Alkyl Transfer Reactivity in the First Octahedral Isocyanide Complex of Nickel(II)

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$[Ni\{S_2P(OEt)_2\}_2]$ (**1**) reacts with 2 equiv of CNXyl (Xyl = 2,6-dimethylphenyl) to afford $[Ni\{S_2P(OEt)_2\}_2(CNXyl)_2]$ (**2**), which, as confirmed by X-ray crystallography, is the first octahedral isocyanide complex of Ni(II). Reaction of **2** with PCy_3 (2 equiv) produces square-planar $[Ni\{S_2P(O)(OEt)\}(PCy_3)(CNXyl)]$ (**3**). When **2** is reacted with only 1 equiv of PCy_3, the final product is the square-planar complex $[Ni\{S_2P(O)(OEt)\}(CNXyl)_2]$ (**4**), containing two isocyanide ligands. Compound **4** reacts with 2-fold excess PCy_3 to give **3** via isocyanide displacement. Both **3** and **4** contain one ethyldithiophosphate ligand, which is produced by the transfer of one ethyl group from a coordinated diethyl dithiophosphate of complex **2** to the leaving diethyl dithiophosphate ligand. Experimental evidence indicates that the phosphine plays a significant role in the alkyl transfer. Moreover, reaction of **1** with 2 equiv of *N*-*p*-tolyl-2-iminopyridine affords octahedral $[Ni\{S_2P(OEt)_2\}\{2\text{-pyCH=NC}_6H_4\text{-Me-4}\}_2][S_2P(OEt)_2]$ (**5**), in which both free and coordinated diethyl dithiophosphate coexist without any transfer of alkyl.

Introduction

The chemistry of nickel(II) isocyanide complexes is dominated by the square-planar geometry. Only a few examples of pentacoordinate Ni(II) complexes containing isocyanides have been reported, and most of them are di- or polymetallic compounds where the pentacoordination is attained by the formation of a direct metal−metal bond.[1] No report of structural characterization of a simple octahedral Ni(II) isocyanide complex can be found in the Cambridge Structural Database and, as far as we know, there has been no report on the preparation of such complexes. This is remarkable, since this class of complexes has attracted some interest in several fields, such as the activation of CO_2,[2] the polymerization of isocyanide catalyzed by Ni(II),[3] and, more recently, the preparation of N-aryl Ni(II) carbenes from Ni(0) isocyanide complexes.[4] Additionally, it is well-known that bis(1,1-dithiolato)nickel(II) complexes are able to add ligands to afford penta- or hexacoordinate complexes, although most of these reactions have been done using N- or P-donor ligands.[5] We wish to report here the preparation of the first octahedral isocyanide complex of nickel(II) and its reactivity with phosphines, which involves a change in the coordination number from 6 to 4, and simultaneous activation of a O−C(alkyl) bond of the dithiophosphate ester.

Results and Discussion

Addition of 2 mol equiv of CNXyl (Xyl = 2,6-C_6H_6-Me_2) to a dichloromethane solution of $[Ni\{S_2P(OEt)_2\}_2]$ (**1**)[6] causes an immediate color change from purple to red, and the IR monitoring indicates the coordination of the isocyanide (ν(CN) 2181 cm^{-1} vs 2123 cm^{-1} for the free ligand).[7]

The resulting complex **2** (Scheme 1) was isolated and characterized by analytical and spectroscopic methods. The octahedral environment around Ni was confirmed by X-ray crystallography (Tables 1 and 2).

The molecule (Figure 1) is centrosymmetric, and the two isocyanide ligands are trans to each other, which is consistent with the appearance of only one ν(CN) band in the IR spectrum. The coordination of the isocyanide

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[7] One reviewer asked for an explanation: when isocyanides are coordinated to a monopositive or dipositive metal ion such as Cr(0) or Ni(0), little or no back-donation occurs, and the CN stretching band is shifted to a higher frequency as a result of the inductive effect of the metal. When isocyanides are coordinated to zero-valent metals, back-donation is extensive and the CN stretching band is shifted to lower frequency. See: Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 5th ed.; Wiley: New York, 1997; Part B (Applications in Coordination, Organometallic, and Bioinorganic Chemistry), p 115. Cotton, F. A.; Zingales, F. *J. Am. Chem. Soc.* **1961**, *83*, 351.

