Supplementary Information

Reduction of CO_2 and SO_2 with low valent Nickel compounds under mild conditions

Lucero González-Sebastián, Marcos Flores-Alamo and Juventino J. García*

Facultad de Química. Universidad Nacional Autónoma de México. México City. 04510. México

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1.- $^{31}P\{1H\}$ NMR of complex (1)

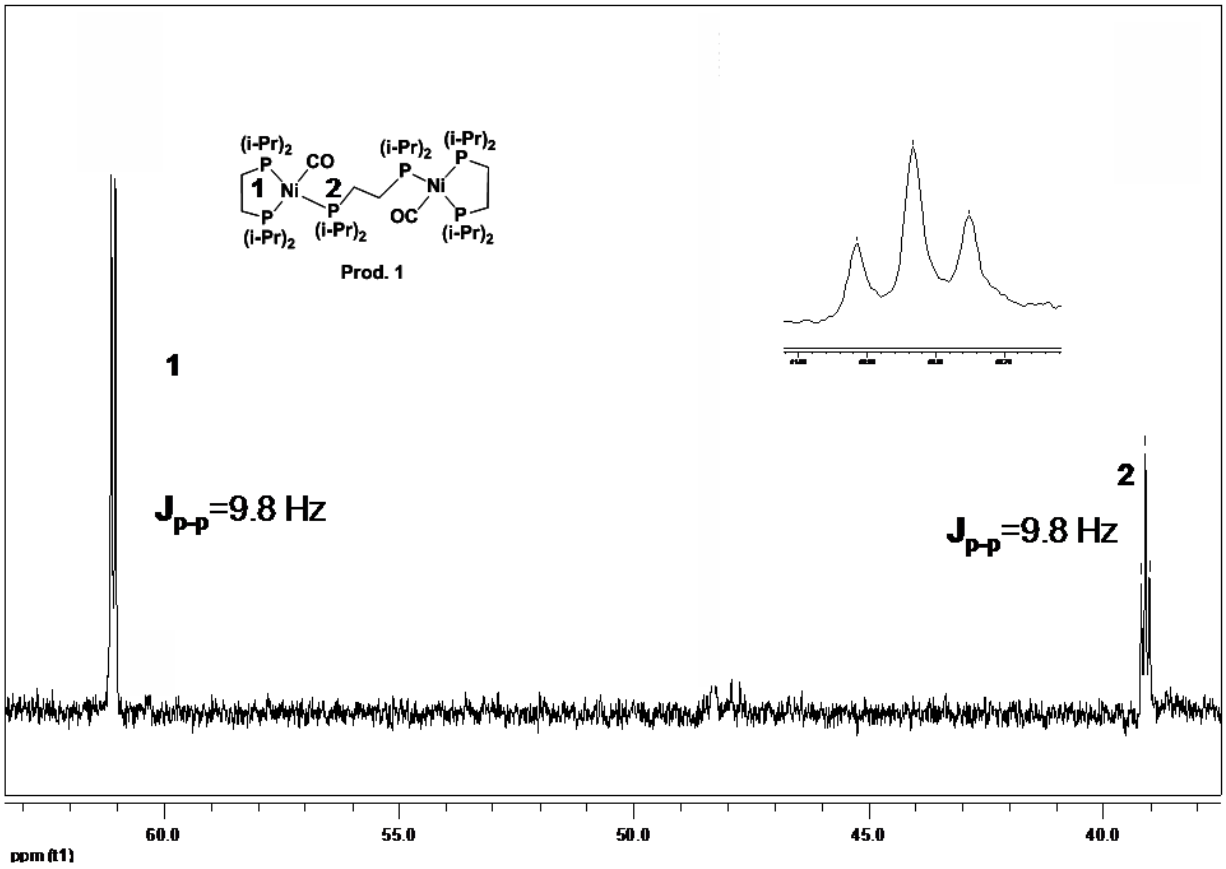

Figure S1. $^{31}P\{^{1}H\}$-NMR spectra of complex (**1**) in Toluene-d_8

2.- $^{31}P\{^{1}H\}$, $^{13}C\{^{1}H\}$ and MS-EI^{+} spectra of complex (2)

