Supporting Information

Janus POCOP Pincer Complexes of Nickel

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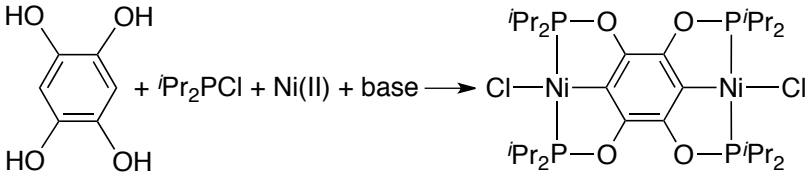
Table S1. Optimization of the one-pot synthesis of **Ni_2Cl_2**[a]

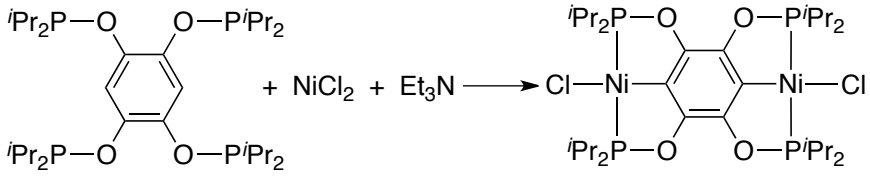


Ni_2Cl_2

Ni(II)	Base	Solvent	Temp (°C)	Time (h)	Heating Method	Isolate Yield (%)
$NiCl_2$	Et_3N	toluene	135	24	oil bath	21
$NiCl_2$	Et_3N	toluene	137	16	oil bath	<1
$NiCl_2$•DME	Et_3N	toluene	135	24	oil bath	13
$NiCl_2$	Et_3N	*o*-xylene	175	24	oil bath	32
$NiCl_2$	Et_3N	*o*-xylene	200	24	Al heating block	6
$NiCl_2$	Et_3N	*o*-xylene	220	24	Al heating block	33
$NiCl_2$	Et_3N	*o*-xylene	250	24	Al heating block	57, 28, 23, 4
$NiCl_2$	NaH	*o*-xylene	250	24	Al heating block	41
$NiCl_2$	Et_3N	toluene	100	1	microwave	1, 1
$NiCl_2$	Et_3N	toluene	150	1	microwave	85, 82
$NiCl_2$	Et_3N	toluene	200	1	microwave	71
$NiCl_2$	Et_3N	*o*-xylene	150	1	microwave	83, 73
$NiCl_2$	Et_3N	*o*-xylene	200	1	microwave	70, 63
$NiCl_2$	Et_3N	*o*-xylene	250	3	microwave	12

[a]Reaction conditions: 1,2,4,5-$(HO)_4C_6H_2$ (0.50 mmol), $^iPr_2PCl$ (2.0 mmol), $NiCl_2$ (1.0 mmol) and Et_3N (12.0 mmol) in 2 mL (for microwave reactions) or 20 mL (for other reactions) of solvent.

Table S2. Optimization of the stepwise synthesis of **Ni_2Cl_2**[a]

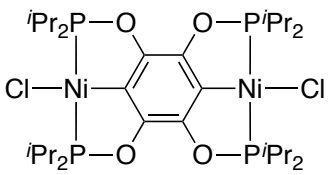
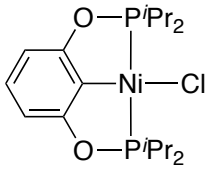


Ni_2Cl_2

Solvent	Temp (°C)	Time (h)	Heating Method	Isolate Yield (%)
o-xylene	250	24	Al heating block	87, 76
o-xylene	250	1	Al heating block	86, 75
o-xylene	175	24	Al heating block	89, 71
o-xylene	175	1	Al heating block	69, 66
o-xylene	150	24	Al heating block	68, 52
toluene	135	24	Al heating block	34, 20

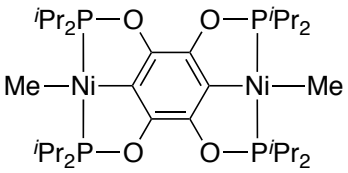
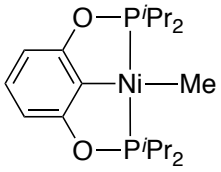
[a]Reaction conditions: 1,2,4,5-$(^iPr_2PO)_4C_6H_2$ (0.5 mmol), $NiCl_2$ (1.0 mmol) and Et_3N (1.0 mmol) in 20 mL of solvent.

Table S3. Comparison of spectroscopic and crystallographic data of {2,3,5,6-(^{i}Pr$_2$PO)$_4$C$_6$}Ni$_2$Cl$_2$ (**Ni$_2$Cl$_2$**) and {2,6-(^{i}Pr$_2$PO)$_2$C$_6$H$_3$}NiCl (**NiCl**)[a]

				
^{1}H NMR (400 MHz, $CDCl_3$, δ)				
PC*H*(CH$_3$)$_2$	2.45-2.35 (m)			2.42 (m)
PCH(C*H*$_3$)$_2$	1.44-1.38 (m), 1.36-1.31 (m)			1.43 (dt, J = 7.2 and 7.4 Hz) 1.34 (dt, J = 7.0 and 7.1 Hz)
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ)				
ortho-Ar*C*	146.33-145.99 (m)			168.97 (t, $J_{P\text{-}C}$ = 10.0 Hz)
ipso-Ar*C*	127.58 (t, $J_{P\text{-}C}$ = 20.9 Hz)			125.20 (t, $J_{P\text{-}C}$ = 21.5 Hz)
P*C*H(CH$_3$)$_2$	28.00 (t, $J_{P\text{-}C}$ = 11.2 Hz)			27.84 (t, $J_{P\text{-}C}$ = 11.1 Hz)
PCH(*C*H$_3$)$_2$	17.76 (s), 16.99 (s)			17.57 (s), 16.79 (s)
^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, δ)				
	185.18 (s)			185.50 (s)
X-Ray Crystallographic Data				
	Structure 1[b]	***Structure 2***[c]		
		Molecule 1	***Molecule 2***	
Ni–P	2.1522(7)	2.1546(7)	2.1618(7)	2.1582(6)
	2.1594(7)	2.1631(7)	2.1650(7)	2.1603(6)
Ni–C$_{ipso}$	1.883(2)	1.880(2)	1.881(2)	1.879(2)
Ni–Cl	2.1918(7)	2.1889(6)	2.1980(6)	2.1944(6)
P–Ni–P	165.28(3)	164.97(2)	164.78(2)	164.01(3)
C$_{ipso}$–Ni–Cl	178.30(8)	178.96(7)	178.10(7)	178.31(6)

[a]Characterization data of **NiCl** were obtained from a previous report.[1]
[b]Crystals were grown from toluene, and the complex co-crystallized with two toluene molecules.
[c]Crystals were grown from CH_2Cl_2 or CH_2Cl_2-pentane. Two independent molecules were found in the crystalline lattice, which are labeled here as Molecules 1 and 2.

Table S4. Comparison of spectroscopic and crystallographic data of {2,3,5,6-(^{i}Pr$_2$PO)$_4$C$_6$}Ni$_2$Me$_2$ (**Ni$_2$Me$_2$**) and {2,6-(^{i}Pr$_2$PO)$_2$C$_6$H$_3$}NiMe (**NiMe**)[a]

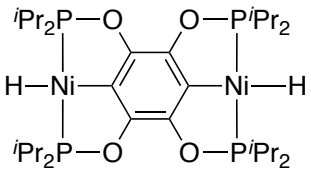
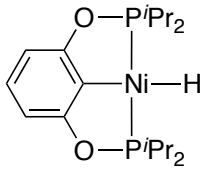
			
^{1}H NMR (400 MHz, δ)[b]			
PC*H*(CH$_3$)$_2$	2.16-2.11 (m)	2.37 (m)	
PCH(C*H*$_3$)$_2$	1.24-1.16 (m)	1.29-1.22 (m)	
NiC*H*$_3$	–0.24 (t, $J_{P\text{-}H}$ = 8.6 Hz)	–0.63 (t, $J_{P\text{-}H}$ = 8.7 Hz)	
^{13}C{^{1}H} NMR (101 MHz, δ)[b]			
ortho-Ar*C*	145.10-144.76 (m)	167.62 (t, $J_{P\text{-}C}$ = 19.2 Hz)	
ipso-Ar*C*	143.41 (t, $J_{P\text{-}C}$ = 18.3 Hz)	139.79 (t, $J_{P\text{-}C}$ = 20.9 Hz)	
P*C*H(CH$_3$)$_2$	28.21 (t, $J_{P\text{-}C}$ = 11.2 Hz)	27.98 (t, $J_{P\text{-}C}$ = 11.0 Hz)	
PCH(*C*H$_3$)$_2$	18.02 (s), 17.39 (s)	17.85 (s), 17.15 (s)	
Ni*C*H$_3$	–20.23 (t, $J_{P\text{-}C}$ = 18.9 Hz)	–21.38 (t, $J_{P\text{-}C}$ = 18.2 Hz)	
^{31}P{^{1}H} NMR (162 MHz, C$_6$D$_6$, δ)			
	189.74 (s)	191.87 (s)	
X-ray Crystallographic Data			
		Molecule 1[c]	***Molecule 2***[c]
Ni–P	2.1225(5)	2.1158(4)	2.1306(4)
	2.1310(5)	2.1287(4)	2.1322(4)
Ni–C$_{ipso}$	1.9049(18)	1.901(2)	1.903(2)
Ni–CH$_3$	1.9885(19)	1.994(2)	1.997(2)
P–Ni–P	164.91(2)	164.28(2)	163.31(2)
C$_{ipso}$–Ni–CH$_3$	176.85(9)	179.07(6)	177.67(7)

[a]Characterization data of **NiMe** were obtained from a previous report.[1]

[b]The ^{1}H and ^{13}C{^{1}H} NMR data of **Ni$_2$Me$_2$** were recorded in C$_6$D$_6$, whereas the ^{1}H and ^{13}C{^{1}H} data of **NiMe** were recorded in CDCl$_3$.

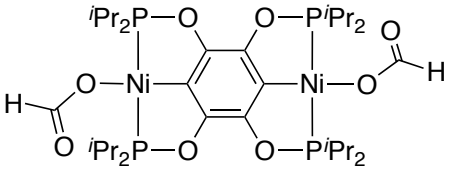
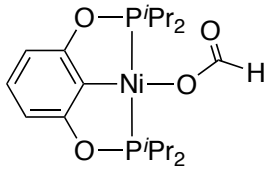
[c]Two independent molecules were found in the crystalline lattice, which are labeled here as Molecules 1 and 2.

Table S5. Comparison of spectroscopic and crystallographic data of {2,3,5,6-(^{i}Pr$_2$PO)$_4$C$_6$}Ni$_2$H$_2$ (**Ni$_2$H$_2$**) and {2,6-(^{i}Pr$_2$PO)$_2$C$_6$H$_3$}NiH (**NiH**)

			
^{1}H NMR (400 MHz, C$_6$D$_6$, δ)			
PC*H*(CH$_3$)$_2$	2.18-2.12 (m)	2.15-2.09 (m)	
PCH(C*H*$_3$)$_2$	1.25-1.17 (m)	1.19-1.09 (m)	
Ni*H*	– 8.25 (t, $J_{P\text{-}H}$ = 55.6 Hz)	– 7.90 (t, $J_{P\text{-}H}$ = 54.0 Hz)	
^{13}C{^{1}H} NMR (101 MHz, C$_6$D$_6$, δ)			
ortho-Ar*C*	145.11-144.77 (m)	168.22 (t, $J_{P\text{-}C}$ = 10.6 Hz)	
ipso-Ar*C*	146.66 (t, $J_{P\text{-}C}$ = 16.8 Hz)	141.75 (t, $J_{P\text{-}C}$ = 17.2 Hz)	
P*C*H(CH$_3$)$_2$	28.97 (t, $J_{P\text{-}C}$ = 12.9 Hz)	28.78 (t, $J_{P\text{-}C}$ = 12.6 Hz)	
PCH(*C*H$_3$)$_2$	19.01 (t, $J_{P\text{-}C}$ = 3.4 Hz), 17.77 (s)	18.76 (t, $J_{P\text{-}C}$ = 3.5 Hz), 17.42 (s)	
^{31}P{^{1}H} NMR (162 MHz, C$_6$D$_6$, δ)			
	205.70 (s)	207.49 (s)	
ATR-IR (solid, cm^{-1})			
ν_{NiH}	1780	1773	
X-ray Crystallographic Data			
		Molecule 1[a]	***Molecule 2***[a]
Ni–P	2.1144(4)	2.1090(5)	2.1103(5)
	2.1149(4)	2.1097(5)	2.1119(5)
Ni–C$_{ipso}$	1.8962(12)	1.8938(18)	1.8921(18)
Ni–H	1.672(15)	1.54(3)	1.47(3)
P–Ni–P	165.983(15)	165.85(2)	166.12(2)
C$_{ipso}$–Ni–H	172.4(5)	178.5(12)	178.9(11)

[a]Two independent molecules were found in the crystalline lattice, which are labeled here as Molecules 1 and 2.

Table S6. Comparison of spectroscopic and crystallographic data of {2,3,5,6-(^{i}Pr$_2$PO)$_4$C$_6$}Ni$_2$(OCHO)$_2$ (**Ni$_2$(OCHO)$_2$**) and {2,6-(^{i}Pr$_2$PO)$_2$C$_6$H$_3$}NiOCHO (**NiOCHO**)[a]

			
^{1}H NMR (400 MHz, C$_6$D$_6$, δ)			
NiOC*H*O	8.31 (t, J_{P-H} = 3.2 Hz)		8.35 (br)
PC*H*(CH$_3$)$_2$	2.30-2.23 (m)		2.32-2.26 (m)
PCH(C*H*$_3$)$_2$	1.37-1.31 (m), 1.26-1.21 (m)		1.36-1.30 (m), 1.21-1.16 (m)
^{13}C{^{1}H} NMR (101 MHz, C$_6$D$_6$, δ)			
NiO*C*HO	166.97 (s)		166.96 (t, J_{P-C} = 3.0 Hz)
ortho-Ar*C*	146.97-146.65 (m)		169.94 (t, J_{P-C} = 10.1 Hz)
ipso-Ar*C*	124.84 (t, J_{P-C} = 22.2 Hz)		122.24 (t, J_{P-C} = 22.7 Hz)
P*C*H(CH$_3$)$_2$	28.99 (t, J_{P-C} = 11.2 Hz)		28.91 (t, J_{P-C} = 11.0 Hz)
PCH(*C*H$_3$)$_2$	17.95 (s), 17.03 (s)		17.87 (t, J_{P-C} = 3.4 Hz), 16.91 (s)
^{31}P{^{1}H} NMR (162 MHz, C$_6$D$_6$, δ)			
	184.36 (s)		184.25 (s)
ATR-IR (solid, cm^{-1})			
ν_{OCO}	1624 (ν_{asym}), 1607 (ν_{asym}) 1305 (ν_{sym}), 1291 (ν_{sym})		1605 (ν_{asym}) 1289 (ν_{asym})
Transmission-IR (in C$_6$H$_6$, cm^{-1})			
ν_{OCO}	1625 (ν_{asym}), 1300 (ν_{sym})		1625 (ν_{asym}), 1304 (ν_{sym})
X-ray Crystallographic Data			
	Molecule 1[b,c]	***Molecule 2***[b]	
Ni–P	2.1668(7)	2.1587(7)	2.1641(7)
	2.1795(7)	2.1779(7)	2.1927(7)
Ni–C$_{ipso}$	1.885(2)	1.885(2)	1.883(2)
Ni–O	1.9120(18)	1.9089(19)	1.9135(17)
P–Ni–P	164.32(3)	164.13(3)	164.31(3)
C$_{ipso}$–Ni–O	172.65(9)	170.29(10)	174.39(8)

[a]Crystallographic data of **Ni(OCHO)** were obtained from a previous report.[2]

[b]Two independent molecules were found in the crystalline lattice, which are labeled here as Molecules 1 and 2.

[c]In Molecule 1, the OCHO groups form hydrogen bonds with the co-crystallized MeOH molecules.

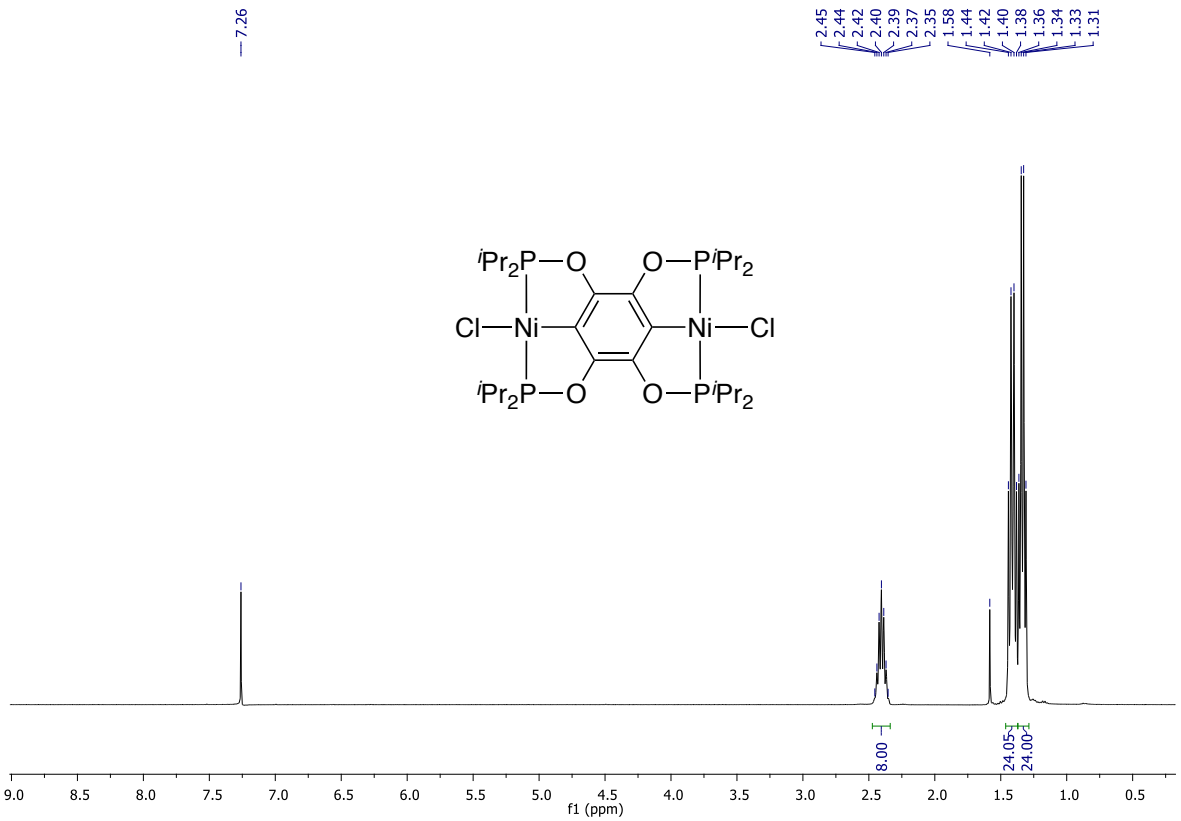


Figure S1. ^{1}H NMR of {2,3,5,6-(^{i}Pr$_2$PO)$_4$C$_6$}Ni$_2$Cl$_2$ (**Ni$_2$Cl$_2$**) in CDCl$_3$