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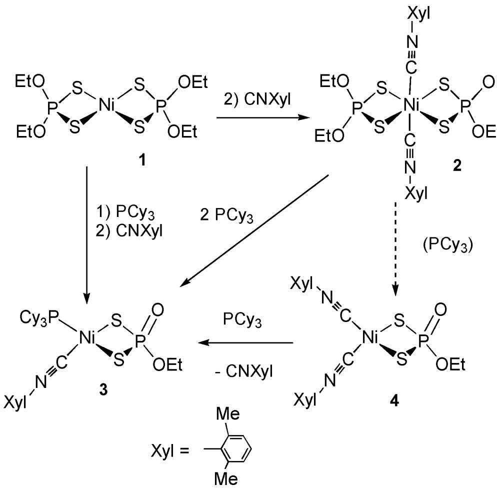
Table 1. Crystal Data and Refinement Details for $[Ni\{S_2P(OEt)_2\}_2(CNXyl)_2]$ (2), $[Ni\{S_2P(O)(OEt)\}(CNXyl)(PCy_3)]$ (3), $[Ni\{S_2P(O)(OEt)\}(CNXyl)_2]$ (4), and $[Ni\{S_2P(OEt)_2\}\{2\text{-}pyCH{=}NC_6H_4\text{-}Me\text{-}4\}_2][S_2P(OEt)_2]$ (5)

	2	3	4	5
formula	$C_{26}H_{38}N_2NiO_4P_2S_4$	$C_{29}H_{47}NNiO_2P_2S_2\cdot CH_2Cl_2$	$C_{20}H_{23}N_2NiO_2PS_4$	$C_{34}H_{44}N_4NiO_4P_2S_4$
fw	691.47	711.37	477.20	821.62
cryst syst	triclinic	monoclinic	monoclinic	triclinic
space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$C2/c$ (No. 15)	$P\bar{1}$ (No. 2)
a, Å	10.911(3)	16.522(1)	15.406(5)	11.657(6)
b, Å	10.932(3)	13.903(1)	13.201(4)	13.101(7)
c, Å	14.640(4)	15.309(1)	22.338(7)	15.337(8)
α, deg	101.227(4)	90	90	98.199(9)
β, deg	90.509(5)	90.104(2)	102.738(6)	109.12(1)
γ, deg	96.954(4)	90	90	110.843(9)
V, Å^3	1699.1(8)	3516.5(4)	4431(2)	1977(2)
Z	2	4	8	2
T, K	293	293	293	293
ρ_{calcd}, g cm^{-3}	1.352	1.344	1.431	1.380
$F(000)$	724	1504	1984	860
λ(Mo Kα), Å	0.710 73	0.710 73	0.710 73	0.710 73
cryst size, mm; color	0.28 × 0.18 × 0.12; pale green	0.22 × 0.21 × 0.17; yellow	0.14 × 0.08 × 0.06; orange	0.23 × 0.14 × 0.08; orange
μ, mm^{-1}	0.943	0.941	1.154	0.824
scan range, deg	$1.42 \leq \theta \leq 23.5$	$1.23 \leq \theta \leq 23.29$	$1.87 \leq \theta \leq 23.28$	$1.47 \leq \theta \leq 23.32$
abs cor	SADABS	SADABS	SADABS	SADABS
corrn factors (min, max)	1.0000, 0.8020	1.000, 0.8673	1.000, 0.4403	1.000, 0.6629
no. of rflns measd	10 582	15 501	9703	8722
no of indep rflns	4825	5065	3186	5541
no of rflns with $I \leq 2\sigma(I)$	4020	4096	1683	3476
GOF on F^2	1.007	1.026	1.003	1.003
no. of params	363	364	258	449
residuals R1, wR2	0.0595, 0.1907	0.0398, 0.1228	0.0514, 0.0812	0.0563, 0.1348

Scheme 1



ligands in **2** is weaker than in the square-planar complexes (cf. Ni−C distances and ν(CN) bands for **2** with those of **3** and **4** below). In the equatorial plane, the Ni atom and the two dithiolato ligands are arranged in a fashion very close to that found in the structural determination[8] of the square-planar starting compound **1**.