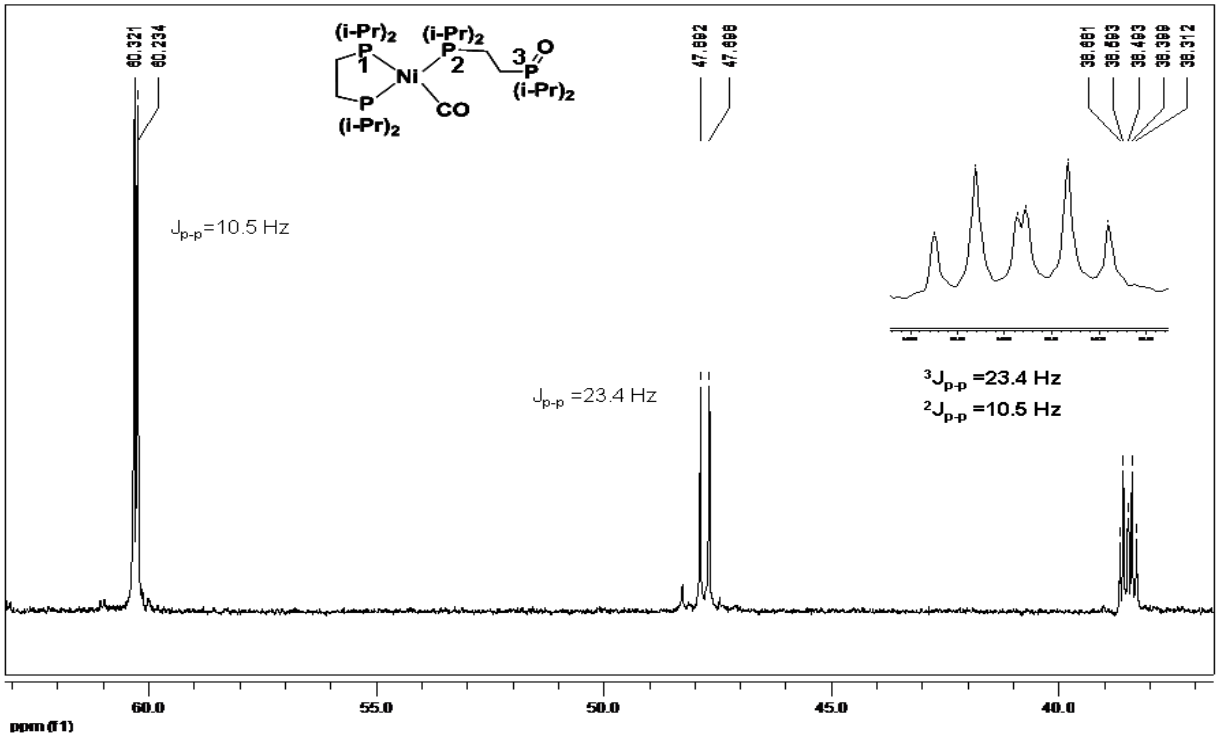

Figure S2. $^{31}P\{^{1}H\}$-NMR spectra of complex (**2**) in Toluene-d_8

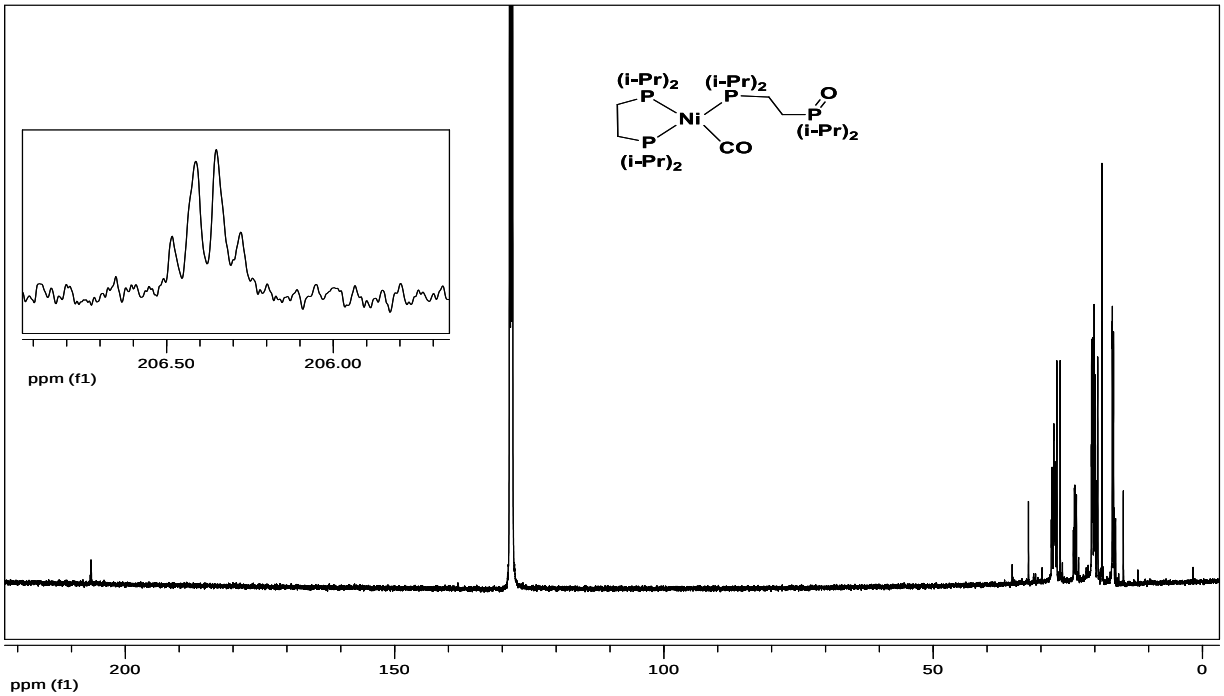

Figure S3. $^{13}C\{^{1}H\}$-NMR