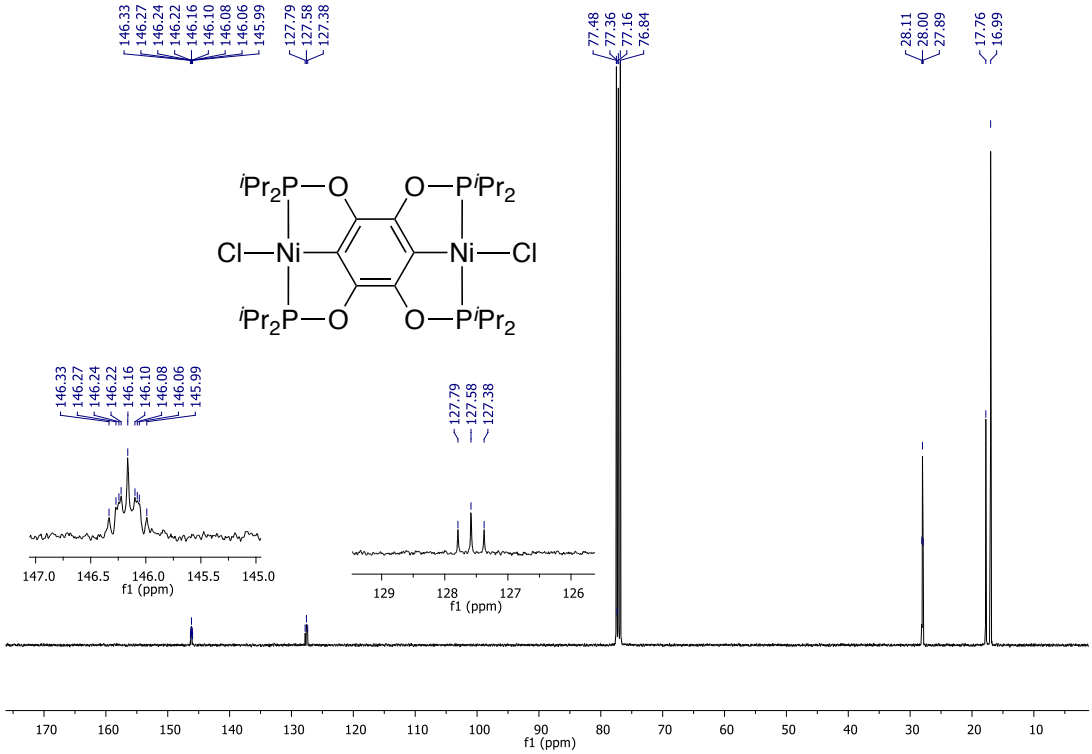


Figure S2. ^{13}C{^{1}H} NMR of {2,3,5,6-(^{i}Pr$_2$PO)$_4$C$_6$}Ni$_2$Cl$_2$ (**Ni$_2$Cl$_2$**) in CDCl$_3$

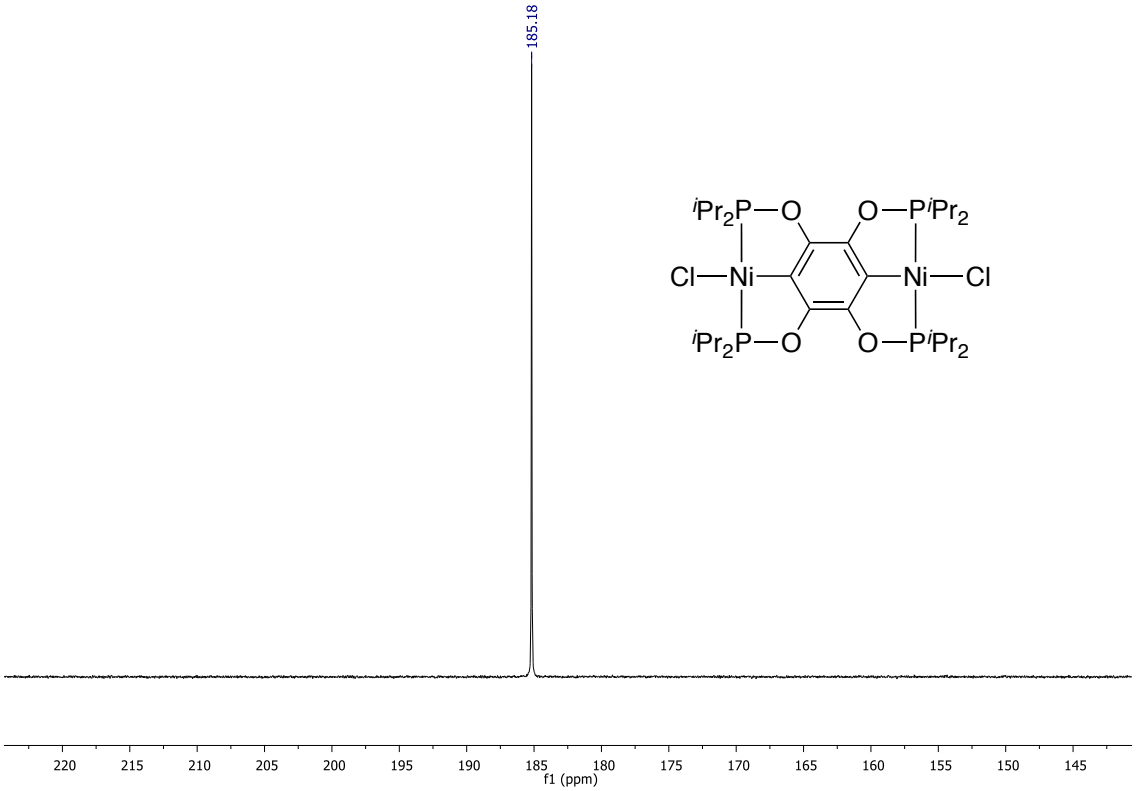


Figure S3. $^{31}P\{^{1}H\}$ NMR of $\{2,3,5,6\text{-}(^{i}Pr_2PO)_4C_6\}Ni_2Cl_2$ (**Ni_2Cl_2**) in $CDCl_3$

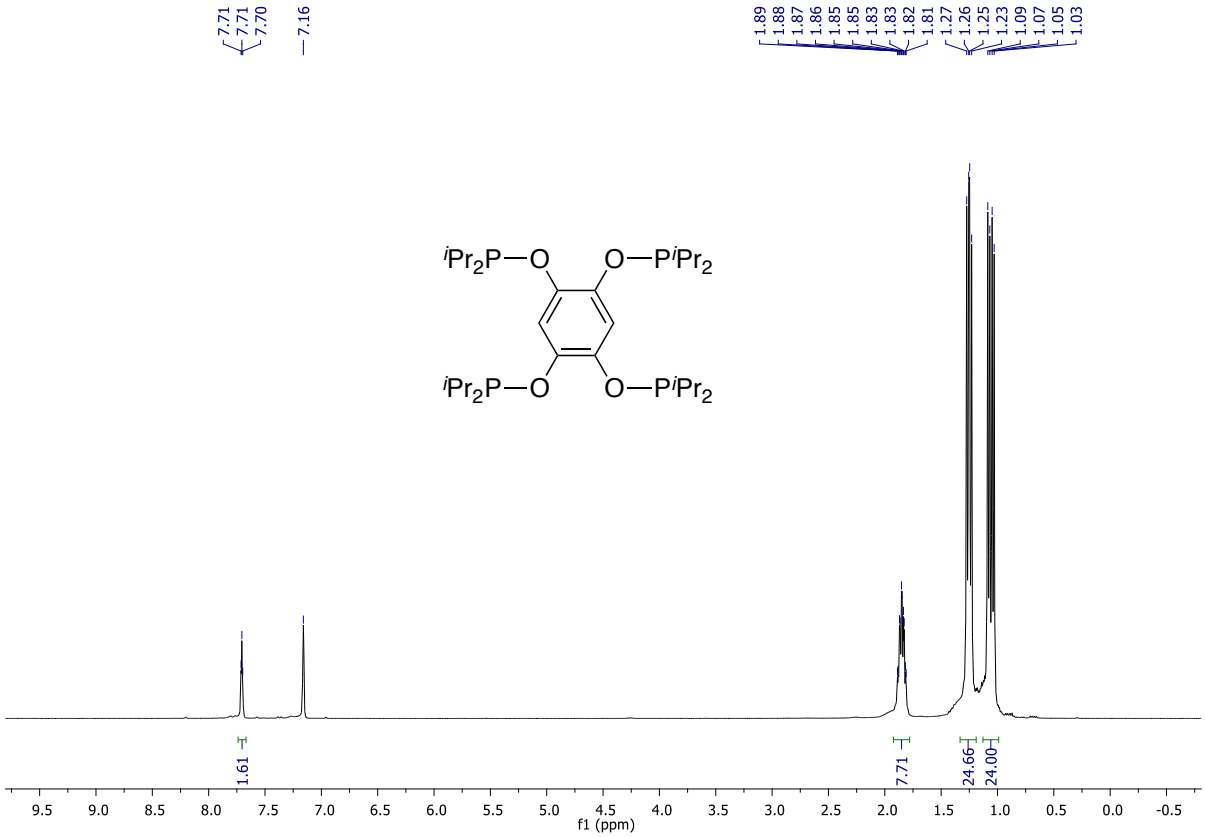


Figure S4. ^{1}H NMR of 1,2,4,5-$(^{i}Pr_2PO)_4C_6H_2$ in C_6D_6

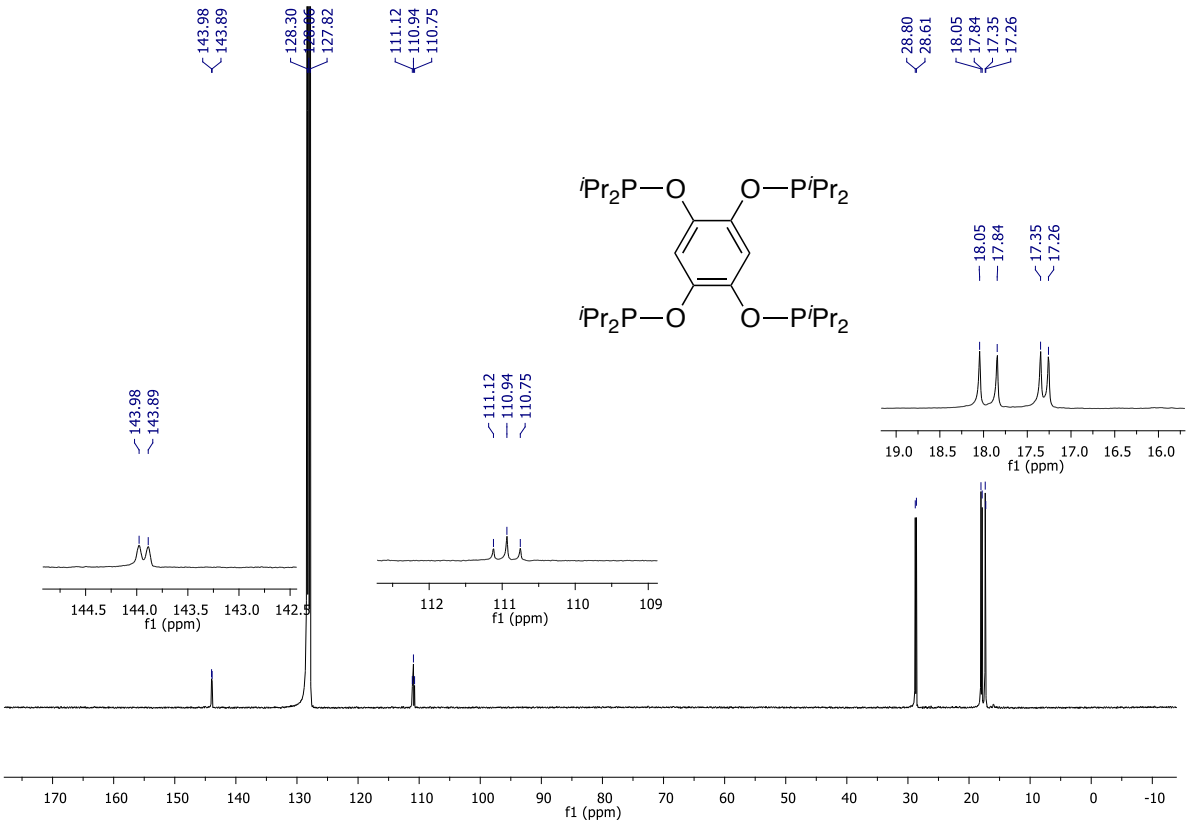


Figure S5. $^{13}C\{^{1}H\}$ NMR of 1,2,4,5-($^{i}Pr_2PO)_4C_6H_2$ in C_6D_6

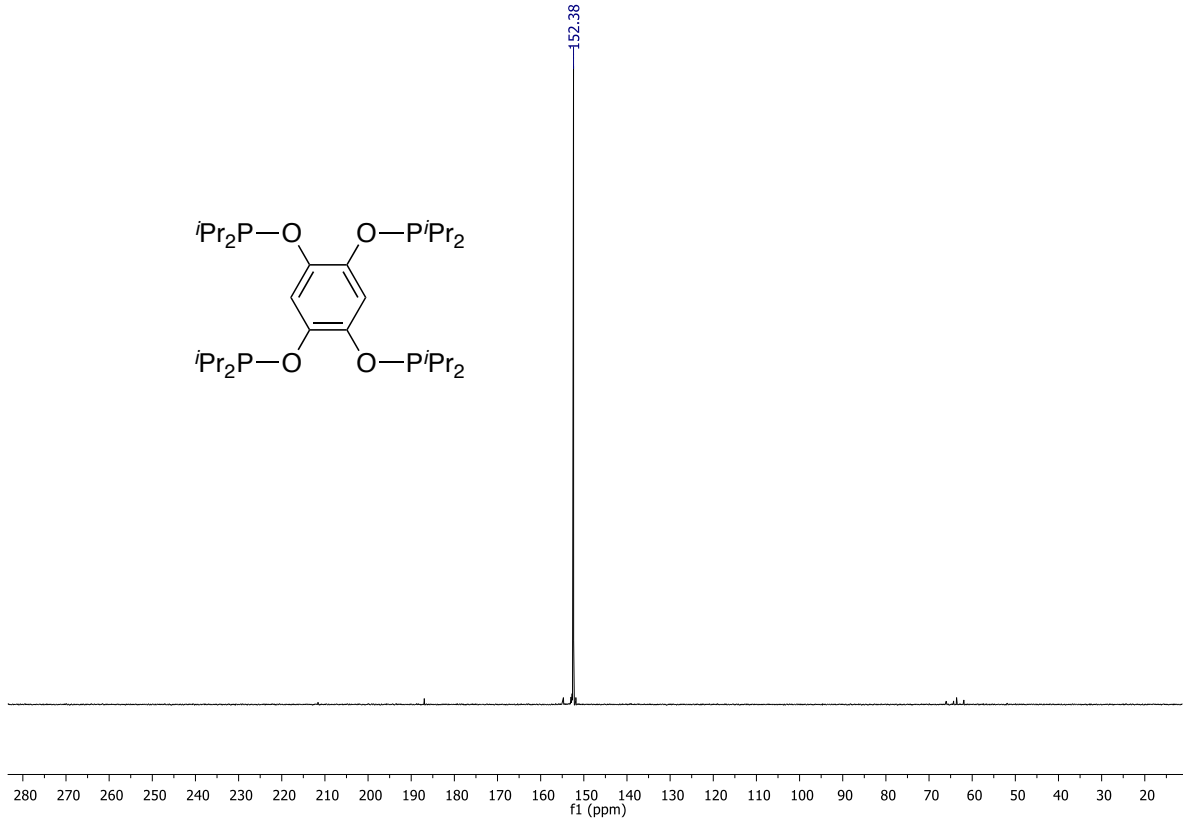


Figure S6. $^{31}P\{^{1}H\}$ NMR of 1,2,4,5-($^{i}Pr_2PO)_4C_6H_2$ in C_6D_6

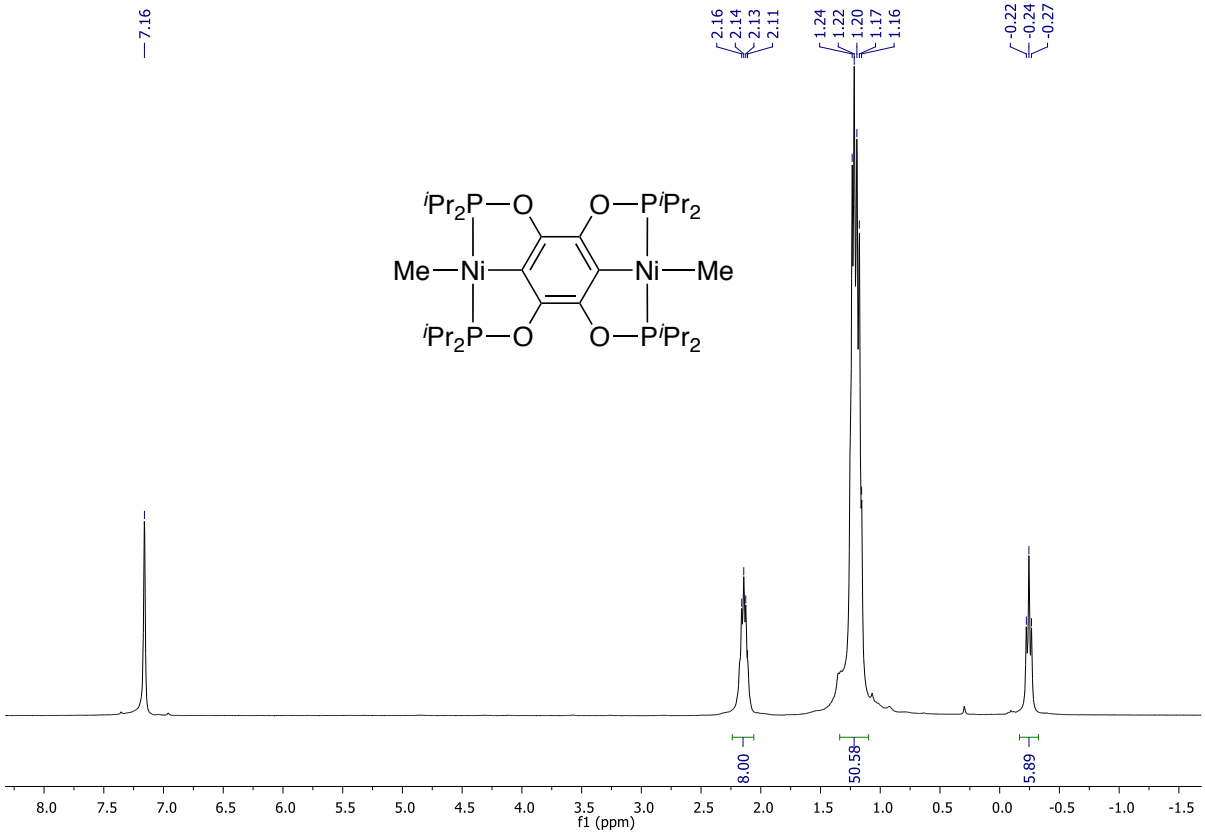


Figure S7. ^{1}H NMR of {2,3,5,6-(^{i}Pr$_2$PO)$_4$C$_6$}Ni$_2$Me$_2$ (**Ni$_2$Me$_2$**) in C$_6$D$_6$