Upon addition of 2 equiv of phosphine, complex **2** slowly undergoes transformation into the new species **3**, in which one phosphine is incorporated into the coordination sphere of Ni, replacing one dithio ligand and one isocyanide, thus affording a four-coordinate square-planar complex. This has been confirmed by X-ray crystallography for **3** (Figure 2 and Table 3).The structure determination revealed also that one ethyl group of the remaining coordinated dithio ligand had been lost to give *O*-ethyl dithiophosphate. As outlined in Scheme 1, complex **3** can also be obtained by reacting **1** successively with 1 equiv of PCy_3 and 1 equiv of isocyanide (see Experimental Section).

Surprisingly, when the octahedral bis(isocyanide) complex **2** was reacted with only 1 equiv of phosphine, the resulting compound retained the two isocyanide ligands, and the phosphine was not incorporated, thus affording compound **4**. Although the phosphine was absent from the final product, its presence in the reaction mixture seems to be necessary, since complex **2** does not transform into **4** even in the presence of excess isocyanide.

Compound **4** undergoes replacement of isocyanide by phosphine, and the complete transformation from **4** to **3** can be achieved by using a 2-fold excess of PCy_3. In contrast, complex **3** does not react even in the presence of excess isocyanide in refluxing toluene for several hours.

As was the case with compound **3**, an X-ray determination (Figure 3 and Table 4) confirmed that in **4** the Ni atom lies in a square-planar four-coordinate environment, and again one ethyl group of the dithiophosphate ligand has been lost.

There are only a few precedents for this O−C activation in Ni(II)[9] and Mo(V)[10] complexes, and its relevance in several fields has been recently emphasized, especially in connection with the enzymatic alkyl transfer from and to phosphate esters.[10,11] It has been generally proposed that the alkyl group is transferred to the leaving dithiophosphate group to afford neutral *O*,*O*′,*S*-triethyl dithiophosphate: $EtSP({=}S)(OEt)_2$.

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Table 2. Selected Interatomic Distances (Å) and Angles (deg) in [Ni{$S_2P(OEt)_2$}$_2$(CNXyl)$_2$] (2)[a]

Ni(1)−C(1)#1	2.006(7)	Ni(1)−C(1)	2.006(7)
Ni(1)−S(2)#1	2.5185(19)	Ni(1)−S(2)	2.5185(19)
Ni(1)−S(1)	2.5564(19)	Ni(1)−S(1)#1	2.5564(19)
S(2)−P(1)	1.986(3)	S(1)−P(1)	1.979(2)
P(1)−O(2)	1.585(5)	P(1)−O(1)	1.612(5)
C(1)−N(1)	1.164(8)	N(1)−C(2)	1.403(8)
Ni(51)−C(51)	2.020(6)	Ni(51)−C(51)#2	2.020(6)
Ni(51)−S(51)	2.5221(18)	Ni(51)−S(51)#2	2.5221(18)
Ni(51)−S(52)	2.5324(19)	Ni(51)−S(52)#2	2.5324(19)
S(51)−P(51)	1.982(3)	S(52)−P(51)	1.985(3)
P(51)−O(52)	1.602(6)	P(51)−O(51)	1.607(6)
C(51)−N(51)	1.151(8)	N(51)−C(52)	1.419(8)
C(1)#1−Ni(1)−C(1)	180.0(3)	C(1)#1−Ni(1)−S(2)#1	91.77(18)
C(1)−Ni(1)−S(2)#1	88.23(18)	C(1)#1−Ni(1)−S(2)	88.23(18)
C(1)−Ni(1)−S(2)	91.77(18)	S(2)#1−Ni(1)−S(2)	180.0
C(1)#1−Ni(1)−S(1)	89.27(17)	C(1)−Ni(1)−S(1)	90.73(17)
S(2)#1−Ni(1)−S(1)	98.75(6)	S(2)−Ni(1)−S(1)	81.25(6)
C(1)#1−Ni(1)−S(1)#1	90.73(17)	C(1)−Ni(1)−S(1)#1	89.27(17)
S(2)#1−Ni(1)−S(1)#1	81.25(6)	S(2)−Ni(1)−S(1)#1	98.75(6)
S(1)−Ni(1)−S(1)#1	180.000(1)	C(1)−N(1)−C(2)	176.5(6)
S(52)−Ni(51)−S(52)#2	180.0	C(51)−Ni(51)−C(51)#2	180.00(15)
C(51)−Ni(51)−S(51)	88.99(17)	C(51)#2−Ni(51)−S(51)	91.01(17)
C(51)−Ni(51)−S(51)#2	91.01(17)	C(51)#2−Ni(51)−S(51)#2	88.99(17)
S(51)−Ni(51)−S(51)#2	180.0	C(51)−Ni(51)−S(52)	90.68(18)
C(51)#2−Ni(51)−S(52)	89.32(18)	S(51)−Ni(51)−S(52)	81.81(6)
S(51)#2−Ni(51)−S(52)	98.19(6)	C(51)−Ni(51)−S(52)#2	89.32(18)
N(51)−C(51)−Ni(51)	177.4(5)	S(51)−Ni(51)−S(52)#2	98.19(6)

