	6019	6421	23
H(4A)	9703	6162	8133	16
H(4B)	8918	5565	8579	16
H(5A)	6305	5933	7834	15
H(5B)	7277	6526	8442	15
H(6A)	8506	7489	7528	19
H(6B)	6908	7619	7852	19
H(6C)	6881	7743	6857	19
H(7A)	9675	5250	6281	17
H(7B)	10968	5603	7063	17
H(8A)	9487	6651	6804	14
H(8B)	10140	6423	5995	14
H(9A)	8036	5743	4827	21
H(9B)	8158	6543	4606	21
H(9C)	6431	6201	4548	21
H(10A)	1490	8705	7773	19
H(10B)	2542	9394	7954	19
H(11A)	4407	8915	7244	16
H(11B)	4295	8468	8066	16
H(12A)	2788	6988	6943	20
H(12B)	2352	7425	7703	20
H(12C)	4188	7214	7769	20
H(13A)	3080	9897	6610	21
H(13B)	1371	10138	6015	21
H(14A)	1414	9211	5051	17
H(14B)	2884	9730	5112	17
H(15A)	5634	9284	6214	23
H(15B)	5392	9202	5192	23
H(15C)	5918	8552	5817	23
H(16A)	-682	9182	5719	19
H(16B)	-1022	8982	6625	19
H(17A)	396	7933	6638	14
H(17B)	-1118	7983	5816	14
H(18A)	-200	8397	4365	19
H(18B)	-694	7621	4523	19

H(18C)	981	7774	4285	19

References

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