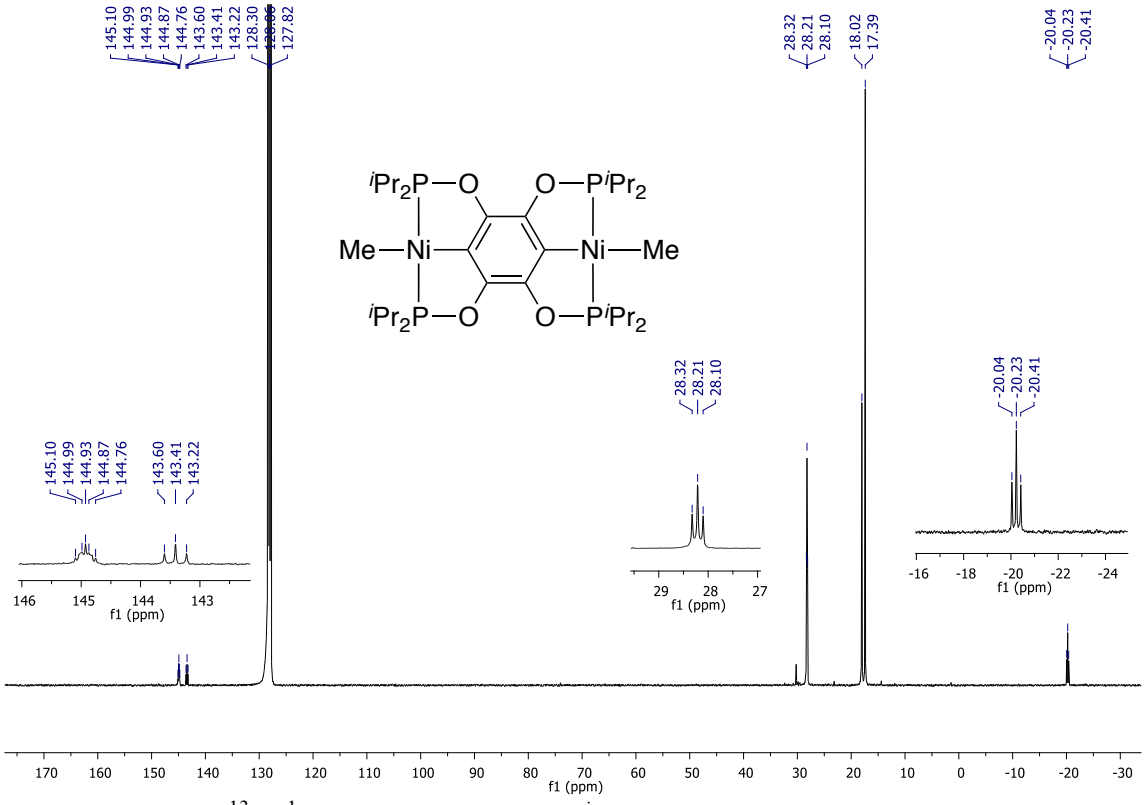


Figure S8. ^{13}C{^{1}H} NMR of {2,3,5,6-(^{i}Pr$_2$PO)$_4$C$_6$}Ni$_2$Me$_2$ (**Ni$_2$Me$_2$**) in C$_6$D$_6$

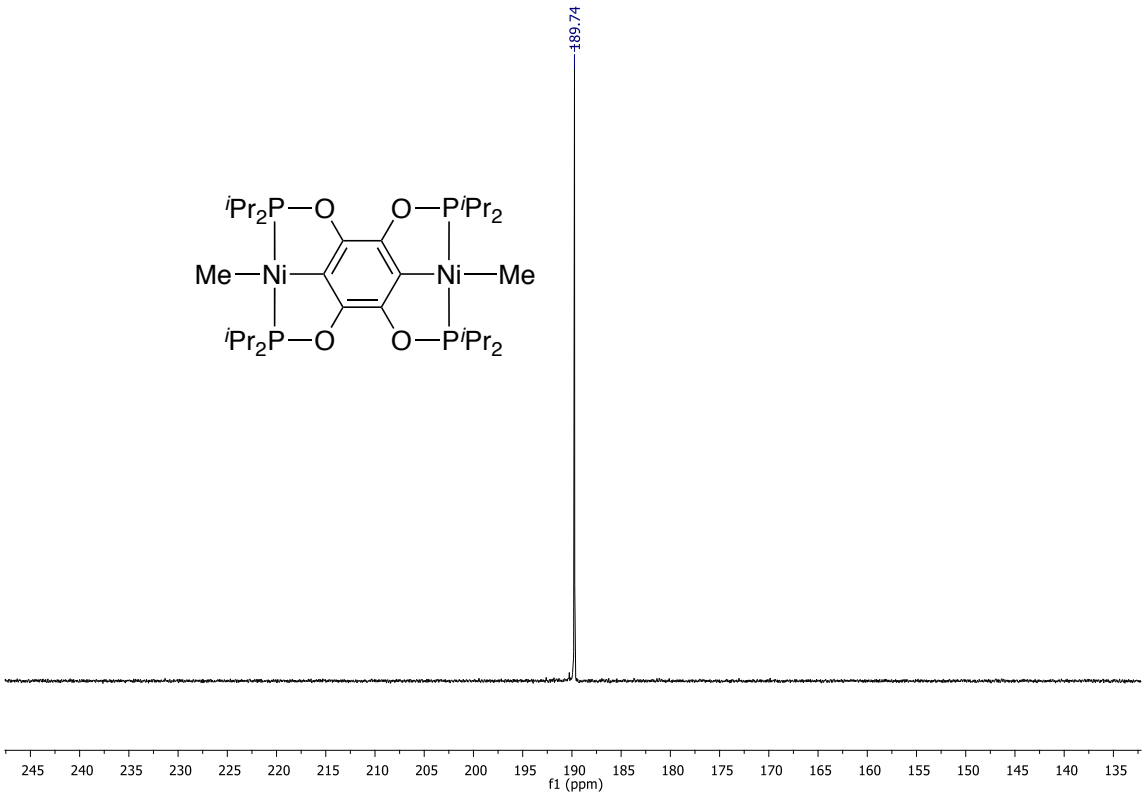


Figure S9. $^{31}P\{^{1}H\}$ NMR of {2,3,5,6-($^{i}Pr_2PO)_4C_6$}Ni_2Me_2 (**Ni_2Me_2**) in C_6D_6

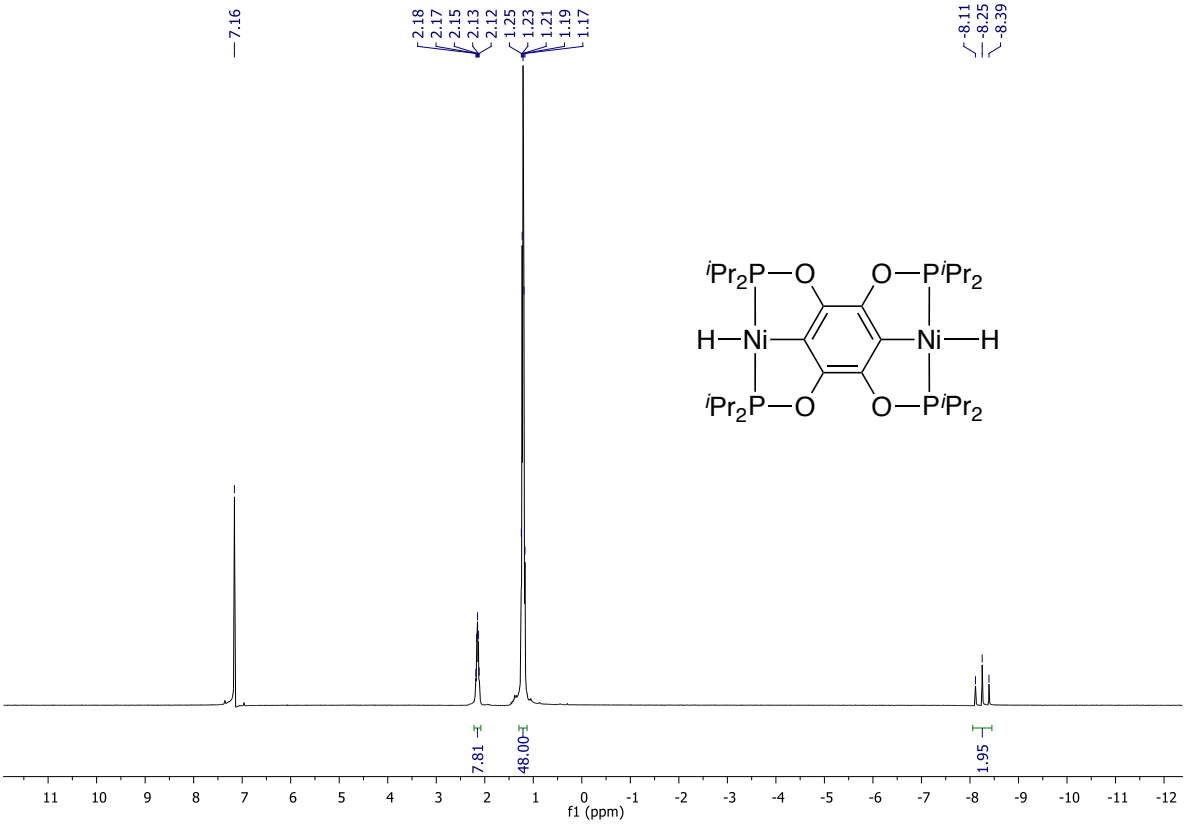


Figure S10. ^{1}H NMR of {2,3,5,6-($^{i}Pr_2PO)_4C_6$}Ni_2H_2 (**Ni_2H_2**) in C_6D_6

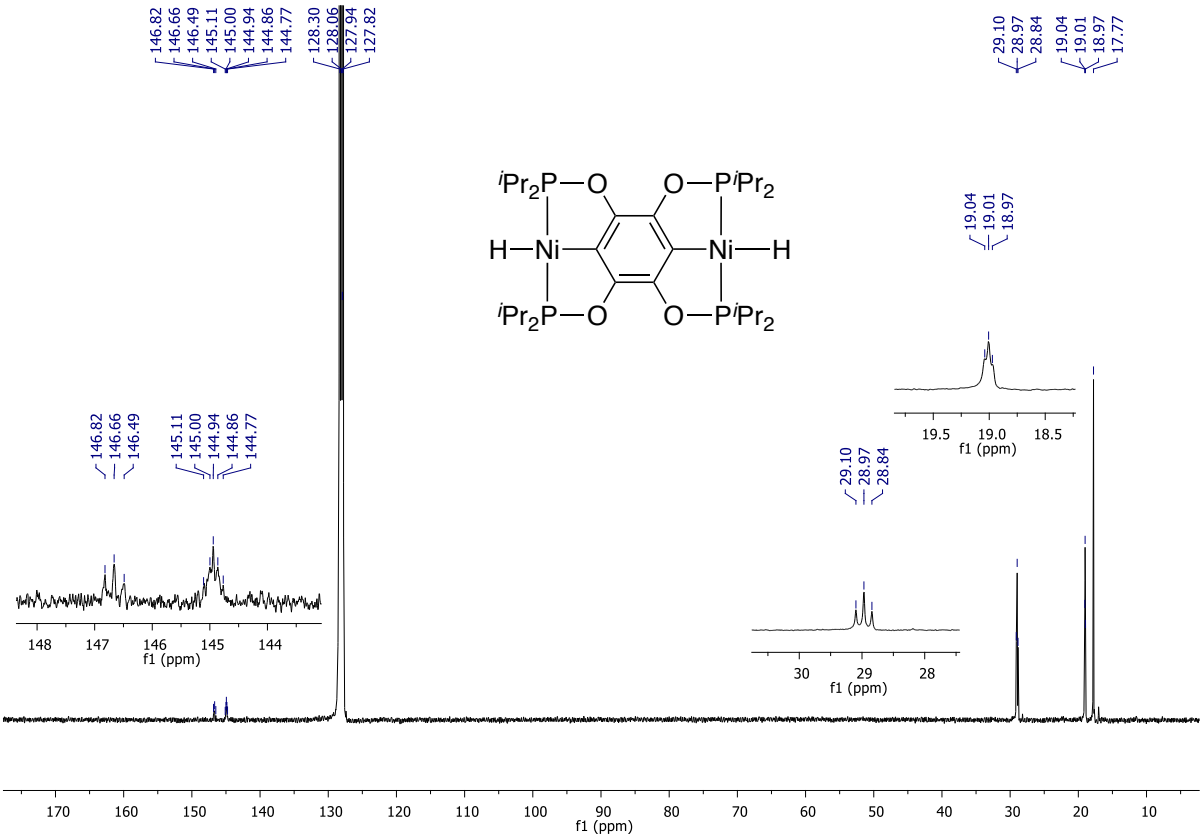


Figure S11. $^{13}C\{^{1}H\}$ NMR of {2,3,5,6-($^{i}Pr_2PO)_4C_6$}Ni_2H_2 (**Ni_2H_2**) in C_6D_6

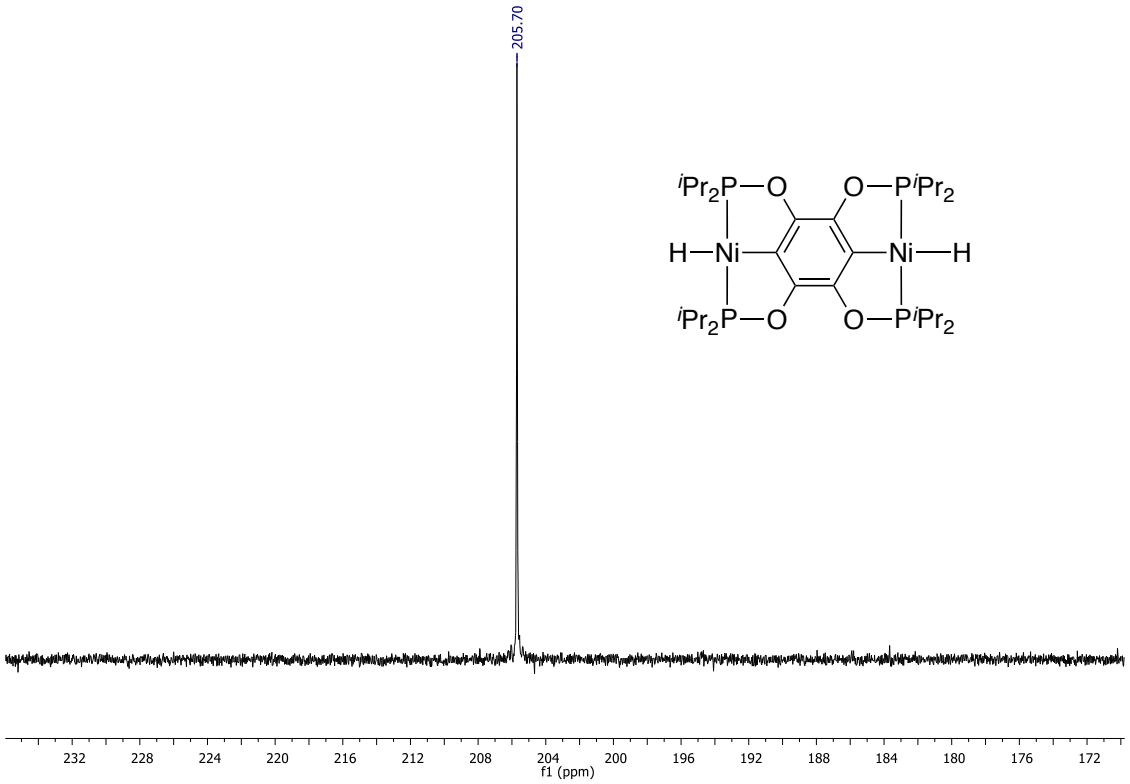


Figure S12. $^{31}P\{^{1}H\}$ NMR of {2,3,5,6-($^{i}Pr_2PO)_4C_6$}Ni_2H_2 (**Ni_2H_2**) in C_6D_6

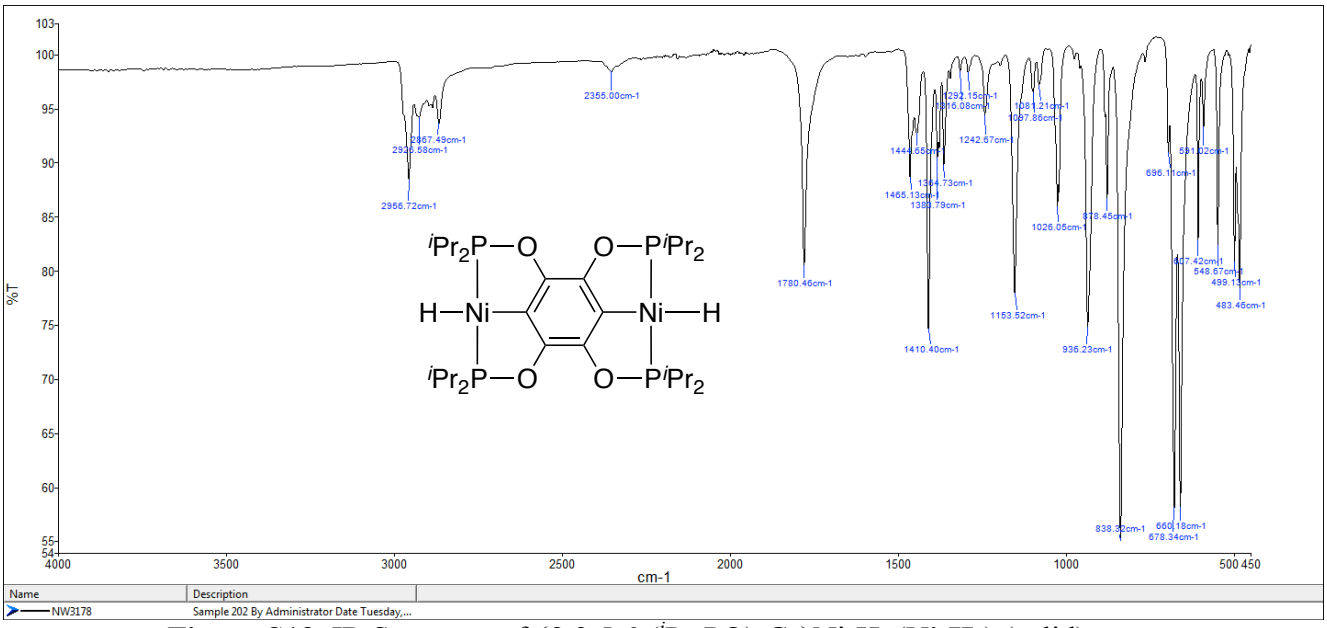


Figure S13. IR Spectrum of {2,3,5,6-(^{i}Pr$_2$PO)$_4$C$_6$}Ni$_2$H$_2$ (**Ni$_2$H$_2$**) (solid)