[a] Symmetry transformations: (#1) $-x, -y, -z + 1$; (#2) $-x + 1, -y + 1, -z + 2$.

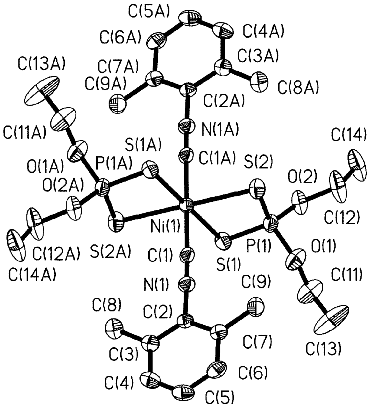


Figure 1. Perspective view of one of the two crystallographically independent but chemically equivalent molecules of [Ni{$S_2P(OEt)_2$}$_2$(CNXyl)$_2$] (**2**), showing the atom numbering. The numbering of the second molecule can be obtained by adding 50 to the number in the label.

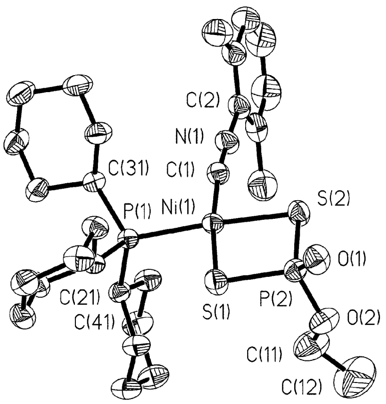


Figure 2. Perspective view of the molecule of [Ni{$S_2P(O)(OEt)$}(CNXyl)(PCy$_3$)] (**3**), showing the atom numbering.

Table 3. Selected Interatomic Distances (Å) and Angles (deg) in [Ni{$S_2P(O)(OEt)$}(CNXyl)(PCy$_3$)] (3)

Ni(1)−C(1)	1.820(4)	Ni(1)−S(1)	2.1855(9)
Ni(1)−P(1)	2.2166(9)	Ni(1)−S(2)	2.2248(10)
S(1)−P(2)	2.0371(12)	S(2)−P(2)	2.0357(13)
P(1)−C(31)	1.846(3)	P(1)−C(41)	1.846(3)
P(1)−C(21)	1.851(3)	P(2)−O(1)	1.460(2)
P(2)−O(2)	1.588(3)	N(1)−C(1)	1.151(4)
C(1)−Ni(1)−S(1)	173.40(11)	C(1)−Ni(1)−P(1)	95.59(10)
S(1)−Ni(1)−P(1)	91.00(3)	C(1)−Ni(1)−S(2)	86.25(11)
S(1)−Ni(1)−S(2)	87.15(4)	P(1)−Ni(1)−S(2)	176.36(4)
P(2)−S(1)−Ni(1)	88.64(4)	P(2)−S(2)−Ni(1)	87.60(4)
C(31)−P(1)−C(41)	105.11(14)	C(31)−P(1)−C(21)	110.91(16)
C(41)−P(1)−C(21)	103.66(14)	C(31)−P(1)−Ni(1)	112.05(11)
C(41)−P(1)−Ni(1)	109.74(11)	C(21)−P(1)−Ni(1)	114.59(11)
O(1)−P(2)−O(2)	106.56(15)	O(1)−P(2)−S(2)	118.87(12)
O(2)−P(2)−S(2)	108.94(12)	O(1)−P(2)−S(1)	116.55(12)
O(2)−P(2)−S(1)	108.84(12)	S(2)−P(2)−S(1)	96.56(5)
C(1)−N(1)−C(2)	176.0(4)	S(2)−P(2)−S(1)	96.56(5)