spectra of complex (**2**) in Benzene-d_6

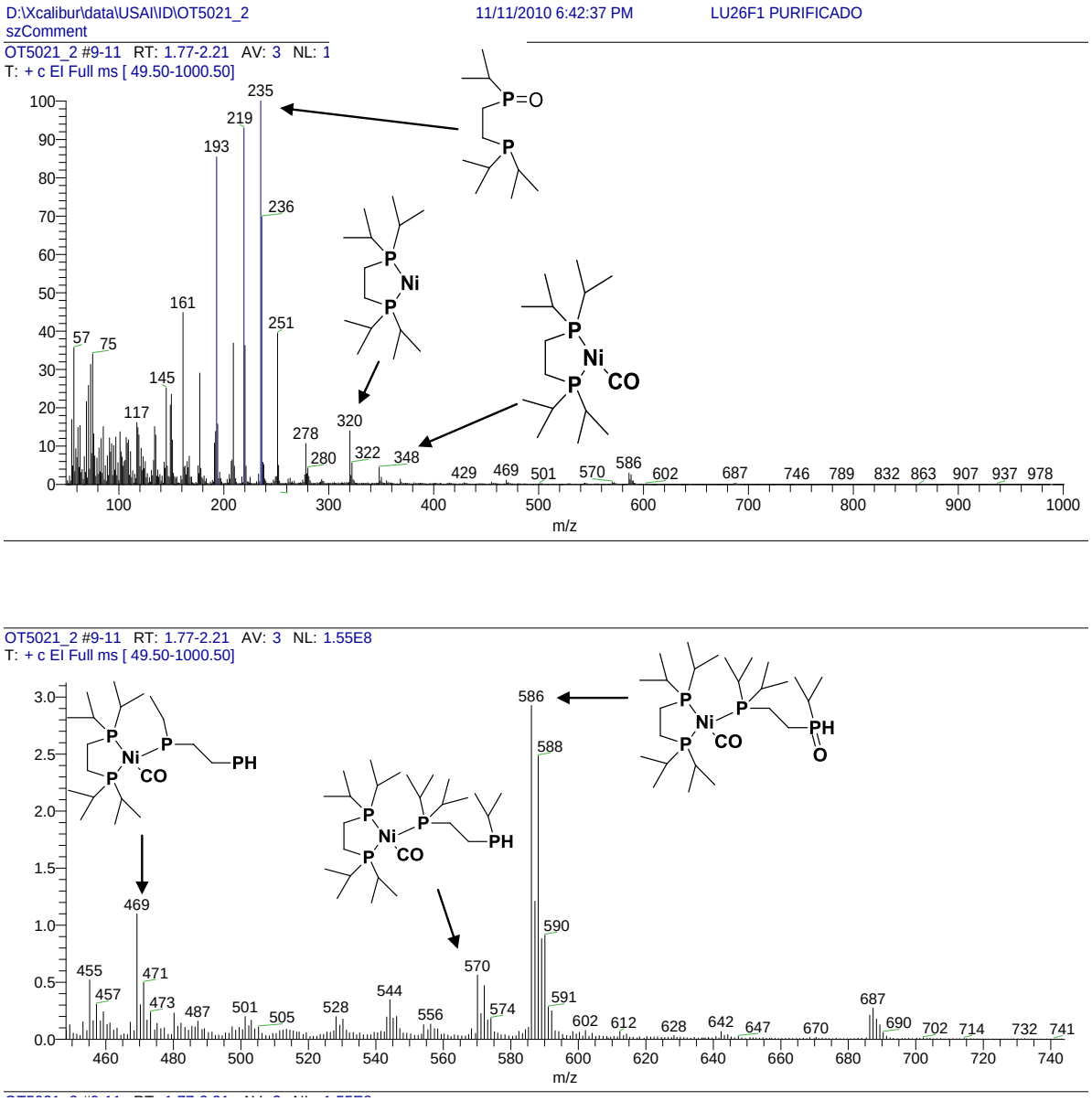

Figure S4. MS-EI^{+} spectra of complex (**2**)

3.- $^{31}P\{^{1}H\}$ and $^{13}C\{^{1}H\}$ spectra of