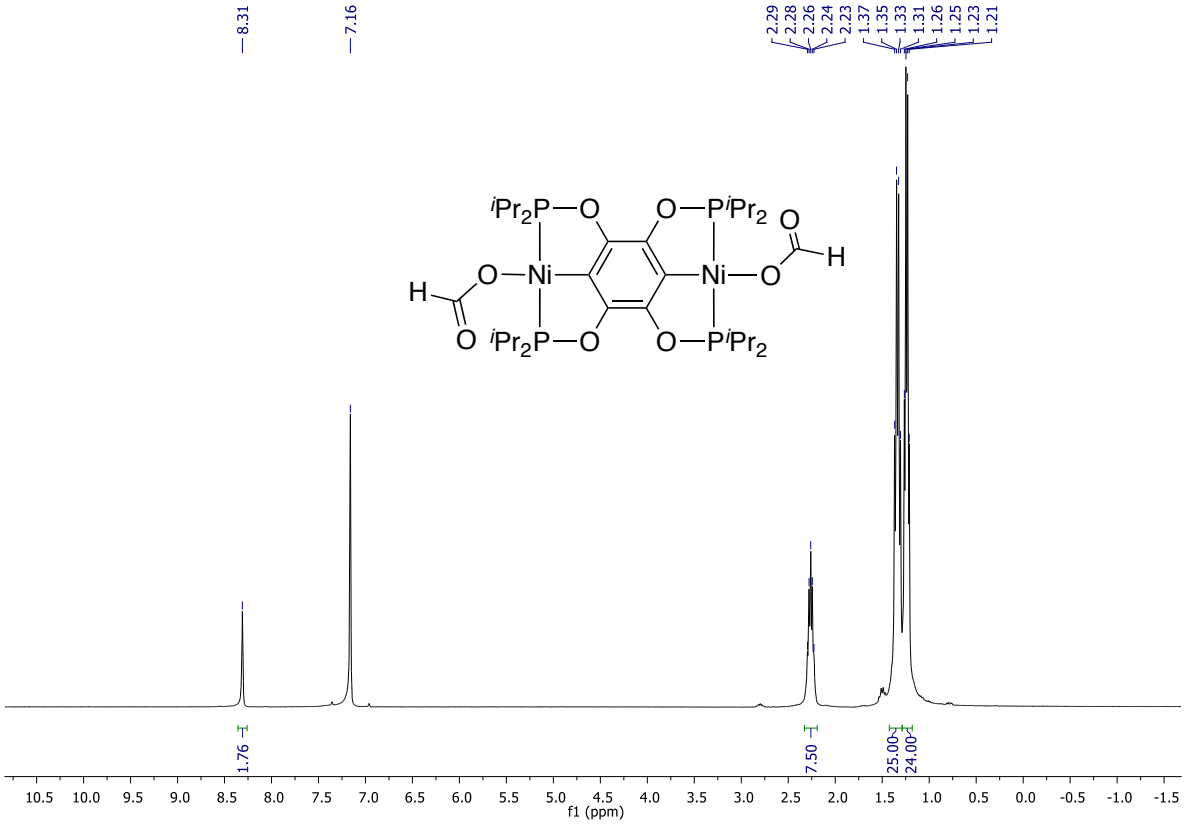


Figure S14. ^{1}H NMR of {2,3,5,6-(^{i}Pr$_2$PO)$_4$C$_6$}Ni$_2$(OCHO)$_2$ (**Ni$_2$(OCHO)$_2$**) in C$_6$D$_6$

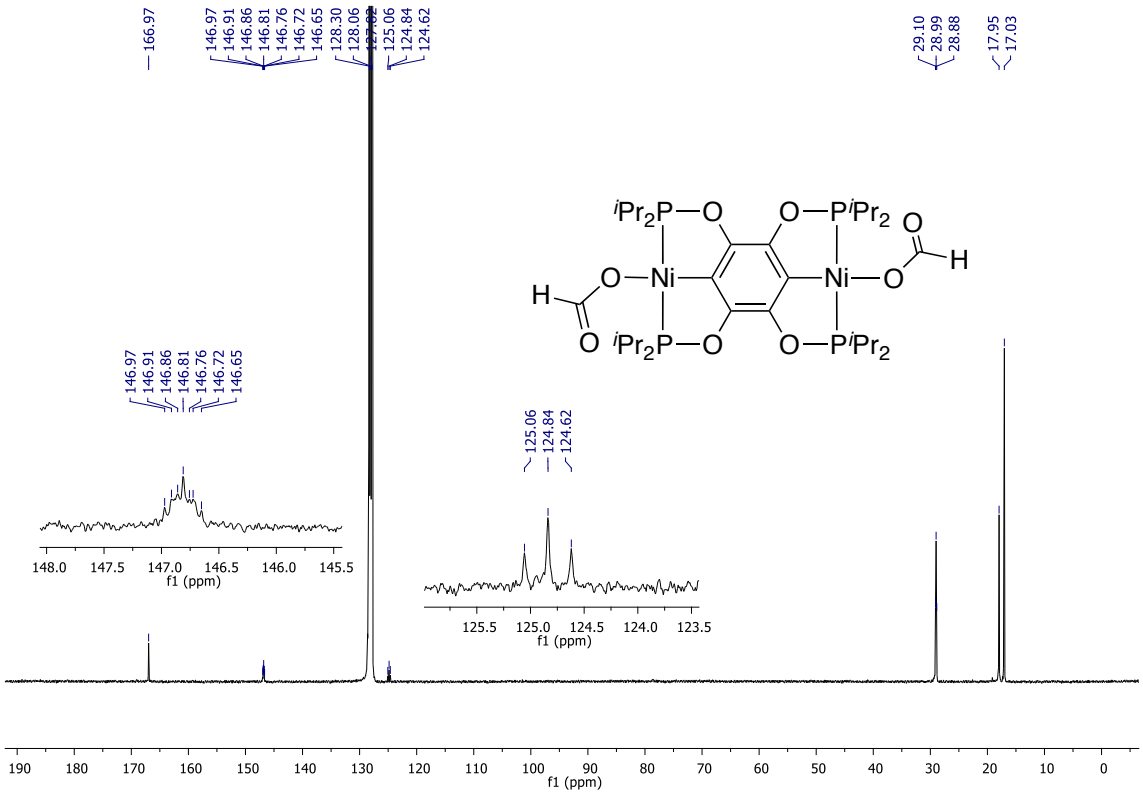


Figure S15. $^{13}C\{^{1}H\}$ NMR of {2,3,5,6-($^{i}Pr_2PO)_4C_6$}$Ni_2(OCHO)_2$ (**$Ni_2(OCHO)_2$**) in C_6D_6

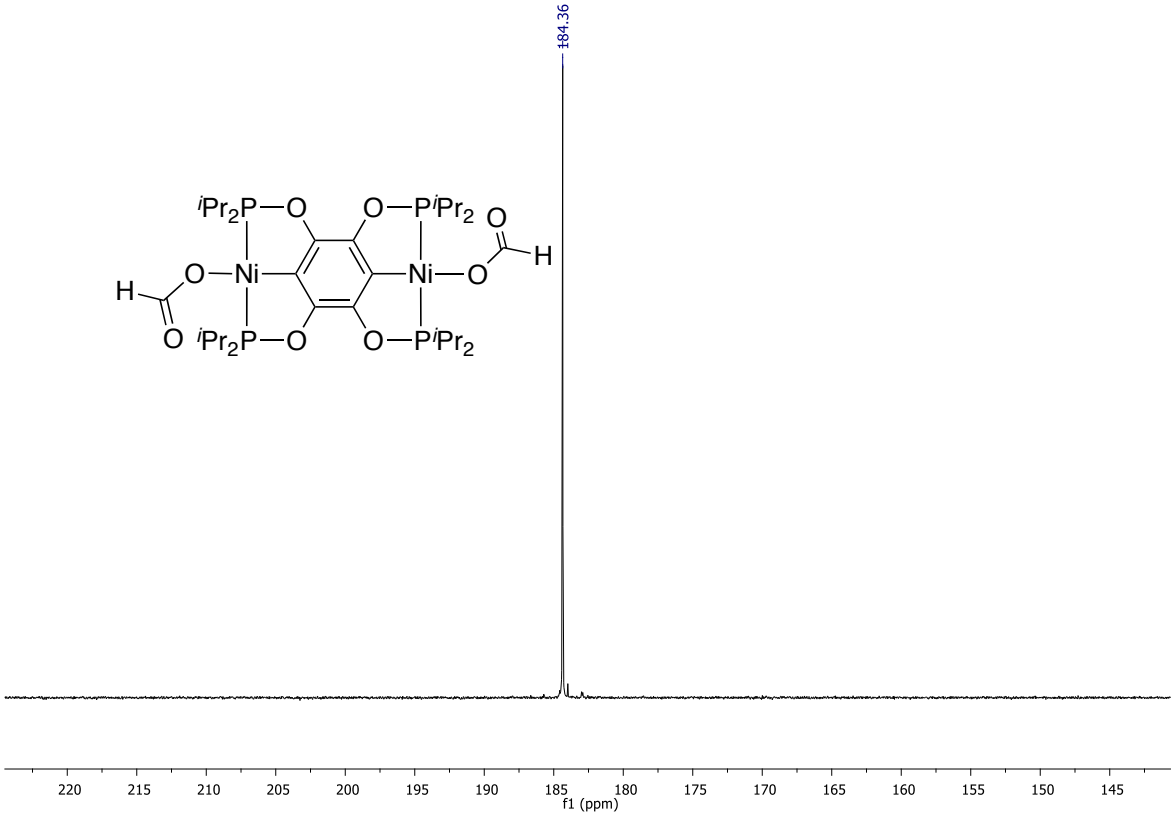


Figure S16. $^{31}P\{^{1}H\}$ NMR of {2,3,5,6-($^{i}Pr_2PO)_4C_6$}$Ni_2(OCHO)_2$ (**$Ni_2(OCHO)_2$**) in C_6D_6

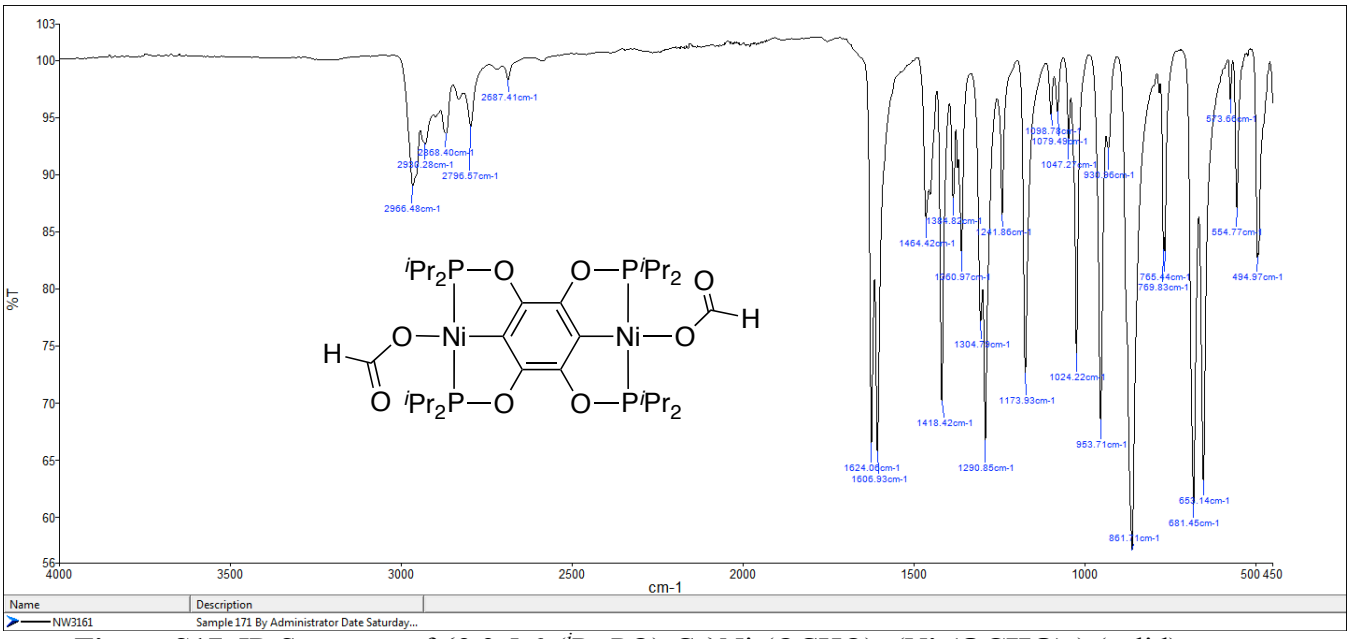


Figure S17. IR Spectrum of {2,3,5,6-(^{i}Pr$_2$PO)$_4$C$_6$}Ni$_2$(OCHO)$_2$ (**Ni$_2$(OCHO)$_2$**) (solid)

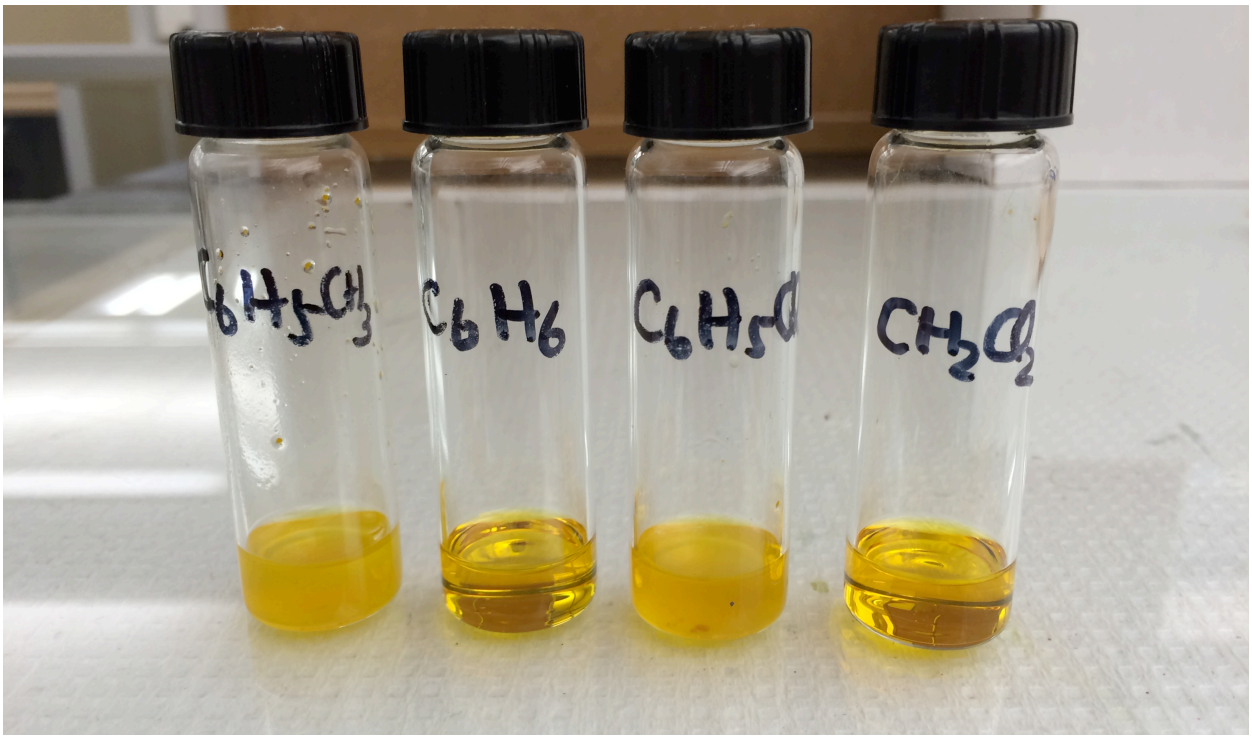
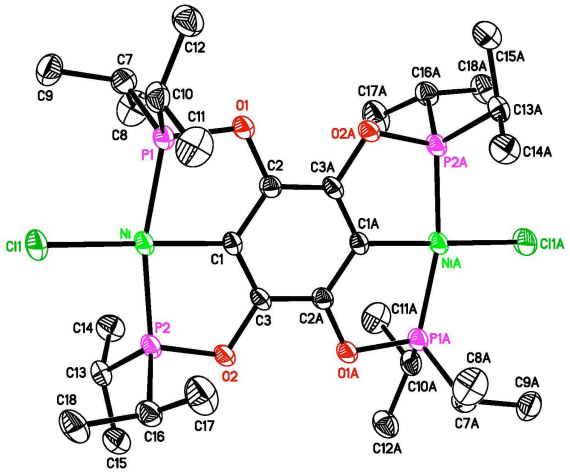


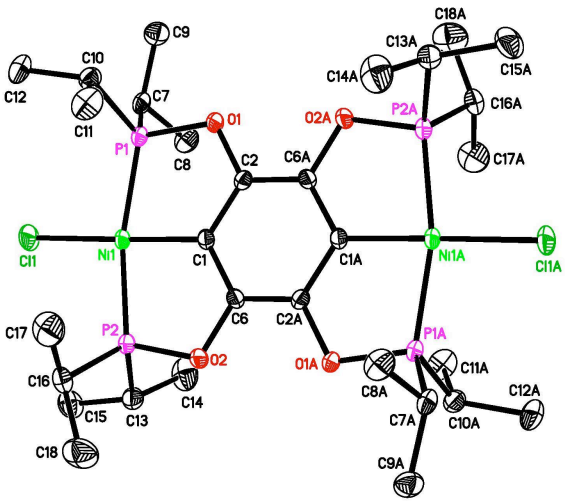
Figure S18. Solubility test for {2,3,5,6-(^{i}Pr$_2$PO)$_4$C$_6$}Ni$_2$Cl$_2$ (**Ni$_2$Cl$_2$**) (10 mg in 1.0 mL of solvent)

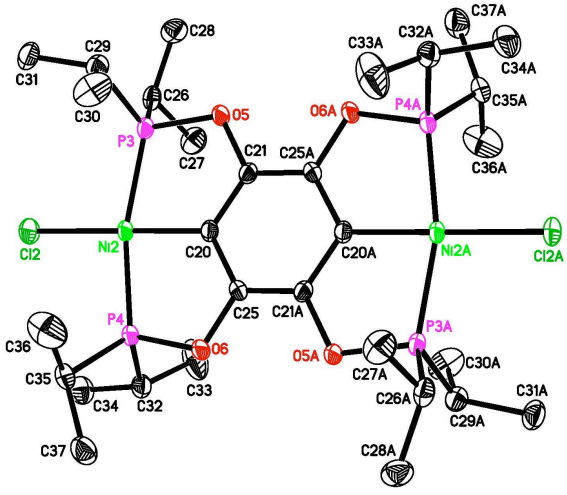
Figure S19. ORTEP drawings of structures determined by X-ray crystallography

(A) $Ni_2Cl_2 \cdot 2C_7H_8$

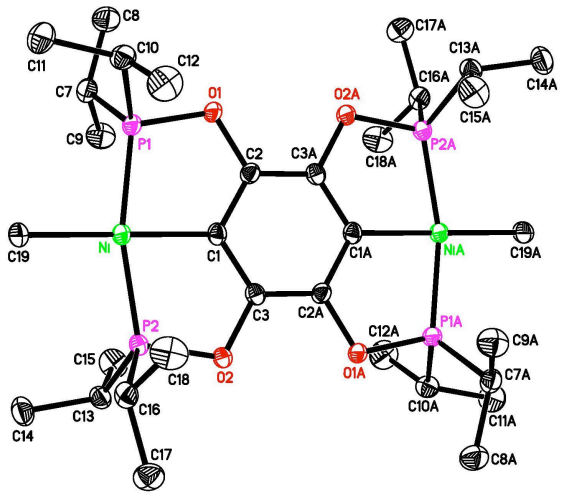


(B) Ni_2Cl_2 (2 independent molecules)