However, there are several experimental facts which suggests a more complex mechanism. In the first place, the presence of a leaving dithiophosphate does not lead necessarily to the transference of alkyl. Thus, the bis(dithiophosphate) complex **1** reacts with 2 equiv of *N*-*p*-tolyl-2-iminopyridine, as depicted in Scheme 2, to afford the salt **5**, via displacement of the O,O′ dithiophosphate anion.

An X-ray determination reveals that **5** contains both coordinated and free dithiophosphate, without any transfer of alkyl (Figure 4 and Table 5).

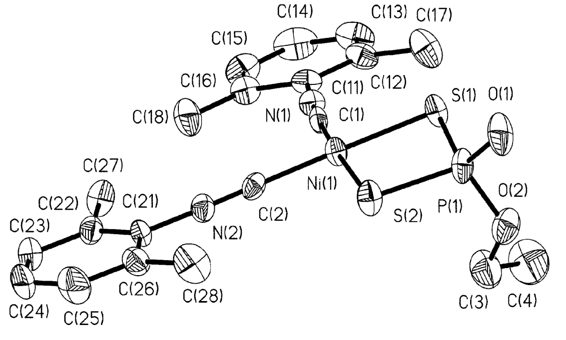
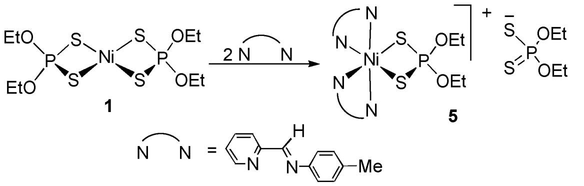


Figure 3. Perspective view of the molecule of [Ni{$S_2P(O)(OEt)$}(CNXyl)$_2$] (**4**), showing the atom numbering.

Table 4. Selected Interatomic Distances (Å) and Angles (deg) in [Ni{$S_2P(O)(OEt)$}$(CNXyl)_2$] (4)

Ni(1)−C(1)	1.821(7)	Ni(1)−C(2)	1.831(6)
Ni(1)−S(1)	2.1887(17)	Ni(1)−S(2)	2.1894(19)
S(1)−P(1)	2.023(2)	S(2)−P(1)	2.032(2)
P(1)−O(1)	1.451(4)	P(1)−O(2)	1.585(5)
N(1)−C(1)	1.148(7)	N(1)−C(11)	1.399(7)
N(2)−C(2)	1.149(6)	N(2)−C(21)	1.393(7)
C(1)−Ni(1)−C(2)	96.4(2)	C(1)−Ni(1)−S(1)	87.96(18)
C(2)−Ni(1)−S(1)	175.5(2)	C(1)−Ni(1)−S(2)	171.2(2)
C(2)−Ni(1)−S(2)	88.39(18)	S(1)−Ni(1)−S(2)	87.45(7)
P(1)−S(1)−Ni(1)	87.72(8)	P(1)−S(2)−Ni(1)	87.47(8)
O(1)−P(1)−O(2)	106.0(3)	O(1)−P(1)−S(1)	118.1(2)
O(2)−P(1)−S(1)	108.64(19)	O(1)−P(1)−S(2)	117.5(2)
O(2)−P(1)−S(2)	109.68(19)	S(1)−P(1)−S(2)	96.53(9)
C(1)−N(1)−C(11)	177.9(6)	C(2)−N(2)−C(21)	177.0(6)
C(3)−O(2)−P(1)	122.8(4)	N(1)−C(1)−Ni(1)	174.2(6)
N(2)−C(2)−Ni(1)	176.7(6)	O(2)−C(3)−C(4)	110.2(7)

Scheme 2



In an early related precedent, the structure of [Ni{$S_2P(OMe)_2$}$_2$(phen-Me_2)] contains both monodentate and bidentate dithiophosphate, again without any alkyl transfer between them.[12] Interestingly, the octahedral bis(isocyanide) complex **2** does not react with an excess of diimine, even in refluxing THF for several hours.