the thermolysis of complex (2)

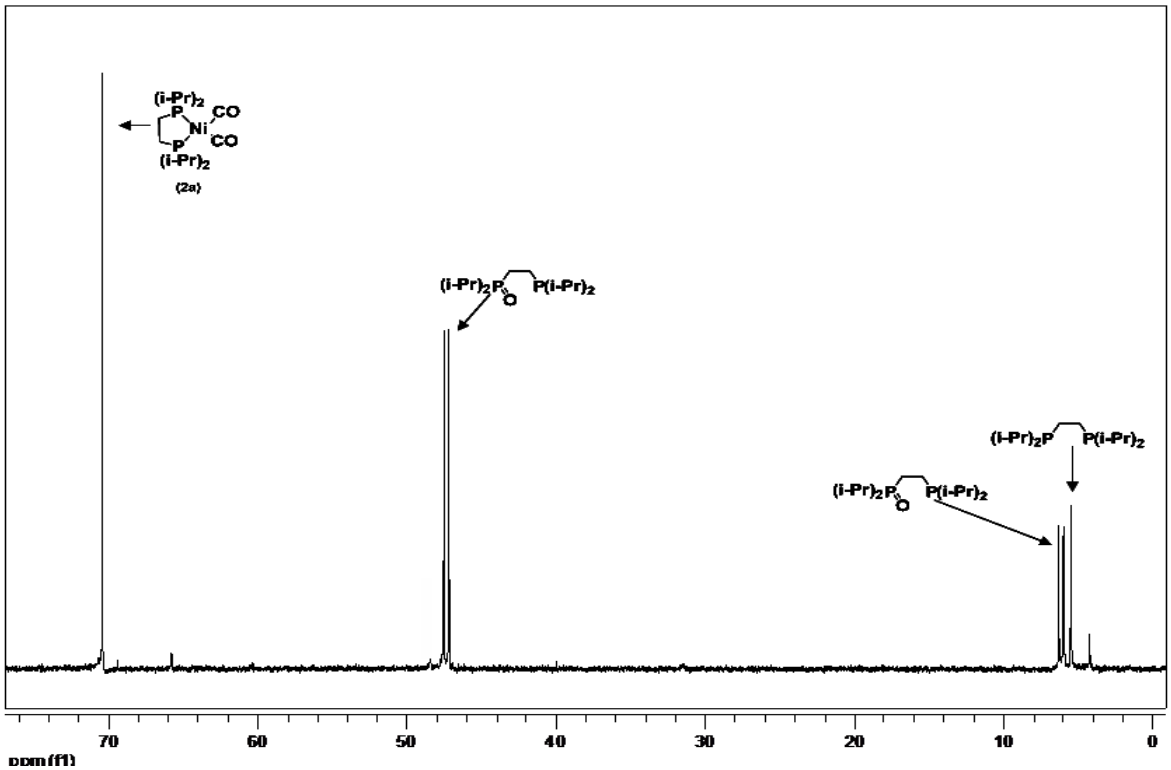

Figure S5. $^{31}P\{^{1}H\}$-NMR spectra of thermolysis of complex (**2**) recorded after 5h at 100ºC in Toluene-d_8