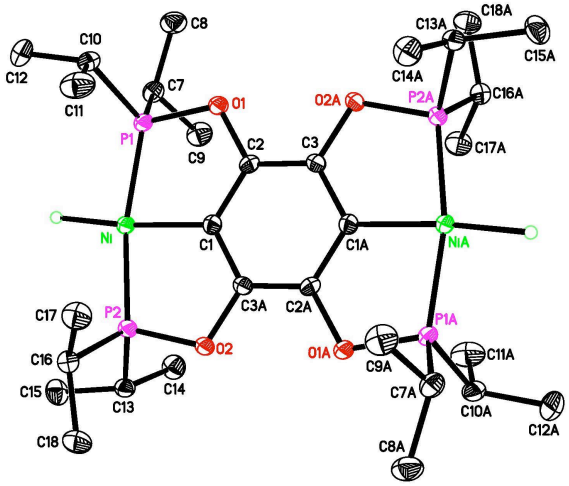




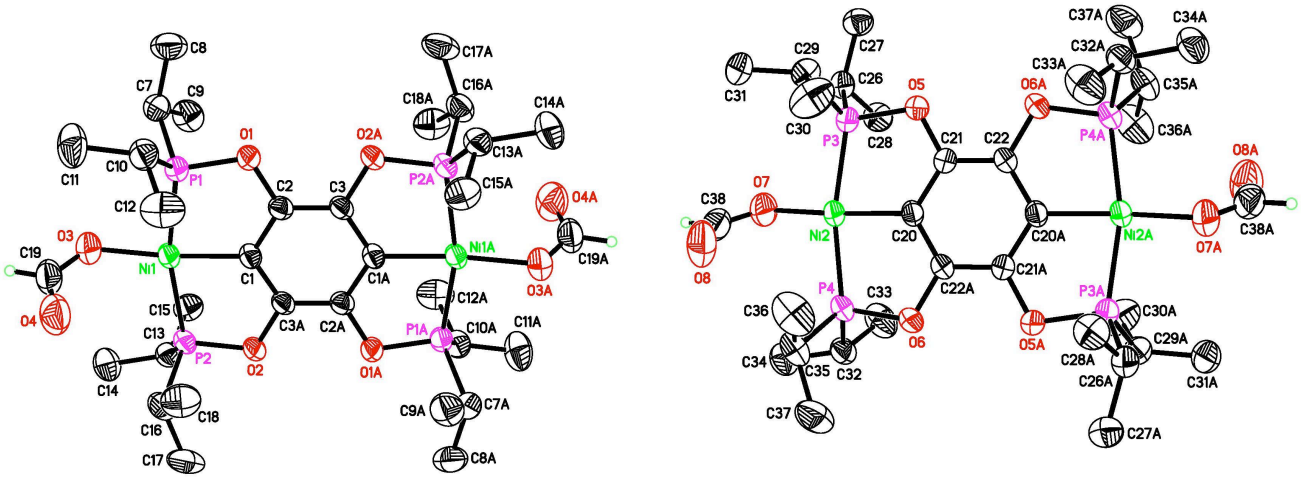
(C) Ni_2Me_2•$2H_2O$



(D) Ni_2H_2



(E) $\mathbf{Ni_2(OCHO)_2}$•3/2MeOH (2 independent molecules)



(F) **NiH**•1/2C_4H_8O (2 independent molecules)

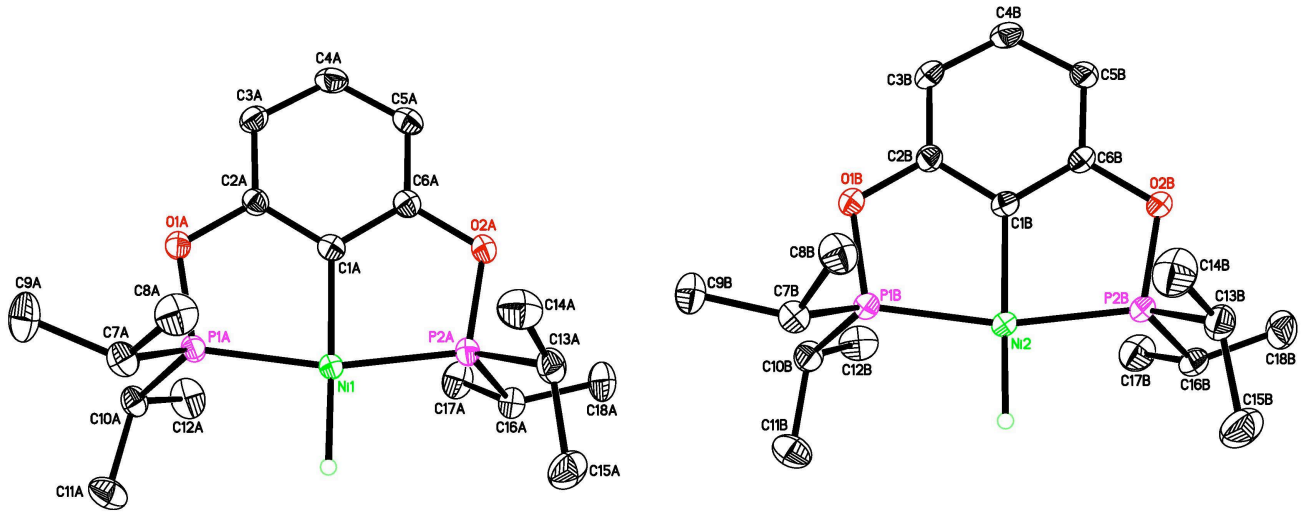


Table S7. Crystal data and structure refinement for **Ni_2Cl_2**.

CCDC deposition number	1864160	
Empirical formula	$C_{30}H_{56}O_4P_4Cl_2Ni_2$	
Formula weight	792.94	
Temperature	150(2) K	
Wavelength	0.7749 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 7.7891(7) Å	α = 83.534(3)°
	b = 11.1624(11) Å	β = 86.323(3)°
	c = 23.194(2) Å	γ = 74.566(3)°
Volume	1930.3(3) $Å^3$	
Z	2	
Density (calculated)	1.364 Mg/m^3	
Absorption coefficient	1.653 mm^{-1}	
F(000)	836	
Crystal size	0.060 x 0.020 x 0.020 mm^3	
θ range for data collection	2.074 to 29.947°	
Index ranges	$-10 \leq h \leq 9$, $-14 \leq k \leq 14$, $-29 \leq l \leq 29$	
Reflections collected	35262	
Independent reflections	8567 [R_{int} = 0.0509]	
Completeness to θ = 27.706°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.971 and 0.896	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8567 / 0 / 395	
Goodness-of-fit on F^2	1.025	
Final R indices [I>2σ(I)]	R1 = 0.0349, wR2 = 0.0682	
R indices (all data)	R1 = 0.0591, wR2 = 0.0748	
Largest diff. peak and hole	0.509 and -0.325 $eÅ^{-3}$	

Table S8. Bond lengths [Å] and angles [°] for **Ni_2Cl_2**.

Ni(1)-C(1)	1.880(2)	Ni(1)-P(1)	2.1546(7)
Ni(1)-P(2)	2.1631(7)	Ni(1)-Cl(1)	2.1889(6)
P(1)-O(1)	1.6474(15)	P(1)-C(7)	1.824(2)
P(1)-C(10)	1.830(2)	P(2)-O(2)	1.6523(15)
P(2)-C(13)	1.823(2)	P(2)-C(16)	1.825(2)
O(1)-C(2)	1.397(2)	O(2)-C(6)	1.398(2)
C(1)-C(6)	1.397(3)	C(1)-C(2)	1.402(3)
C(2)-C(6)#1	1.378(3)	C(6)-C(2)#1	1.378(3)
C(7)-C(9)	1.527(3)	C(7)-C(8)	1.530(3)
C(10)-C(12)	1.526(3)	C(10)-C(11)	1.533(3)
C(13)-C(15)	1.529(3)	C(13)-C(14)	1.534(3)
C(16)-C(17)	1.523(3)	C(16)-C(18)	1.524(3)
Ni(2)-C(20)	1.881(2)	Ni(2)-P(4)	2.1618(7)
Ni(2)-P(3)	2.1650(7)	Ni(2)-Cl(2)	2.1980(6)
P(3)-O(5)	1.6504(15)	P(3)-C(29)	1.827(2)
P(3)-C(26)	1.830(2)	P(4)-O(6)	1.6472(15)
P(4)-C(35)	1.824(2)	P(4)-C(32)	1.825(2)
O(5)-C(21)	1.400(2)	O(6)-C(25)	1.397(2)
C(20)-C(21)	1.394(3)	C(20)-C(25)	1.406(3)
C(21)-C(25)#2	1.374(3)	C(25)-C(21)#2	1.375(3)
C(26)-C(28)	1.528(3)	C(26)-C(27)	1.529(3)
C(29)-C(30)	1.526(3)	C(29)-C(31)	1.530(3)
C(32)-C(34)	1.522(3)	C(32)-C(33)	1.537(3)
C(35)-C(37)	1.523(3)	C(35)-C(36)	1.526(3)

C(1)-Ni(1)-P(1)	82.64(7)	C(1)-Ni(1)-P(2)	82.64(7)
P(1)-Ni(1)-P(2)	164.97(2)	C(1)-Ni(1)-Cl(1)	178.96(7)
P(1)-Ni(1)-Cl(1)	96.33(2)	P(2)-Ni(1)-Cl(1)	98.39(2)
O(1)-P(1)-C(7)	102.71(9)	O(1)-P(1)-C(10)	101.19(9)
C(7)-P(1)-C(10)	107.10(10)	O(1)-P(1)-Ni(1)	106.63(6)
C(7)-P(1)-Ni(1)	118.85(8)	C(10)-P(1)-Ni(1)	117.77(8)
O(2)-P(2)-C(13)	101.00(9)	O(2)-P(2)-C(16)	102.93(9)
C(13)-P(2)-C(16)	107.05(11)	O(2)-P(2)-Ni(1)	106.26(6)
C(13)-P(2)-Ni(1)	120.99(8)	C(16)-P(2)-Ni(1)	115.99(8)
C(2)-O(1)-P(1)	110.76(13)	C(6)-O(2)-P(2)	111.19(13)
C(6)-C(1)-C(2)	117.49(19)	C(6)-C(1)-Ni(1)	121.48(16)
C(2)-C(1)-Ni(1)	121.02(15)	C(6)#1-C(2)-O(1)	120.44(19)
C(6)#1-C(2)-C(1)	120.99(19)	O(1)-C(2)-C(1)	118.57(18)
C(2)#1-C(6)-C(1)	121.5(2)	C(2)#1-C(6)-O(2)	120.06(19)
C(1)-C(6)-O(2)	118.42(18)	C(9)-C(7)-C(8)	111.70(19)
C(9)-C(7)-P(1)	113.00(15)	C(8)-C(7)-P(1)	108.87(15)
C(12)-C(10)-C(11)	111.31(19)	C(12)-C(10)-P(1)	112.11(15)
C(11)-C(10)-P(1)	108.93(16)	C(15)-C(13)-C(14)	111.6(2)
C(15)-C(13)-P(2)	112.01(16)	C(14)-C(13)-P(2)	108.85(16)
C(17)-C(16)-C(18)	111.5(2)	C(17)-C(16)-P(2)	108.81(17)

C(18)-C(16)-P(2)	113.33(17)	C(20)-Ni(2)-P(4)	82.57(7)
C(20)-Ni(2)-P(3)	82.21(7)	P(4)-Ni(2)-P(3)	164.78(2)
C(20)-Ni(2)-Cl(2)	178.10(7)	P(4)-Ni(2)-Cl(2)	96.83(2)
P(3)-Ni(2)-Cl(2)	98.38(2)	O(5)-P(3)-C(29)	101.01(9)
O(5)-P(3)-C(26)	101.44(9)	C(29)-P(3)-C(26)	107.43(11)
O(5)-P(3)-Ni(2)	106.42(6)	C(29)-P(3)-Ni(2)	118.19(8)
C(26)-P(3)-Ni(2)	119.30(8)	O(6)-P(4)-C(35)	102.53(9)
O(6)-P(4)-C(32)	101.35(9)	C(35)-P(4)-C(32)	106.82(11)
O(6)-P(4)-Ni(2)	106.50(6)	C(35)-P(4)-Ni(2)	118.17(8)
C(32)-P(4)-Ni(2)	118.84(8)	C(21)-O(5)-P(3)	111.11(13)
C(25)-O(6)-P(4)	111.11(13)	C(21)-C(20)-C(25)	116.72(19)
C(21)-C(20)-Ni(2)	122.05(16)	C(25)-C(20)-Ni(2)	121.23(16)
C(25)#2-C(21)-C(20)	122.0(2)	C(25)#2-C(21)-O(5)	119.94(19)
C(20)-C(21)-O(5)	118.04(19)	C(21)#2-C(25)-O(6)	120.39(19)
C(21)#2-C(25)-C(20)	121.3(2)	O(6)-C(25)-C(20)	118.34(19)
C(28)-C(26)-C(27)	111.9(2)	C(28)-C(26)-P(3)	112.34(16)
C(27)-C(26)-P(3)	108.55(16)	C(30)-C(29)-C(31)	111.7(2)
C(30)-C(29)-P(3)	108.04(16)	C(31)-C(29)-P(3)	112.31(16)
C(34)-C(32)-C(33)	111.3(2)	C(34)-C(32)-P(4)	111.69(16)
C(33)-C(32)-P(4)	109.09(17)	C(37)-C(35)-C(36)	112.5(2)
C(37)-C(35)-P(4)	112.59(16)	C(36)-C(35)-P(4)	109.05(17)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y,-z+1 #2 -x+1,-y+1,-z+2

Table S9. Torsion angles [°] for **Ni_2Cl_2**.

C(7)-P(1)-O(1)-C(2)	-132.09(14)	C(10)-P(1)-O(1)-C(2)	117.31(14)
Ni(1)-P(1)-O(1)-C(2)	-6.38(14)	C(13)-P(2)-O(2)-C(6)	126.20(15)
C(16)-P(2)-O(2)-C(6)	-123.25(14)	Ni(1)-P(2)-O(2)-C(6)	-0.89(14)
P(1)-Ni(1)-C(1)-C(6)	176.21(18)	P(2)-Ni(1)-C(1)-C(6)	-0.74(16)
P(1)-Ni(1)-C(1)-C(2)	-3.19(16)	P(2)-Ni(1)-C(1)-C(2)	179.86(17)
P(1)-O(1)-C(2)-C(6)#1	-175.03(16)	P(1)-O(1)-C(2)-C(1)	4.7(2)
C(6)-C(1)-C(2)-C(6)#1	0.1(3)	Ni(1)-C(1)-C(2)-C(6)#1	179.56(15)
C(6)-C(1)-C(2)-O(1)	-179.60(18)	Ni(1)-C(1)-C(2)-O(1)	-0.2(3)
C(2)-C(1)-C(6)-C(2)#1	-0.1(3)	Ni(1)-C(1)-C(6)-C(2)#1	-179.55(15)
C(2)-C(1)-C(6)-O(2)	179.78(18)	Ni(1)-C(1)-C(6)-O(2)	0.4(3)
P(2)-O(2)-C(6)-C(2)#1	-179.63(16)	P(2)-O(2)-C(6)-C(1)	0.4(2)
O(1)-P(1)-C(7)-C(9)	-60.01(17)	C(10)-P(1)-C(7)-C(9)	46.10(18)
Ni(1)-P(1)-C(7)-C(9)	-177.35(12)	O(1)-P(1)-C(7)-C(8)	64.72(17)
C(10)-P(1)-C(7)-C(8)	170.83(15)	Ni(1)-P(1)-C(7)-C(8)	-52.62(17)
O(1)-P(1)-C(10)-C(12)	166.04(16)	C(7)-P(1)-C(10)-C(12)	58.85(19)
Ni(1)-P(1)-C(10)-C(12)	-78.25(17)	O(1)-P(1)-C(10)-C(11)	-70.33(17)
C(7)-P(1)-C(10)-C(11)	-177.52(16)	Ni(1)-P(1)-C(10)-C(11)	45.38(18)
O(2)-P(2)-C(13)-C(15)	168.56(16)	C(16)-P(2)-C(13)-C(15)	61.22(19)

Ni(1)-P(2)-C(13)-C(15)	-74.74(18)	O(2)-P(2)-C(13)-C(14)	-67.56(18)
C(16)-P(2)-C(13)-C(14)	-174.89(17)	Ni(1)-P(2)-C(13)-C(14)	49.15(19)
O(2)-P(2)-C(16)-C(17)	78.23(18)	C(13)-P(2)-C(16)-C(17)	-175.80(17)
Ni(1)-P(2)-C(16)-C(17)	-37.32(19)	O(2)-P(2)-C(16)-C(18)	-46.4(2)
C(13)-P(2)-C(16)-C(18)	59.5(2)	Ni(1)-P(2)-C(16)-C(18)	-162.00(16)
C(29)-P(3)-O(5)-C(21)	119.95(15)	C(26)-P(3)-O(5)-C(21)	-129.52(15)
Ni(2)-P(3)-O(5)-C(21)	-4.05(15)	C(35)-P(4)-O(6)-C(25)	-129.80(15)
C(32)-P(4)-O(6)-C(25)	119.90(15)	Ni(2)-P(4)-O(6)-C(25)	-5.03(15)
P(4)-Ni(2)-C(20)-C(21)	177.41(19)	P(3)-Ni(2)-C(20)-C(21)	-2.41(17)
P(4)-Ni(2)-C(20)-C(25)	-3.05(17)	P(3)-Ni(2)-C(20)-C(25)	177.14(18)
C(25)-C(20)-C(21)-C(25)#2	0.0(4)	Ni(2)-C(20)-C(21)-C(25)#2	179.52(16)
C(25)-C(20)-C(21)-O(5)	-179.17(19)	Ni(2)-C(20)-C(21)-O(5)	0.4(3)
P(3)-O(5)-C(21)-C(25)#2	-176.42(16)	P(3)-O(5)-C(21)-C(20)	2.7(2)
P(4)-O(6)-C(25)-C(21)#2	-176.58(16)	P(4)-O(6)-C(25)-C(20)	3.3(2)
C(21)-C(20)-C(25)-C(21)#2	0.0(4)	Ni(2)-C(20)-C(25)-C(21)#2	-179.52(16)
C(21)-C(20)-C(25)-O(6)	-179.86(18)	Ni(2)-C(20)-C(25)-O(6)	0.6(3)
O(5)-P(3)-C(26)-C(28)	-55.80(17)	C(29)-P(3)-C(26)-C(28)	49.73(18)
Ni(2)-P(3)-C(26)-C(28)	-172.19(13)	O(5)-P(3)-C(26)-C(27)	68.47(17)
C(29)-P(3)-C(26)-C(27)	174.01(16)	Ni(2)-P(3)-C(26)-C(27)	-47.91(18)
O(5)-P(3)-C(29)-C(30)	-70.81(18)	C(26)-P(3)-C(29)-C(30)	-176.65(17)
Ni(2)-P(3)-C(29)-C(30)	44.72(19)	O(5)-P(3)-C(29)-C(31)	165.51(16)
C(26)-P(3)-C(29)-C(31)	59.67(19)	Ni(2)-P(3)-C(29)-C(31)	-78.95(17)
O(6)-P(4)-C(32)-C(34)	169.68(16)	C(35)-P(4)-C(32)-C(34)	62.70(19)
Ni(2)-P(4)-C(32)-C(34)	-74.14(18)	O(6)-P(4)-C(32)-C(33)	-66.9(2)
C(35)-P(4)-C(32)-C(33)	-173.89(19)	Ni(2)-P(4)-C(32)-C(33)	49.3(2)
O(6)-P(4)-C(35)-C(37)	-48.70(18)	C(32)-P(4)-C(35)-C(37)	57.44(19)
Ni(2)-P(4)-C(35)-C(37)	-165.38(14)	O(6)-P(4)-C(35)-C(36)	76.92(19)
C(32)-P(4)-C(35)-C(36)	-176.95(18)	Ni(2)-P(4)-C(35)-C(36)	-39.8(2)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y,-z+1 #2 -x+1,-y+1,-z+2

Table S10. Crystal data and structure refinement for **Ni_2Cl_2**•$2C_7H_8$.