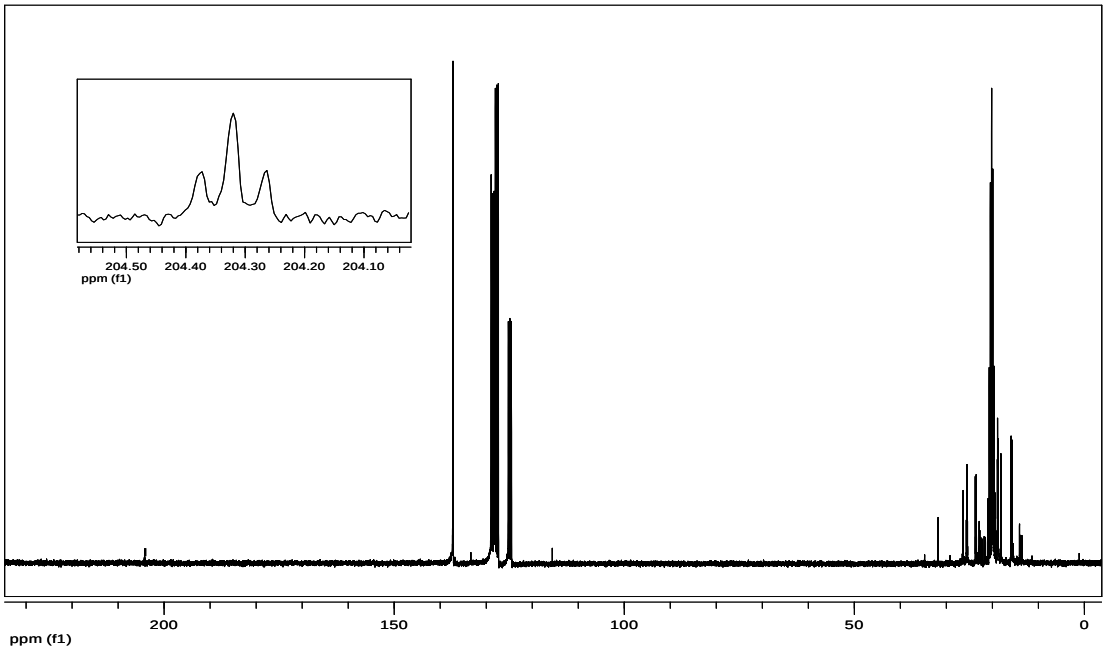

Figure S6. $^{13}C\{^{1}H\}$-NMR spectra of thermolysis of complex (**2**) recorded after 5h at 100ºC in Toluene-d_8

4.- $^{31}P\{^{1}H\}$ spectrum of the reaction of complex (2) with CO_2

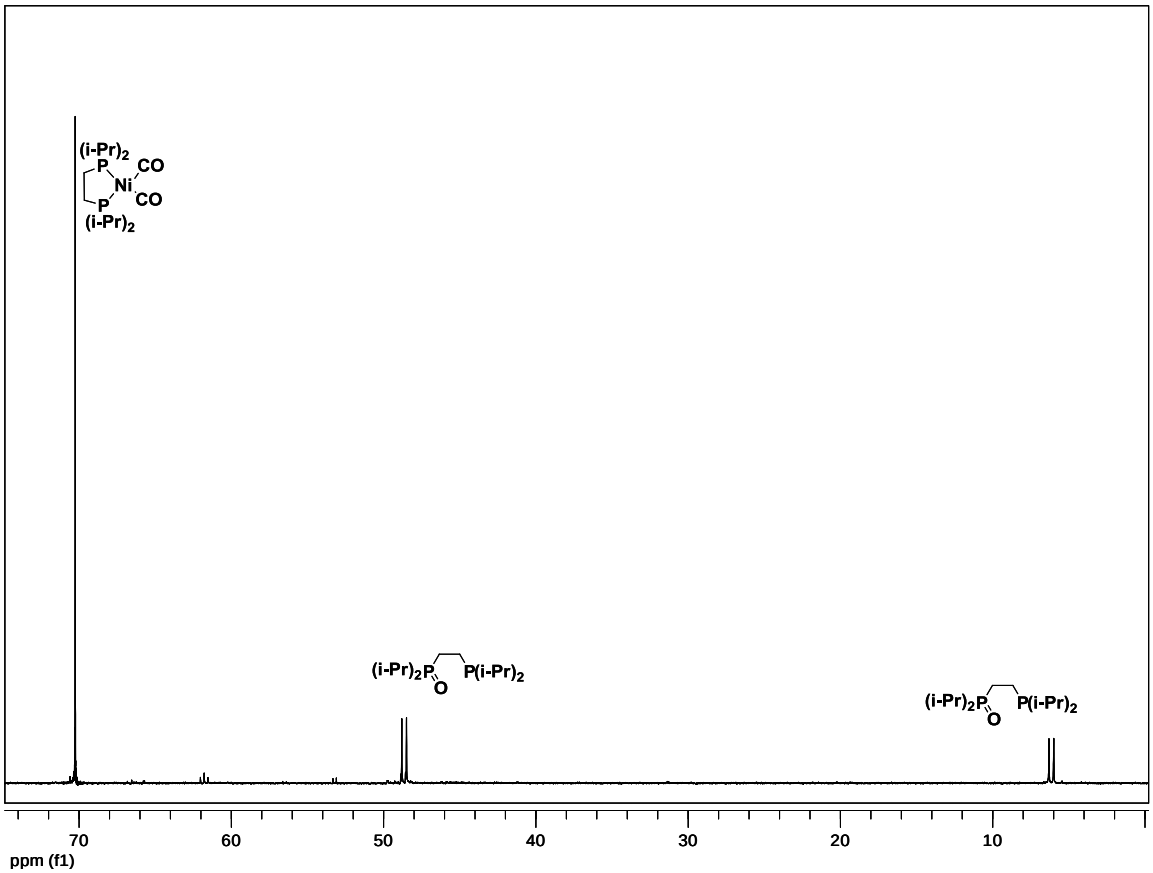

Figure S7. $^{31}P\{^{1}H\}$ spectrum of the reaction of complex (**2**) with CO_2

5.-Crystalographic data of complexes (1) and (5)

Table SI. Summary of crystallographic data for complex (**1**)

Empirical formula	C44 H96 Ni2 O2 P6	
Formula weight	960.45	
Temperature	130(2) K	
Wavelength	1.54180 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.7220(6) Å	α= 102.320(6)°.
	b = 11.5158(8) Å	β= 91.092(6)°.
	c = 14.3744(10) Å	γ = 112.112(7)°.
Volume	1298.88(16) $Å^3$	
Z	1	
Density (calculated)	1.228 Mg/m^3	
Absorption coefficient	2.881 mm^{-1}	
F(000)	522	
Crystal size	0.28 x0.18 x 0.049 mm^3	
Theta range for data collection	4.27 to 68.11°.	
Index ranges	-10<=h<=7, -12<=k<=13, -17<=l<=17	
Reflections collected	8546	
Independent reflections	4721 [R(int) = 0.0298]	
Completeness to theta = 68.11°	99.3 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4721 / 0 / 256	
Goodness-of-fit on F^2	1.083	
Final R indices [I>2sigma(I)]	R1 = 0.0394, wR2 = 0.0905	
R indices (all data)	R1 = 0.0499, wR2 = 0.0957	
Largest diff. peak and hole	0.472 and -0.357 $e.Å^{-3}$	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for (**1**).U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ni(1)	3656(1)	2554(1)	2918(1)	12(1)
P(1)	5299(1)	3219(1)	1829(1)	14(1)
P(2)	2720(1)	554(1)	2073(1)	14(1)
P(3)	4635(1)	2886(1)	4432(1)	11(1)
O(1)	1190(3)	3706(2)	2992(2)	30(1)
C(1)	-414(4)	431(3)	1405(2)	30(1)
C(2)	434(4)	-378(3)	1747(2)	23(1)
C(3)	-394(4)	-865(3)	2588(2)	31(1)
C(4)	2548(5)	-2069(3)	1736(2)	34(1)
C(5)	3387(4)	-702(3)	2369(2)	20(1)
C(6)	5276(4)	-260(3)	2392(2)	30(1)
C(7)	2963(4)	3410(3)	549(2)	31(1)
C(8)	4707(4)	4167(3)	1087(2)	22(1)
C(9)	4799(5)	5457(3)	1695(2)	33(1)
C(10)	8239(4)	5237(3)	2834(2)	32(1)
C(11)	7625(4)	4022(3)	2019(2)	22(1)
C(12)	8521(4)	4296(4)	1131(2)	38(1)
C(13)	5086(4)	1748(3)	905(2)	20(1)
C(14)	3421(4)	623(3)	864(2)	20(1)
C(15)	6878(4)	2698(3)	5842(2)	24(1)
C(16)	6372(3)	2421(3)	4768(2)	17(1)
C(17)	7897(4)	3020(3)	4263(2)	29(1)
C(18)	1455(3)	2293(3)	5062(2)	19(1)
C(19)	3060(3)	2084(3)	5206(2)	15(1)
C(20)	2669(4)	639(3)	5029(2)	22(1)
C(21)	5412(3)	4579(2)	5152(2)	14(1)
C(22)	2152(3)	3236(3)	2974(2)	17(1)