CCDC deposition number	1864161	
Formula	$C_{30}H_{56}O_4P_4Cl_2Ni_2.2C_7H_8$	
Formula weight	977.21	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 7.6816(5) Å	α = 114.2602(18)°
	b = 13.3319(9) Å	β = 94.503(2)°
	c = 13.6700(9) Å	γ = 97.699(2)°
Volume	1250.92(14) $Å^3$	
Z	1	
Density (calculated)	1.297 Mg/m^3	
Absorption coefficient	1.025 mm^{-1}	
F(000)	518	
Crystal size	0.130 x 0.070 x 0.040 mm^3	
θ range for data collection	1.652 to 28.231°	
Index ranges	$-10 \leq h \leq 10$, $-17 \leq k \leq 17$, $-18 \leq l \leq 18$	
Reflections collected	33123	
Independent reflections	6174 [R_{int} = 0.0663]	
Completeness to θ = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.928 and 0.769	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6174 / 189 / 312	
Goodness-of-fit on F^2	1.006	
Final R indices [I>2σ(I)]	R1 = 0.0457, wR2 = 0.1026	
R indices (all data)	R1 = 0.0688, wR2 = 0.1126	
Largest diff. peak and hole	0.801 and -0.408 $eÅ^{-3}$	

Table S11. Bond lengths [Å] and angles [°] for **Ni_2Cl_2**•$2C_7H_8$.

Ni-C(1)	1.883(2)	Ni-P(2)	2.1522(7)
Ni-P(1)	2.1594(7)	Ni-Cl(1)	2.1918(7)
P(1)-O(1)	1.6547(16)	P(1)-C(7)	1.819(3)
P(1)-C(10)	1.824(3)	P(2)-O(2)	1.6519(17)
P(2)-C(13)	1.827(3)	P(2)-C(16)	1.829(3)
O(1)-C(2)	1.387(3)	O(2)-C(3)	1.396(3)
C(1)-C(3)	1.390(3)	C(1)-C(2)	1.399(3)
C(2)-C(3)#1	1.391(3)	C(3)-C(2)#1	1.390(3)
C(7)-C(9)	1.532(4)	C(7)-C(8)	1.534(4)
C(10)-C(11)	1.524(4)	C(10)-C(12)	1.530(4)
C(13)-C(14)	1.524(4)	C(13)-C(15)	1.532(4)
C(16)-C(17)	1.518(4)	C(16)-C(18)	1.524(3)
C(51)-C(52)	1.4022	C(51)-C(56)	1.4022
C(51)-C(57)	1.5070	C(52)-C(53)	1.3965
C(53)-C(54)	1.3964	C(54)-C(55)	1.3965
C(55)-C(56)	1.3962	C(61)-C(66)	1.352(11)
C(61)-C(62)	1.425(11)	C(61)-C(67)	1.474(9)
C(62)-C(63)	1.352(9)	C(63)-C(64)	1.394(10)
C(64)-C(65)	1.379(10)	C(65)-C(66)	1.390(10)

C(1)-Ni-P(2)	82.44(8)	C(1)-Ni-P(1)	82.84(8)
P(2)-Ni-P(1)	165.28(3)	C(1)-Ni-Cl(1)	178.30(8)
P(2)-Ni-Cl(1)	97.11(3)	P(1)-Ni-Cl(1)	97.60(3)
O(1)-P(1)-C(7)	101.75(11)	O(1)-P(1)-C(10)	102.84(11)
C(7)-P(1)-C(10)	106.69(13)	O(1)-P(1)-Ni	106.14(7)
C(7)-P(1)-Ni	118.57(9)	C(10)-P(1)-Ni	118.35(9)
O(2)-P(2)-C(13)	101.98(11)	O(2)-P(2)-C(16)	101.05(11)
C(13)-P(2)-C(16)	107.15(12)	O(2)-P(2)-Ni	106.71(6)
C(13)-P(2)-Ni	119.09(9)	C(16)-P(2)-Ni	118.04(10)
C(2)-O(1)-P(1)	111.01(14)	C(3)-O(2)-P(2)	110.60(15)
C(3)-C(1)-C(2)	117.9(2)	C(3)-C(1)-Ni	121.43(17)
C(2)-C(1)-Ni	120.69(18)	O(1)-C(2)-C(3)#1	120.2(2)
O(1)-C(2)-C(1)	119.2(2)	C(3)#1-C(2)-C(1)	120.6(2)
C(1)-C(3)-C(2)#1	121.5(2)	C(1)-C(3)-O(2)	118.7(2)
C(2)#1-C(3)-O(2)	119.8(2)	C(9)-C(7)-C(8)	111.3(2)
C(9)-C(7)-P(1)	111.47(19)	C(8)-C(7)-P(1)	109.2(2)
C(11)-C(10)-C(12)	112.1(2)	C(11)-C(10)-P(1)	109.2(2)
C(12)-C(10)-P(1)	112.75(19)	C(14)-C(13)-C(15)	111.8(2)
C(14)-C(13)-P(2)	108.79(17)	C(15)-C(13)-P(2)	112.26(18)
C(17)-C(16)-C(18)	112.1(2)	C(17)-C(16)-P(2)	108.27(18)
C(18)-C(16)-P(2)	111.39(19)	C(52)-C(51)-C(56)	118.1
C(52)-C(51)-C(57)	120.9	C(56)-C(51)-C(57)	121.0
C(53)-C(52)-C(51)	121.1	C(54)-C(53)-C(52)	120.1
C(53)-C(54)-C(55)	119.4	C(56)-C(55)-C(54)	120.1
C(55)-C(56)-C(51)	121.1	C(66)-C(61)-C(62)	119.9(7)

C(66)-C(61)-C(67)	129.9(10)	C(62)-C(61)-C(67)	110.2(9)
C(63)-C(62)-C(61)	117.8(8)	C(62)-C(63)-C(64)	123.0(9)
C(65)-C(64)-C(63)	118.0(8)	C(64)-C(65)-C(66)	120.2(9)
C(61)-C(66)-C(65)	120.9(9)		

Symmetry transformations used to generate equivalent atoms: #1 -x,-y+1,-z+1

Table S12. Torsion angles [°] for **Ni_2Cl_2•**$2C_7H_8$.

C(7)-P(1)-O(1)-C(2)	-121.49(17)	C(10)-P(1)-O(1)-C(2)	128.12(17)
Ni-P(1)-O(1)-C(2)	3.17(17)	C(13)-P(2)-O(2)-C(3)	128.87(17)
C(16)-P(2)-O(2)-C(3)	-120.74(17)	Ni-P(2)-O(2)-C(3)	3.23(17)
P(2)-Ni-C(1)-C(3)	1.17(19)	P(1)-Ni-C(1)-C(3)	-178.8(2)
P(2)-Ni-C(1)-C(2)	-177.4(2)	P(1)-Ni-C(1)-C(2)	2.71(19)
P(1)-O(1)-C(2)-C(3)#1	178.46(19)	P(1)-O(1)-C(2)-C(1)	-1.5(3)
C(3)-C(1)-C(2)-O(1)	-180.0(2)	Ni-C(1)-C(2)-O(1)	-1.4(3)
C(3)-C(1)-C(2)-C(3)#1	0.0(4)	Ni-C(1)-C(2)-C(3)#1	178.63(18)
C(2)-C(1)-C(3)-C(2)#1	-0.1(4)	Ni-C(1)-C(3)-C(2)#1	-178.62(19)
C(2)-C(1)-C(3)-O(2)	179.3(2)	Ni-C(1)-C(3)-O(2)	0.7(3)
P(2)-O(2)-C(3)-C(1)	-2.7(3)	P(2)-O(2)-C(3)-C(2)#1	176.60(19)
O(1)-P(1)-C(7)-C(9)	-168.35(19)	C(10)-P(1)-C(7)-C(9)	-60.9(2)
Ni-P(1)-C(7)-C(9)	75.8(2)	O(1)-P(1)-C(7)-C(8)	68.2(2)
C(10)-P(1)-C(7)-C(8)	175.64(19)	Ni-P(1)-C(7)-C(8)	-47.7(2)
O(1)-P(1)-C(10)-C(11)	-73.2(2)	C(7)-P(1)-C(10)-C(11)	-179.87(19)
Ni-P(1)-C(10)-C(11)	43.3(2)	O(1)-P(1)-C(10)-C(12)	52.0(2)
C(7)-P(1)-C(10)-C(12)	-54.6(2)	Ni-P(1)-C(10)-C(12)	168.57(16)
O(2)-P(2)-C(13)-C(14)	-66.5(2)	C(16)-P(2)-C(13)-C(14)	-172.19(18)
Ni-P(2)-C(13)-C(14)	50.5(2)	O(2)-P(2)-C(13)-C(15)	57.76(19)
C(16)-P(2)-C(13)-C(15)	-47.9(2)	Ni-P(2)-C(13)-C(15)	174.78(14)
O(2)-P(2)-C(16)-C(17)	67.4(2)	C(13)-P(2)-C(16)-C(17)	173.8(2)
Ni-P(2)-C(16)-C(17)	-48.4(2)	O(2)-P(2)-C(16)-C(18)	-168.89(19)
C(13)-P(2)-C(16)-C(18)	-62.5(2)	Ni-P(2)-C(16)-C(18)	75.3(2)
C(56)-C(51)-C(52)-C(53)	0.3	C(57)-C(51)-C(52)-C(53)	-178.5
C(51)-C(52)-C(53)-C(54)	-0.1	C(52)-C(53)-C(54)-C(55)	-0.1
C(53)-C(54)-C(55)-C(56)	0.1	C(54)-C(55)-C(56)-C(51)	0.1
C(52)-C(51)-C(56)-C(55)	-0.3	C(57)-C(51)-C(56)-C(55)	178.5
C(66)-C(61)-C(62)-C(63)	-4.0(11)	C(67)-C(61)-C(62)-C(63)	176.8(7)
C(61)-C(62)-C(63)-C(64)	3.1(11)	C(62)-C(63)-C(64)-C(65)	-1.6(11)
C(63)-C(64)-C(65)-C(66)	0.8(10)	C(62)-C(61)-C(66)-C(65)	3.3(12)
C(67)-C(61)-C(66)-C(65)	-177.6(8)	C(64)-C(65)-C(66)-C(61)	-1.8(11)

Symmetry transformations used to generate equivalent atoms: #1 -x,-y+1,-z+1

Table S13. Crystal data and structure refinement for **Ni_2Me_2**•$2H_2O$.

CCDC deposition number	1864162	
Formula	$C_{32}H_{62}O_4P_4Ni_2.2H_2O$	
Formula weight	788.14	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 7.6206(4) Å	α = 111.4434(13)°
	b = 10.9712(5) Å	β = 92.3629(14)°
	c = 12.8787(6) Å	γ = 97.0512(14)°
Volume	990.31(8) $Å^3$	
Z	1	
Density (calculated)	1.322 Mg/m^3	
Absorption coefficient	1.150 mm^{-1}	
F(000)	422	
Crystal size	0.220 x 0.050 x 0.040 mm^3	
θ range for data collection	1.706 to 28.353°	
Index ranges	$-10 \leq h \leq 10$, $-14 \leq k \leq 14$, $-17 \leq l \leq 17$	
Reflections collected	29347	
Independent reflections	4952 [R_{int} = 0.0427]	
Completeness to θ = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.928 and 0.815	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4952 / 0 / 217	
Goodness-of-fit on F^2	1.044	
Final R indices [I>2σ(I)]	R1 = 0.0365, wR2 = 0.0932	
R indices (all data)	R1 = 0.0471, wR2 = 0.0982	
Largest diff. peak and hole	0.846 and -0.366 $eÅ^{-3}$	

Table S14. Bond lengths [Å] and angles [°] for **Ni_2Me_2**•$2H_2O$.

Ni-C(1)	1.9049(18)	Ni-C(19)	1.9885(19)
Ni-P(2)	2.1225(5)	Ni-P(1)	2.1310(5)
P(1)-O(1)	1.6566(13)	P(1)-C(7)	1.827(2)
P(1)-C(10)	1.834(2)	P(2)-O(2)	1.6605(13)
P(2)-C(13)	1.827(2)	P(2)-C(16)	1.829(2)
O(1)-C(2)	1.403(2)	O(2)-C(3)	1.409(2)
C(1)-C(3)	1.391(3)	C(1)-C(2)	1.397(3)
C(2)-C(3)#1	1.383(3)	C(3)-C(2)#1	1.383(3)
C(7)-C(8)	1.521(3)	C(7)-C(9)	1.538(3)
C(10)-C(12)	1.528(3)	C(10)-C(11)	1.533(3)
C(13)-C(15)	1.525(3)	C(13)-C(14)	1.533(3)
C(16)-C(17)	1.523(3)	C(16)-C(18)	1.527(3)
C(1)-Ni-C(19)	176.85(9)	C(1)-Ni-P(2)	82.26(6)
C(19)-Ni-P(2)	97.33(6)	C(1)-Ni-P(1)	82.71(6)
C(19)-Ni-P(1)	97.75(6)	P(2)-Ni-P(1)	164.91(2)
O(1)-P(1)-C(7)	101.44(8)	O(1)-P(1)-C(10)	100.07(9)
C(7)-P(1)-C(10)	106.30(10)	O(1)-P(1)-Ni	107.21(5)
C(7)-P(1)-Ni	118.59(7)	C(10)-P(1)-Ni	120.00(7)
O(2)-P(2)-C(13)	99.80(8)	O(2)-P(2)-C(16)	102.33(8)
C(13)-P(2)-C(16)	106.62(9)	O(2)-P(2)-Ni	107.87(5)
C(13)-P(2)-Ni	120.51(7)	C(16)-P(2)-Ni	116.84(7)
C(2)-O(1)-P(1)	111.13(11)	C(3)-O(2)-P(2)	110.32(11)
C(3)-C(1)-C(2)	117.26(17)	C(3)-C(1)-Ni	121.67(14)
C(2)-C(1)-Ni	121.06(14)	C(3)#1-C(2)-C(1)	121.05(18)
C(3)#1-C(2)-O(1)	121.07(17)	C(1)-C(2)-O(1)	117.88(16)
C(2)#1-C(3)-C(1)	121.68(17)	C(2)#1-C(3)-O(2)	120.56(17)
C(1)-C(3)-O(2)	117.76(16)	C(8)-C(7)-C(9)	111.11(18)
C(8)-C(7)-P(1)	113.09(15)	C(9)-C(7)-P(1)	108.66(15)
C(12)-C(10)-C(11)	111.32(19)	C(12)-C(10)-P(1)	109.00(15)
C(11)-C(10)-P(1)	112.32(15)	C(15)-C(13)-C(14)	111.07(18)
C(15)-C(13)-P(2)	109.29(14)	C(14)-C(13)-P(2)	112.31(15)
C(17)-C(16)-C(18)	111.38(18)	C(17)-C(16)-P(2)	114.73(14)
C(18)-C(16)-P(2)	108.62(14)		

Symmetry transformations used to generate equivalent atoms: #1 -x,-y,-z+1

Table S15. Torsion angles [°] for **Ni_2Me_2**•2H_2O.

C(7)-P(1)-O(1)-C(2)	-124.11(13)	C(10)-P(1)-O(1)-C(2)	126.82(13)
Ni-P(1)-O(1)-C(2)	0.90(13)	C(13)-P(2)-O(2)-C(3)	123.04(13)
C(16)-P(2)-O(2)-C(3)	-127.39(13)	Ni-P(2)-O(2)-C(3)	-3.61(13)
C(3)-C(1)-C(2)-C(3)#1	1.2(3)	Ni-C(1)-C(2)-C(3)#1	-179.71(15)
C(3)-C(1)-C(2)-O(1)	-178.74(16)	Ni-C(1)-C(2)-O(1)	0.3(3)
P(1)-O(1)-C(2)-C(3)#1	179.22(15)	P(1)-O(1)-C(2)-C(1)	-0.8(2)
C(2)-C(1)-C(3)-C(2)#1	-1.2(3)	Ni-C(1)-C(3)-C(2)#1	179.71(15)
C(2)-C(1)-C(3)-O(2)	179.38(16)	Ni-C(1)-C(3)-O(2)	0.3(3)
P(2)-O(2)-C(3)-C(2)#1	-177.05(15)	P(2)-O(2)-C(3)-C(1)	2.4(2)
O(1)-P(1)-C(7)-C(8)	-54.98(16)	C(10)-P(1)-C(7)-C(8)	49.20(17)
Ni-P(1)-C(7)-C(8)	-171.98(13)	O(1)-P(1)-C(7)-C(9)	68.88(15)
C(10)-P(1)-C(7)-C(9)	173.07(15)	Ni-P(1)-C(7)-C(9)	-48.11(16)
O(1)-P(1)-C(10)-C(12)	-74.30(16)	C(7)-P(1)-C(10)-C(12)	-179.48(15)
Ni-P(1)-C(10)-C(12)	42.41(18)	O(1)-P(1)-C(10)-C(11)	161.84(15)
C(7)-P(1)-C(10)-C(11)	56.67(17)	Ni-P(1)-C(10)-C(11)	-81.45(16)
O(2)-P(2)-C(13)-C(15)	-70.23(16)	C(16)-P(2)-C(13)-C(15)	-176.35(15)
Ni-P(2)-C(13)-C(15)	47.37(17)	O(2)-P(2)-C(13)-C(14)	166.04(14)
C(16)-P(2)-C(13)-C(14)	59.91(17)	Ni-P(2)-C(13)-C(14)	-76.37(16)
O(2)-P(2)-C(16)-C(17)	-55.67(17)	C(13)-P(2)-C(16)-C(17)	48.64(18)
Ni-P(2)-C(16)-C(17)	-173.23(13)	O(2)-P(2)-C(16)-C(18)	69.70(16)
C(13)-P(2)-C(16)-C(18)	174.00(15)	Ni-P(2)-C(16)-C(18)	-47.87(16)

Symmetry transformations used to generate equivalent atoms: #1 -x,-y,-z+1

Table S16. Crystal data and structure refinement for **Ni_2H_2**.

CCDC deposition number	1864163	
Empirical formula	$C_{30}H_{58}O_4P_4Ni_2$	
Formula weight	724.06	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 7.5342(2) Å	α = 90°
	b = 20.0626(6) Å	β = 99.1380(10)°
	c = 12.1446(4) Å	γ = 90°
Volume	1812.43(9) $Å^3$	
Z	2	
Density (calculated)	1.327 Mg/m^3	
Absorption coefficient	1.246 mm^{-1}	
F(000)	772	
Crystal size	0.125 x 0.060 x 0.035 mm^3	
θ range for data collection	2.921 to 28.308°	
Index ranges	$-10\leq h\leq 10$, $-26\leq k\leq 26$, $-16\leq l\leq 16$	
Reflections collected	53874	
Independent reflections	4506 [R_{int} = 0.0371]	
Completeness to θ = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.862 and 0.794	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4506 / 0 / 192	
Goodness-of-fit on F^2	1.071	
Final R indices [I>2σ(I)]	R1 = 0.0225, wR2 = 0.0534	
R indices (all data)	R1 = 0.0273, wR2 = 0.0554	
Largest diff. peak and hole	0.536 and -0.383 $eÅ^{-3}$	

Table S17. Bond lengths [Å] and angles [°] for **Ni_2H_2**.

Ni-H(1)	1.672(15)	Ni-C(1)	1.8962(12)
Ni-P(1)	2.1144(4)	Ni-P(2)	2.1149(4)
P(1)-O(1)	1.6617(9)	P(1)-C(7)	1.8313(13)
P(1)-C(10)	1.8316(13)	P(2)-O(2)	1.6619(9)
P(2)-C(13)	1.8258(13)	P(2)-C(16)	1.8289(13)
O(1)-C(2)	1.4013(14)	O(2)-C(3)#1	1.4009(14)
C(1)-C(3)#1	1.3989(17)	C(1)-C(2)	1.3991(17)
C(2)-C(3)	1.3817(17)	C(3)-C(1)#1	1.3990(17)
C(3)-O(2)#1	1.4009(14)	C(7)-C(8)	1.5318(19)
C(7)-C(9)	1.5330(19)	C(10)-C(12)	1.527(2)
C(10)-C(11)	1.533(2)	C(13)-C(15)	1.5272(18)
C(13)-C(14)	1.5313(19)	C(16)-C(18)	1.5289(18)
C(16)-C(17)	1.5324(19)		

H(1)-Ni-C(1)	172.4(5)	H(1)-Ni-P(1)	90.4(5)
C(1)-Ni-P(1)	83.40(4)	H(1)-Ni-P(2)	103.4(5)
C(1)-Ni-P(2)	82.99(4)	P(1)-Ni-P(2)	165.983(15)
O(1)-P(1)-C(7)	101.10(6)	O(1)-P(1)-C(10)	100.99(6)
C(7)-P(1)-C(10)	106.98(6)	O(1)-P(1)-Ni	106.96(3)
C(7)-P(1)-Ni	120.30(5)	C(10)-P(1)-Ni	117.44(5)
O(2)-P(2)-C(13)	99.95(5)	O(2)-P(2)-C(16)	101.74(6)
C(13)-P(2)-C(16)	106.60(6)	O(2)-P(2)-Ni	107.18(3)
C(13)-P(2)-Ni	121.22(4)	C(16)-P(2)-Ni	116.99(4)
C(2)-O(1)-P(1)	111.08(8)	C(3)#1-O(2)-P(2)	110.79(7)
C(3)#1-C(1)-C(2)	118.45(11)	C(3)#1-C(1)-Ni	120.95(9)
C(2)-C(1)-Ni	120.60(9)	C(3)-C(2)-C(1)	120.74(11)
C(3)-C(2)-O(1)	121.33(11)	C(1)-C(2)-O(1)	117.93(11)
C(2)-C(3)-C(1)#1	120.81(11)	C(2)-C(3)-O(2)#1	121.43(11)
C(1)#1-C(3)-O(2)#1	117.76(11)	C(8)-C(7)-C(9)	111.55(12)
C(8)-C(7)-P(1)	113.42(10)	C(9)-C(7)-P(1)	108.01(9)
C(12)-C(10)-C(11)	111.54(13)	C(12)-C(10)-P(1)	111.88(10)
C(11)-C(10)-P(1)	108.01(9)	C(15)-C(13)-C(14)	111.88(11)
C(15)-C(13)-P(2)	110.88(9)	C(14)-C(13)-P(2)	108.83(9)
C(18)-C(16)-C(17)	111.25(11)	C(18)-C(16)-P(2)	113.68(9)
C(17)-C(16)-P(2)	108.41(9)		

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+1,-z+1

Table S18. Torsion angles [°] for **Ni_2H_2**.

C(7)-P(1)-O(1)-C(2)	-125.27(9)	C(10)-P(1)-O(1)-C(2)	124.78(9)
Ni-P(1)-O(1)-C(2)	1.40(9)	C(13)-P(2)-O(2)-C(3)#1	132.89(9)
C(16)-P(2)-O(2)-C(3)#1	-117.67(9)	Ni-P(2)-O(2)-C(3)#1	5.65(9)
P(1)-Ni-C(1)-C(3)#1	-179.61(10)	P(2)-Ni-C(1)-C(3)#1	3.76(10)
P(1)-Ni-C(1)-C(2)	-0.33(10)	P(2)-Ni-C(1)-C(2)	-176.96(10)
C(3)#1-C(1)-C(2)-C(3)	0.5(2)	Ni-C(1)-C(2)-C(3)	-178.77(9)
C(3)#1-C(1)-C(2)-O(1)	-179.31(11)	Ni-C(1)-C(2)-O(1)	1.40(16)
P(1)-O(1)-C(2)-C(3)	178.37(10)	P(1)-O(1)-C(2)-C(1)	-1.79(14)
C(1)-C(2)-C(3)-C(1)#1	-0.5(2)	O(1)-C(2)-C(3)-C(1)#1	179.29(11)
C(1)-C(2)-C(3)-O(2)#1	179.65(11)	O(1)-C(2)-C(3)-O(2)#1	-0.52(19)
O(1)-P(1)-C(7)-C(8)	-55.23(11)	C(10)-P(1)-C(7)-C(8)	50.02(12)
Ni-P(1)-C(7)-C(8)	-172.55(8)	O(1)-P(1)-C(7)-C(9)	68.95(10)
C(10)-P(1)-C(7)-C(9)	174.20(10)	Ni-P(1)-C(7)-C(9)	-48.37(11)
O(1)-P(1)-C(10)-C(12)	163.71(10)	C(7)-P(1)-C(10)-C(12)	58.38(12)
Ni-P(1)-C(10)-C(12)	-80.46(11)	O(1)-P(1)-C(10)-C(11)	-73.15(11)
C(7)-P(1)-C(10)-C(11)	-178.47(10)	Ni-P(1)-C(10)-C(11)	42.68(11)
O(2)-P(2)-C(13)-C(15)	168.01(9)	C(16)-P(2)-C(13)-C(15)	62.47(11)
Ni-P(2)-C(13)-C(15)	-74.79(10)	O(2)-P(2)-C(13)-C(14)	-68.52(10)
C(16)-P(2)-C(13)-C(14)	-174.06(9)	Ni-P(2)-C(13)-C(14)	48.68(11)
O(2)-P(2)-C(16)-C(18)	-58.29(11)	C(13)-P(2)-C(16)-C(18)	45.96(11)
Ni-P(2)-C(16)-C(18)	-174.68(8)	O(2)-P(2)-C(16)-C(17)	65.98(10)
C(13)-P(2)-C(16)-C(17)	170.23(9)	Ni-P(2)-C(16)-C(17)	-50.40(10)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+1,-z+1

Table S19. Crystal data and structure refinement for **$Ni_2(OCHO)_2$**•3/2MeOH.

CCDC deposition number	1864164	
Formula	$C_{32}H_{58}O_8P_4Ni_2.3/2CH_3OH$	
Formula weight	860.14	
Temperature	150(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 7.7567(4) Å	α = 103.073(2)°
	b = 13.9995(7) Å	β = 97.291(2)°
	c = 20.7945(10) Å	γ = 91.116(2)°
Volume	2179.05(19) $Å^3$	
Z	2	
Density (calculated)	1.311 Mg/m^3	
Absorption coefficient	2.844 mm^{-1}	
F(000)	914	
Crystal size	0.085 x 0.017 x 0.010 mm^3	
θ range for data collection	2.201 to 75.335°	
Index ranges	$-9 \le h \le 9$, $-17 \le k \le 17$, $-26 \le l \le 25$	
Reflections collected	92902	
Independent reflections	8929 [R_{int} = 0.0808]	
Completeness to θ = 67.679°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.860 and 0.756	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8929 / 0 / 471	
Goodness-of-fit on F^2	1.041	
Final R indices [I>2σ(I)]	R1 = 0.0428, wR2 = 0.1174	
R indices (all data)	R1 = 0.0499, wR2 = 0.1242	
Largest diff. peak and hole	0.531 and -0.307 $eÅ^{-3}$	

Table S20. Bond lengths [Å] and angles [°] for **$Ni_2(OCHO)_2$**•3/2MeOH.

Ni(1)-C(1)	1.885(2)	Ni(1)-O(3)	1.9120(18)
Ni(1)-P(1)	2.1668(7)	Ni(1)-P(2)	2.1795(7)
P(1)-O(1)	1.6478(16)	P(1)-C(7)	1.822(3)
P(1)-C(10)	1.824(3)	P(2)-O(2)	1.6490(16)
P(2)-C(13)	1.821(3)	P(2)-C(16)	1.823(3)
O(1)-C(2)	1.396(3)	O(2)-C(3)#1	1.395(2)
O(3)-C(19)	1.244(4)	O(4)-C(19)	1.234(4)
C(1)-C(2)	1.393(3)	C(1)-C(3)#1	1.402(3)
C(2)-C(3)	1.376(3)	C(3)-O(2)#1	1.395(2)
C(3)-C(1)#1	1.402(3)	C(7)-C(9)	1.528(4)
C(7)-C(8)	1.534(4)	C(10)-C(12)	1.524(4)
C(10)-C(11)	1.527(4)	C(13)-C(15)	1.532(4)
C(13)-C(14)	1.537(4)	C(16)-C(18)	1.516(4)
C(16)-C(17)	1.529(4)		
Ni(2)-C(20)	1.885(2)	Ni(2)-O(7)	1.9089(19)
Ni(2)-P(3)	2.1587(7)	Ni(2)-P(4)	2.1779(7)
P(3)-O(5)	1.6455(16)	P(3)-C(29)	1.823(3)
P(3)-C(26)	1.826(3)	P(4)-O(6)	1.6506(17)
P(4)-C(32)	1.823(3)	P(4)-C(35)	1.824(3)
O(5)-C(21)	1.393(3)	O(6)-C(22)#2	1.391(3)
O(7)-C(38)	1.208(4)	O(8)-C(38)	1.224(4)
C(20)-C(21)	1.390(3)	C(20)-C(22)#2	1.399(3)
C(21)-C(22)	1.389(3)	C(22)-O(6)#2	1.391(3)
C(22)-C(20)#2	1.399(3)	C(26)-C(28)	1.529(4)
C(26)-C(27)	1.531(4)	C(29)-C(30)	1.527(4)
C(29)-C(31)	1.530(4)	C(32)-C(34)	1.528(4)
C(32)-C(33)	1.532(4)	C(35)-C(36)	1.514(4)
C(35)-C(37)	1.526(4)	O(9)-C(39)	1.386(6)
O(10)-C(40)	1.361(7)		
C(1)-Ni(1)-O(3)	172.65(9)	C(1)-Ni(1)-P(1)	82.20(7)
O(3)-Ni(1)-P(1)	95.14(6)	C(1)-Ni(1)-P(2)	82.62(7)
O(3)-Ni(1)-P(2)	100.40(6)	P(1)-Ni(1)-P(2)	164.32(3)
O(1)-P(1)-C(7)	102.36(10)	O(1)-P(1)-C(10)	101.48(11)
C(7)-P(1)-C(10)	107.80(13)	O(1)-P(1)-Ni(1)	106.65(6)
C(7)-P(1)-Ni(1)	118.47(9)	C(10)-P(1)-Ni(1)	117.53(9)
O(2)-P(2)-C(13)	101.28(10)	O(2)-P(2)-C(16)	101.75(11)
C(13)-P(2)-C(16)	107.20(12)	O(2)-P(2)-Ni(1)	105.63(6)
C(13)-P(2)-Ni(1)	119.08(8)	C(16)-P(2)-Ni(1)	118.87(10)
C(2)-O(1)-P(1)	110.83(13)	C(3)#1-O(2)-P(2)	111.78(13)
C(19)-O(3)-Ni(1)	120.9(2)	C(2)-C(1)-C(3)#1	117.2(2)
C(2)-C(1)-Ni(1)	121.52(17)	C(3)#1-C(1)-Ni(1)	121.22(16)
C(3)-C(2)-C(1)	121.6(2)	C(3)-C(2)-O(1)	119.66(19)
C(1)-C(2)-O(1)	118.76(19)	C(2)-C(3)-O(2)#1	120.41(19)

C(2)-C(3)-C(1)#1	121.2(2)	O(2)#1-C(3)-C(1)#1	118.41(19)
C(9)-C(7)-C(8)	111.5(2)	C(9)-C(7)-P(1)	108.79(19)
C(8)-C(7)-P(1)	112.8(2)	C(12)-C(10)-C(11)	111.7(3)
C(12)-C(10)-P(1)	108.55(19)	C(11)-C(10)-P(1)	112.0(2)
C(15)-C(13)-C(14)	111.6(2)	C(15)-C(13)-P(2)	108.53(17)
C(14)-C(13)-P(2)	110.94(19)	C(18)-C(16)-C(17)	111.1(2)
C(18)-C(16)-P(2)	108.74(19)	C(17)-C(16)-P(2)	112.7(2)
O(4)-C(19)-O(3)	126.4(3)		

C(20)-Ni(2)-O(7)	170.29(10)	C(20)-Ni(2)-P(3)	82.14(7)
O(7)-Ni(2)-P(3)	94.57(7)	C(20)-Ni(2)-P(4)	82.49(7)
O(7)-Ni(2)-P(4)	101.23(7)	P(3)-Ni(2)-P(4)	164.13(3)
O(5)-P(3)-C(29)	102.28(11)	O(5)-P(3)-C(26)	102.25(10)
C(29)-P(3)-C(26)	107.27(12)	O(5)-P(3)-Ni(2)	106.65(6)
C(29)-P(3)-Ni(2)	117.32(9)	C(26)-P(3)-Ni(2)	118.68(8)
O(6)-P(4)-C(32)	100.93(11)	O(6)-P(4)-C(35)	102.08(12)
C(32)-P(4)-C(35)	107.38(12)	O(6)-P(4)-Ni(2)	105.86(6)
C(32)-P(4)-Ni(2)	118.38(9)	C(35)-P(4)-Ni(2)	119.22(10)
C(21)-O(5)-P(3)	110.71(13)	C(22)#2-O(6)-P(4)	111.64(14)
C(38)-O(7)-Ni(2)	123.3(2)	C(21)-C(20)-C(22)#2	117.3(2)
C(21)-C(20)-Ni(2)	121.28(17)	C(22)#2-C(20)-Ni(2)	121.34(16)
C(22)-C(21)-C(20)	121.4(2)	C(22)-C(21)-O(5)	119.75(19)
C(20)-C(21)-O(5)	118.84(19)	C(21)-C(22)-O(6)#2	120.1(2)
C(21)-C(22)-C(20)#2	121.3(2)	O(6)#2-C(22)-C(20)#2	118.65(19)
C(28)-C(26)-C(27)	111.9(2)	C(28)-C(26)-P(3)	108.66(18)
C(27)-C(26)-P(3)	112.76(18)	C(30)-C(29)-C(31)	111.2(3)
C(30)-C(29)-P(3)	109.85(19)	C(31)-C(29)-P(3)	110.19(19)
C(34)-C(32)-C(33)	111.2(3)	C(34)-C(32)-P(4)	111.99(19)
C(33)-C(32)-P(4)	107.96(18)	C(36)-C(35)-C(37)	111.7(3)
C(36)-C(35)-P(4)	109.2(2)	C(37)-C(35)-P(4)	112.9(2)
O(7)-C(38)-O(8)	128.0(3)		

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z #2 -x+1,-y+2,-z+1

Table S21. Torsion angles [°] for **$Ni_2(OCHO)_2$**•3/2MeOH.

C(7)-P(1)-O(1)-C(2)	-126.56(16)	C(10)-P(1)-O(1)-C(2)	122.11(16)
Ni(1)-P(1)-O(1)-C(2)	-1.46(16)	C(13)-P(2)-O(2)-C(3)#1	130.71(16)
C(16)-P(2)-O(2)-C(3)#1	-118.84(16)	Ni(1)-P(2)-O(2)-C(3)#1	5.93(16)
P(1)-Ni(1)-C(1)-C(2)	-1.56(18)	P(2)-Ni(1)-C(1)-C(2)	-177.63(19)
P(1)-Ni(1)-C(1)-C(3)#1	179.62(19)	P(2)-Ni(1)-C(1)-C(3)#1	3.55(17)
C(3)#1-C(1)-C(2)-C(3)	-0.5(4)	Ni(1)-C(1)-C(2)-C(3)	-179.41(17)
C(3)#1-C(1)-C(2)-O(1)	179.92(19)	Ni(1)-C(1)-C(2)-O(1)	1.1(3)
P(1)-O(1)-C(2)-C(3)	-179.07(17)	P(1)-O(1)-C(2)-C(1)	0.5(3)
C(1)-C(2)-C(3)-O(2)#1	-179.5(2)	O(1)-C(2)-C(3)-O(2)#1	0.1(3)
C(1)-C(2)-C(3)-C(1)#1	0.6(4)	O(1)-C(2)-C(3)-C(1)#1	-179.9(2)

O(1)-P(1)-C(7)-C(9)	65.8(2)	C(10)-P(1)-C(7)-C(9)	172.31(19)
Ni(1)-P(1)-C(7)-C(9)	-51.1(2)	O(1)-P(1)-C(7)-C(8)	-58.5(2)
C(10)-P(1)-C(7)-C(8)	48.0(2)	Ni(1)-P(1)-C(7)-C(8)	-175.40(18)
O(1)-P(1)-C(10)-C(12)	-71.2(2)	C(7)-P(1)-C(10)-C(12)	-178.3(2)
Ni(1)-P(1)-C(10)-C(12)	44.7(2)	O(1)-P(1)-C(10)-C(11)	165.1(2)
C(7)-P(1)-C(10)-C(11)	58.0(2)	Ni(1)-P(1)-C(10)-C(11)	-79.1(2)
O(2)-P(2)-C(13)-C(15)	-71.02(19)	C(16)-P(2)-C(13)-C(15)	-177.23(18)
Ni(1)-P(2)-C(13)-C(15)	44.1(2)	O(2)-P(2)-C(13)-C(14)	166.00(19)
C(16)-P(2)-C(13)-C(14)	59.8(2)	Ni(1)-P(2)-C(13)-C(14)	-78.8(2)
O(2)-P(2)-C(16)-C(18)	69.3(2)	C(13)-P(2)-C(16)-C(18)	175.2(2)
Ni(1)-P(2)-C(16)-C(18)	-46.1(2)	O(2)-P(2)-C(16)-C(17)	-54.4(2)
C(13)-P(2)-C(16)-C(17)	51.5(2)	Ni(1)-P(2)-C(16)-C(17)	-169.75(17)
Ni(1)-O(3)-C(19)-O(4)	-0.7(5)		
C(29)-P(3)-O(5)-C(21)	118.38(17)	C(26)-P(3)-O(5)-C(21)	-130.63(17)
Ni(2)-P(3)-O(5)-C(21)	-5.36(17)	C(32)-P(4)-O(6)-C(22)#2	124.25(18)
C(35)-P(4)-O(6)-C(22)#2	-125.11(18)	Ni(2)-P(4)-O(6)-C(22)#2	0.33(18)
P(3)-Ni(2)-C(20)-C(21)	-5.01(18)	P(4)-Ni(2)-C(20)-C(21)	178.9(2)
P(3)-Ni(2)-C(20)-C(22)#2	177.7(2)	P(4)-Ni(2)-C(20)-C(22)#2	1.69(18)
C(22)#2-C(20)-C(21)-C(22)	-0.4(4)	Ni(2)-C(20)-C(21)-C(22)	-177.74(18)
C(22)#2-C(20)-C(21)-O(5)	-179.7(2)	Ni(2)-C(20)-C(21)-O(5)	3.0(3)
P(3)-O(5)-C(21)-C(22)	-177.10(18)	P(3)-O(5)-C(21)-C(20)	2.2(3)
C(20)-C(21)-C(22)-O(6)#2	-179.4(2)	O(5)-C(21)-C(22)-O(6)#2	-0.1(3)
C(20)-C(21)-C(22)-C(20)#2	0.4(4)	O(5)-C(21)-C(22)-C(20)#2	179.7(2)
O(5)-P(3)-C(26)-C(28)	67.40(19)	C(29)-P(3)-C(26)-C(28)	174.58(18)
Ni(2)-P(3)-C(26)-C(28)	-49.5(2)	O(5)-P(3)-C(26)-C(27)	-57.3(2)
C(29)-P(3)-C(26)-C(27)	49.9(2)	Ni(2)-P(3)-C(26)-C(27)	-174.21(15)
O(5)-P(3)-C(29)-C(30)	-67.8(2)	C(26)-P(3)-C(29)-C(30)	-175.0(2)
Ni(2)-P(3)-C(29)-C(30)	48.5(3)	O(5)-P(3)-C(29)-C(31)	169.34(19)
C(26)-P(3)-C(29)-C(31)	62.2(2)	Ni(2)-P(3)-C(29)-C(31)	-74.4(2)
O(6)-P(4)-C(32)-C(34)	166.21(19)	C(35)-P(4)-C(32)-C(34)	59.7(2)
Ni(2)-P(4)-C(32)-C(34)	-78.9(2)	O(6)-P(4)-C(32)-C(33)	-71.0(2)
C(35)-P(4)-C(32)-C(33)	-177.5(2)	Ni(2)-P(4)-C(32)-C(33)	43.9(2)
O(6)-P(4)-C(35)-C(36)	71.9(3)	C(32)-P(4)-C(35)-C(36)	177.6(2)
Ni(2)-P(4)-C(35)-C(36)	-44.2(3)	O(6)-P(4)-C(35)-C(37)	-53.0(2)
C(32)-P(4)-C(35)-C(37)	52.6(2)	Ni(2)-P(4)-C(35)-C(37)	-169.14(18)
Ni(2)-O(7)-C(38)-O(8)	2.9(5)		

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z #2 -x+1,-y+2,-z+1

Table S22. Hydrogen bonding interactions [Å and °] in **$Ni_2(OCHO)_2$**•3/2MeOH.