Table S3.Summary of crystallographic data for complex (**5**)

Empirical formula	C14 H32 Ni O3 P2 S2	
Formula weight	433.17	
Temperature	130 (2) K	
Wavelength	0.71073 Å	
Crystal system	Tetragonal	
Space group	P42/n	
Unit cell dimensions	a = 22.7088(3) Å	α= 90°.
	b = 22.7088(3) Å	β= 90°.
	c = 7.9025(2) Å	γ = 90°.
Volume	4075.24(13) $Å^3$	
Z	8	
Density (calculated)	1.412 Mg/m^3	
Absorption coefficient	1.322 mm^{-1}	
F(000)	1840	
Crystal size	0.266 x 0.0823 x 0.0443 mm^3	
Theta range for data collection	3.59 to 26.05°.	
Index ranges	-28<=h<=28, -21<=k<=28, -9<=l<=9	
Reflections collected	29432	
Independent reflections	4020 [R(int) = 0.0494]	
Completeness to theta = 26.05°	99.8 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4020 / 0 / 207	
Goodness-of-fit on F^2	1.096	
Final R indices [I>2sigma(I)]	R1 = 0.0361, wR2 = 0.0961	
R indices (all data)	R1 = 0.0488, wR2 = 0.0989	
Largest diff. peak and hole	0.887 and -0.905 e.$Å^{-3}$	

Table S4. 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)
C(1)	8927(1)	4071(1)	9618(4)	32(1)
C(2)	9100(2)	4557(2)	10852(4)	41(1)
C(3)	9450(2)	3660(2)	9242(5)	43(1)
C(4)	8431(1)	3749(1)	6297(4)	33(1)
C(5)	8049(2)	3286(2)	7165(6)	55(1)
C(6)	8169(2)	3940(2)	4630(5)	45(1)
C(7)	7863(1)	5952(1)	4924(4)	27(1)
C(8)	7644(1)	5489(2)	3686(4)	37(1)
C(9)	8161(2)	6461(2)	3989(4)	46(1)
C(10)	8539(1)	6241(1)	7947(4)	23(1)
C(11)	7998(1)	6520(1)	8785(4)	31(1)
C(12)	8991(1)	6059(1)	9264(4)	31(1)
C(13)	8977(1)	5309(1)	5596(4)	24(1)
C(14)	9205(1)	4781(1)	6608(4)	26(1)
Ni(1)	7862(1)	4948(1)	8031(1)	18(1)
O(1)	7138(1)	5379(1)	8171(3)	27(1)
O(2)	6639(1)	5348(1)	10857(3)	52(1)
O(3)	6279(1)	4757(1)	8638(3)	40(1)
P(1)	8314(1)	5618(1)	6595(1)	19(1)
P(2)	8601(1)	4381(1)	7673(1)	23(1)
S(1)	6792(1)	5005(1)	9406(1)	24(1)
S(2)	7413(1)	4395(1)	9881(1)	44(1)