D-H...A	**d(D-H)**	**d(H...A)**	**d(D...A)**	**<(DHA)**
O9-H9...O4	0.90	1.83	2.711(3)	165
O10-H10…O9	0.90	1.92	2.810(6)	167

Table S23. Crystal data and structure refinement for **NiH**•1/2C_4H_8O.

CCDC deposition number	1864165	
Formula	$C_{18}H_{32}O_2P_2Ni.1/2C_4H_8O$	
Formula weight	437.14	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 12.3740(5) Å	α = 70.1809(14)°
	b = 14.0249(6) Å	β = 69.4817(12)°
	c = 14.8782(6) Å	γ = 78.7225(14)°
Volume	2266.34(16) $Å^3$	
Z	4	
Density (calculated)	1.281 Mg/m^3	
Absorption coefficient	1.010 mm^{-1}	
F(000)	936	
Crystal size	0.136 x 0.104 x 0.073 mm^3	
θ range for data collection	2.840 to 28.341°	
Index ranges	$-16 \leq h \leq 16$, $-18 \leq k \leq 18$, $-19 \leq l \leq 19$	
Reflections collected	74676	
Independent reflections	11291 [R_{int} = 0.0369]	
Completeness to θ = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.862 and 0.792	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11291 / 120 / 529	
Goodness-of-fit on F^2	1.047	
Final R indices [I>2σ(I)]	R1 = 0.0383, wR2 = 0.0995	
R indices (all data)	R1 = 0.0445, wR2 = 0.1048	
Largest diff. peak and hole	1.618 and -0.569 $eÅ^{-3}$	

Table S24. Bond lengths [Å] and angles [°] for **NiH**•1/2C_4H_8O.

Ni(1)-C(1A)	1.8938(18)	Ni(1)-P(1A)	2.1090(5)
Ni(1)-P(2A)	2.1097(5)	Ni(1)-H(1)	1.54(3)
P(1A)-O(1A)	1.6687(14)	P(1A)-C(7A)	1.8259(19)
P(1A)-C(10A)	1.8286(19)	P(2A)-O(2A)	1.6681(14)
P(2A)-C(13A)	1.8258(19)	P(2A)-C(16A)	1.826(2)
O(1A)-C(2A)	1.393(2)	O(2A)-C(6A)	1.394(2)
C(1A)-C(6A)	1.395(2)	C(1A)-C(2A)	1.395(2)
C(2A)-C(3A)	1.389(2)	C(3A)-C(4A)	1.406(3)
C(4A)-C(5A)	1.390(3)	C(5A)-C(6A)	1.386(3)
C(7A)-C(9A)	1.529(3)	C(7A)-C(8A)	1.531(3)
C(10A)-C(11A)	1.527(3)	C(10A)-C(12A)	1.535(3)
C(13A)-C(15A)	1.523(3)	C(13A)-C(14A)	1.531(3)
C(16A)-C(18A)	1.528(3)	C(16A)-C(17A)	1.532(3)
Ni(2)-C(1B)	1.8921(18)	Ni(2)-P(2B)	2.1103(5)
Ni(2)-P(1B)	2.1119(5)	Ni(2)-H(2)	1.47(3)
P(1B)-O(1B)	1.6721(13)	P(1B)-C(10B)	1.822(2)
P(1B)-C(7B)	1.824(2)	P(2B)-O(2B)	1.6716(14)
P(2B)-C(16B)	1.830(2)	P(2B)-C(13B)	1.830(2)
O(1B)-C(2B)	1.390(2)	O(2B)-C(6B)	1.395(2)
C(1B)-C(6B)	1.392(3)	C(1B)-C(2B)	1.394(2)
C(2B)-C(3B)	1.389(3)	C(3B)-C(4B)	1.391(3)
C(4B)-C(5B)	1.397(3)	C(5B)-C(6B)	1.396(3)
C(7B)-C(9B)	1.528(3)	C(7B)-C(8B)	1.533(3)
C(10B)-C(11B)	1.528(3)	C(10B)-C(12B)	1.529(3)
C(13B)-C(15B)	1.525(3)	C(13B)-C(14B)	1.529(3)
C(16B)-C(17B)	1.526(3)	C(16B)-C(18B)	1.532(3)
O(20A)-C(24A)	1.385(10)	O(20A)-C(21A)	1.489(14)
C(21A)-C(22A)	1.471(16)	C(22A)-C(23A)	1.468(11)
C(23A)-C(24A)	1.225(12)	O(20B)-C(21B)	1.319(13)
O(20B)-C(24B)	1.381(8)	C(21B)-C(22B)	1.383(15)
C(22B)-C(23B)	1.513(10)	C(23B)-C(24B)	1.687(11)
C(1A)-Ni(1)-P(1A)	83.08(6)	C(1A)-Ni(1)-P(2A)	82.79(6)
P(1A)-Ni(1)-P(2A)	165.85(2)	C(1A)-Ni(1)-H(1)	178.5(12)
P(1A)-Ni(1)-H(1)	95.5(11)	P(2A)-Ni(1)-H(1)	98.6(11)
O(1A)-P(1A)-C(7A)	102.03(8)	O(1A)-P(1A)-C(10A)	100.59(8)
C(7A)-P(1A)-C(10A)	106.75(9)	O(1A)-P(1A)-Ni(1)	106.62(5)
C(7A)-P(1A)-Ni(1)	118.29(6)	C(10A)-P(1A)-Ni(1)	119.57(7)
O(2A)-P(2A)-C(13A)	100.04(8)	O(2A)-P(2A)-C(16A)	101.12(8)
C(13A)-P(2A)-C(16A)	107.02(9)	O(2A)-P(2A)-Ni(1)	106.99(5)
C(13A)-P(2A)-Ni(1)	120.47(7)	C(16A)-P(2A)-Ni(1)	117.86(6)
C(2A)-O(1A)-P(1A)	111.79(11)	C(6A)-O(2A)-P(2A)	111.40(11)
C(6A)-C(1A)-C(2A)	116.44(16)	C(6A)-C(1A)-Ni(1)	121.88(14)

C(2A)-C(1A)-Ni(1)	121.68(13)	C(3A)-C(2A)-O(1A)	119.62(16)
C(3A)-C(2A)-C(1A)	123.56(17)	O(1A)-C(2A)-C(1A)	116.82(16)
C(2A)-C(3A)-C(4A)	116.92(17)	C(5A)-C(4A)-C(3A)	122.09(17)
C(6A)-C(5A)-C(4A)	117.88(17)	C(5A)-C(6A)-O(2A)	120.00(16)
C(5A)-C(6A)-C(1A)	123.09(17)	O(2A)-C(6A)-C(1A)	116.91(16)
C(9A)-C(7A)-C(8A)	111.60(18)	C(9A)-C(7A)-P(1A)	113.27(14)
C(8A)-C(7A)-P(1A)	109.50(14)	C(11A)-C(10A)-C(12A)	111.36(18)
C(11A)-C(10A)-P(1A)	111.59(13)	C(12A)-C(10A)-P(1A)	109.03(14)
C(15A)-C(13A)-C(14A)	111.56(18)	C(15A)-C(13A)-P(2A)	110.78(14)
C(14A)-C(13A)-P(2A)	109.18(14)	C(18A)-C(16A)-C(17A)	111.83(17)
C(18A)-C(16A)-P(2A)	113.71(14)	C(17A)-C(16A)-P(2A)	107.96(14)

C(1B)-Ni(2)-P(2B)	83.21(6)	C(1B)-Ni(2)-P(1B)	82.92(6)
P(2B)-Ni(2)-P(1B)	166.12(2)	C(1B)-Ni(2)-H(2)	178.9(11)
P(2B)-Ni(2)-H(2)	95.7(11)	P(1B)-Ni(2)-H(2)	98.1(11)
O(1B)-P(1B)-C(10B)	99.93(8)	O(1B)-P(1B)-C(7B)	101.62(8)
C(10B)-P(1B)-C(7B)	107.35(9)	O(1B)-P(1B)-Ni(2)	106.62(5)
C(10B)-P(1B)-Ni(2)	120.84(7)	C(7B)-P(1B)-Ni(2)	117.22(6)
O(2B)-P(2B)-C(16B)	101.94(8)	O(2B)-P(2B)-C(13B)	100.43(9)
C(16B)-P(2B)-C(13B)	107.11(9)	O(2B)-P(2B)-Ni(2)	106.53(5)
C(16B)-P(2B)-Ni(2)	118.14(7)	C(13B)-P(2B)-Ni(2)	119.64(7)
C(2B)-O(1B)-P(1B)	111.64(11)	C(6B)-O(2B)-P(2B)	111.50(11)
C(6B)-C(1B)-C(2B)	116.57(16)	C(6B)-C(1B)-Ni(2)	121.55(13)
C(2B)-C(1B)-Ni(2)	121.87(14)	C(3B)-C(2B)-O(1B)	120.07(16)
C(3B)-C(2B)-C(1B)	122.99(17)	O(1B)-C(2B)-C(1B)	116.94(16)
C(2B)-C(3B)-C(4B)	117.84(17)	C(3B)-C(4B)-C(5B)	122.17(17)
C(6B)-C(5B)-C(4B)	117.08(17)	C(1B)-C(6B)-O(2B)	117.20(16)
C(1B)-C(6B)-C(5B)	123.31(17)	O(2B)-C(6B)-C(5B)	119.48(16)
C(9B)-C(7B)-C(8B)	112.17(17)	C(9B)-C(7B)-P(1B)	114.15(14)
C(8B)-C(7B)-P(1B)	108.22(13)	C(11B)-C(10B)-C(12B)	111.58(18)
C(11B)-C(10B)-P(1B)	110.54(15)	C(12B)-C(10B)-P(1B)	109.00(15)
C(15B)-C(13B)-C(14B)	111.1(2)	C(15B)-C(13B)-P(2B)	111.16(15)
C(14B)-C(13B)-P(2B)	108.46(15)	C(17B)-C(16B)-C(18B)	111.57(19)
C(17B)-C(16B)-P(2B)	108.77(14)	C(18B)-C(16B)-P(2B)	113.57(14)

C(24A)-O(20A)-C(21A)	112.9(7)	C(22A)-C(21A)-O(20A)	94.1(9)
C(23A)-C(22A)-C(21A)	111.1(7)	C(24A)-C(23A)-C(22A)	107.8(8)
C(23A)-C(24A)-O(20A)	110.7(8)	C(21B)-O(20B)-C(24B)	106.8(8)
O(20B)-C(21B)-C(22B)	117.3(10)	C(21B)-C(22B)-C(23B)	102.9(7)
C(22B)-C(23B)-C(24B)	96.7(6)	O(20B)-C(24B)-C(23B)	106.4(5)

Table S25. Torsion angles [°] for **NiH**•1/2C_4H_8O.

C(7A)-P(1A)-O(1A)-C(2A)	123.81(13)	C(10A)-P(1A)-O(1A)-C(2A)	-126.33(13)
Ni(1)-P(1A)-O(1A)-C(2A)	-0.90(13)	C(13A)-P(2A)-O(2A)-C(6A)	-128.35(13)
C(16A)-P(2A)-O(2A)-C(6A)	121.92(13)	Ni(1)-P(2A)-O(2A)-C(6A)	-2.01(13)
P(1A)-Ni(1)-C(1A)-C(6A)	179.78(15)	P(2A)-Ni(1)-C(1A)-C(6A)	-1.01(14)
P(1A)-Ni(1)-C(1A)-C(2A)	-0.80(14)	P(2A)-Ni(1)-C(1A)-C(2A)	178.41(15)
P(1A)-O(1A)-C(2A)-C(3A)	180.00(14)	P(1A)-O(1A)-C(2A)-C(1A)	0.4(2)
C(6A)-C(1A)-C(2A)-C(3A)	0.3(3)	Ni(1)-C(1A)-C(2A)-C(3A)	-179.16(15)
C(6A)-C(1A)-C(2A)-O(1A)	179.88(15)	Ni(1)-C(1A)-C(2A)-O(1A)	0.4(2)
O(1A)-C(2A)-C(3A)-C(4A)	178.80(17)	C(1A)-C(2A)-C(3A)-C(4A)	-1.6(3)
C(2A)-C(3A)-C(4A)-C(5A)	2.0(3)	C(3A)-C(4A)-C(5A)-C(6A)	-1.1(3)
C(4A)-C(5A)-C(6A)-O(2A)	179.89(17)	C(4A)-C(5A)-C(6A)-C(1A)	-0.4(3)
P(2A)-O(2A)-C(6A)-C(5A)	-178.81(14)	P(2A)-O(2A)-C(6A)-C(1A)	1.4(2)
C(2A)-C(1A)-C(6A)-C(5A)	0.8(3)	Ni(1)-C(1A)-C(6A)-C(5A)	-179.79(14)
C(2A)-C(1A)-C(6A)-O(2A)	-179.50(15)	Ni(1)-C(1A)-C(6A)-O(2A)	-0.1(2)
O(1A)-P(1A)-C(7A)-C(9A)	46.89(17)	C(10A)-P(1A)-C(7A)-C(9A)	-58.21(18)
Ni(1)-P(1A)-C(7A)-C(9A)	163.43(13)	O(1A)-P(1A)-C(7A)-C(8A)	-78.38(15)
C(10A)-P(1A)-C(7A)-C(8A)	176.52(14)	Ni(1)-P(1A)-C(7A)-C(8A)	38.16(16)
O(1A)-P(1A)-C(10A)-C(11A)	-158.52(14)	C(7A)-P(1A)-C(10A)-C(11A)	-52.40(17)
Ni(1)-P(1A)-C(10A)-C(11A)	85.33(15)	O(1A)-P(1A)-C(10A)-C(12A)	78.05(15)
C(7A)-P(1A)-C(10A)-C(12A)	-175.82(15)	Ni(1)-P(1A)-C(10A)-C(12A)	-38.10(17)
O(2A)-P(2A)-C(13A)-C(15A)	-166.84(14)	C(16A)-P(2A)-C(13A)-C(15A)	-61.83(17)
Ni(1)-P(2A)-C(13A)-C(15A)	76.52(16)	O(2A)-P(2A)-C(13A)-C(14A)	69.91(15)
C(16A)-P(2A)-C(13A)-C(14A)	174.93(14)	Ni(1)-P(2A)-C(13A)-C(14A)	-46.73(16)
O(2A)-P(2A)-C(16A)-C(18A)	57.86(16)	C(13A)-P(2A)-C(16A)-C(18A)	-46.38(17)
Ni(1)-P(2A)-C(16A)-C(18A)	174.00(13)	O(2A)-P(2A)-C(16A)-C(17A)	-66.84(15)
C(13A)-P(2A)-C(16A)-C(17A)	-171.08(14)	Ni(1)-P(2A)-C(16A)-C(17A)	49.31(16)
C(10B)-P(1B)-O(1B)-C(2B)	-127.27(13)	C(7B)-P(1B)-O(1B)-C(2B)	122.54(13)
Ni(2)-P(1B)-O(1B)-C(2B)	-0.74(13)	C(16B)-P(2B)-O(2B)-C(6B)	123.74(13)
C(13B)-P(2B)-O(2B)-C(6B)	-126.10(13)	Ni(2)-P(2B)-O(2B)-C(6B)	-0.71(13)
P(2B)-Ni(2)-C(1B)-C(6B)	-0.27(15)	P(1B)-Ni(2)-C(1B)-C(6B)	179.11(16)
P(2B)-Ni(2)-C(1B)-C(2B)	179.57(16)	P(1B)-Ni(2)-C(1B)-C(2B)	-1.05(15)
P(1B)-O(1B)-C(2B)-C(3B)	-179.89(14)	P(1B)-O(1B)-C(2B)-C(1B)	0.0(2)
C(6B)-C(1B)-C(2B)-C(3B)	0.6(3)	Ni(2)-C(1B)-C(2B)-C(3B)	-179.22(14)
C(6B)-C(1B)-C(2B)-O(1B)	-179.29(15)	Ni(2)-C(1B)-C(2B)-O(1B)	0.9(2)
O(1B)-C(2B)-C(3B)-C(4B)	179.21(17)	C(1B)-C(2B)-C(3B)-C(4B)	-0.7(3)
C(2B)-C(3B)-C(4B)-C(5B)	-0.6(3)	C(3B)-C(4B)-C(5B)-C(6B)	1.9(3)
C(2B)-C(1B)-C(6B)-O(2B)	-179.98(16)	Ni(2)-C(1B)-C(6B)-O(2B)	-0.1(2)
C(2B)-C(1B)-C(6B)-C(5B)	0.8(3)	Ni(2)-C(1B)-C(6B)-C(5B)	-179.39(15)
P(2B)-O(2B)-C(6B)-C(1B)	0.6(2)	P(2B)-O(2B)-C(6B)-C(5B)	179.86(14)
C(4B)-C(5B)-C(6B)-C(1B)	-2.0(3)	C(4B)-C(5B)-C(6B)-O(2B)	178.80(17)
O(1B)-P(1B)-C(7B)-C(9B)	59.15(16)	C(10B)-P(1B)-C(7B)-C(9B)	-45.25(17)
Ni(2)-P(1B)-C(7B)-C(9B)	174.88(12)	O(1B)-P(1B)-C(7B)-C(8B)	-66.51(14)
C(10B)-P(1B)-C(7B)-C(8B)	-170.91(14)	Ni(2)-P(1B)-C(7B)-C(8B)	49.21(15)
O(1B)-P(1B)-C(10B)-C(11B)	-165.88(15)	C(7B)-P(1B)-C(10B)-C(11B)	-60.28(17)

Ni(2)-P(1B)-C(10B)-C(11B)	77.85(16)	O(1B)-P(1B)-C(10B)-C(12B)	71.13(15)
C(7B)-P(1B)-C(10B)-C(12B)	176.73(14)	Ni(2)-P(1B)-C(10B)-C(12B)	-45.14(17)
O(2B)-P(2B)-C(13B)-C(15B)	-162.94(16)	C(16B)-P(2B)-C(13B)-C(15B)	-56.87(18)
Ni(2)-P(2B)-C(13B)-C(15B)	81.11(17)	O(2B)-P(2B)-C(13B)-C(14B)	74.63(17)
C(16B)-P(2B)-C(13B)-C(14B)	-179.30(16)	Ni(2)-P(2B)-C(13B)-C(14B)	-41.32(18)
O(2B)-P(2B)-C(16B)-C(17B)	-76.29(16)	C(13B)-P(2B)-C(16B)-C(17B)	178.72(15)
Ni(2)-P(2B)-C(16B)-C(17B)	40.00(17)	O(2B)-P(2B)-C(16B)-C(18B)	48.60(17)
C(13B)-P(2B)-C(16B)-C(18B)	-56.39(18)	Ni(2)-P(2B)-C(16B)-C(18B)	164.89(13)

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