The experimental results known so far indicate that the transfer of alkyl occurs only when phosphine is present in the reaction mixture, even in the case (formation of **4**) when the phosphine is not incorporated into the final product.

Additionally, IR monitoring of the reaction mixtures of **1** and **2** with PCy_3/isocyanide reveals the formation, in the initial steps, of the complex [$Ni(CNXyl)_4$], as deduced from the ν(CN) bands at 2030 and 2000 cm^{-1}, identical with those of an authentic sample prepared as described in the literature.[13] The Ni(0) complex slowly transforms into the final products **3** and **4**, depending on the amount of phosphine available. This implies that some reduction and oxidation processes are involved in the mechanism. On the other hand, the monitoring of the crude reaction mixtures by $^{31}P\{^1H\}$ NMR shows the presence of $EtSP(=S)(OEt)_2$ (at δ 96.1 ppm), together with small amounts of phosphine sulfide and phosphine oxide, and no trace of the signal of [PCy_3-Et]$^+$, suggesting that the phosphine activates the process through coordination to the metal atom in an intermediate, rather than being involved directly in the alkyl transfer. Some work is now in progress attempting to obtain conclusive information about the mechanism of this interesting C−O activation.

Experimental Section

All reactions were carried out in dry solvents under a nitrogen atmosphere. Details of the instrumentation and experimental procedures have been given elsewhere.[14] Literature procedures for the preparation of starting materials are quoted in each case. Ligands and other reagents were purchased and used without purification, unless otherwise stated.

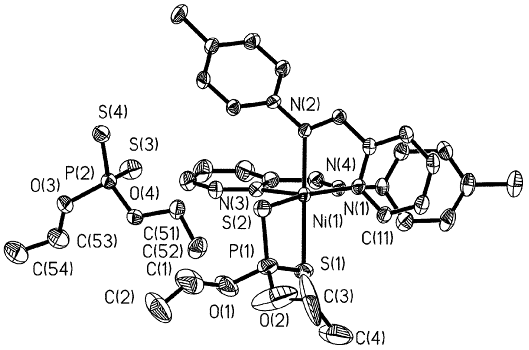


Figure 4. Perspective view of the molecule of [Ni{$S_2P(OEt)_2$}{2-pyCH=NC_6H_4-Me-4}$_2$][$S_2P(OEt)_2$] (**5**), showing the atom numbering.

Table 5. Selected Interatomic Distances (Å) and Angles (deg) in [Ni{$S_2P(OEt)_2$}{2-pyCH=NC_6H_4-Me-4}$_2$][$S_2P(OEt)_2$] (5)

Ni(1)−N(1)	2.084(5)	Ni(1)−N(4)	2.090(4)
Ni(1)−N(2)	2.095(4)	Ni(1)−N(3)	2.110(5)
Ni(1)−S(2)	2.4403(19)	Ni(1)−S(1)	2.468(2)
S(1)−P(1)	1.933(3)	S(2)−P(1)	1.968(3)
P(1)−O(1)	1.5057	P(1)−O(2)	1.527(6)
N(1)−C(11)	1.322(7)	N(1)−C(15)	1.353(7)
N(2)−C(16)	1.282(7)	N(2)−C(17)	1.432(7)
N(3)−C(31)	1.331(7)	N(3)−C(35)	1.343(7)
N(4)−C(36)	1.257(7)	N(4)−C(37)	1.429(7)
N(1)−Ni(1)−N(4)	89.92(18)	N(1)−Ni(1)−N(2)	78.11(18)
N(4)−Ni(1)−N(2)	90.57(16)	N(1)−Ni(1)−N(3)	164.03(17)
N(4)−Ni(1)−N(3)	78.36(19)	N(2)−Ni(1)−N(3)	91.06(18)
N(1)−Ni(1)−S(2)	93.08(13)	N(4)−Ni(1)−S(2)	174.83(14)
N(2)−Ni(1)−S(2)	94.16(12)	N(3)−Ni(1)−S(2)	99.46(14)
N(1)−Ni(1)−S(1)	99.56(14)	N(4)−Ni(1)−S(1)	92.80(13)
N(2)−Ni(1)−S(1)	175.90(13)	N(3)−Ni(1)−S(1)	91.89(13)
S(2)−Ni(1)−S(1)	82.55(6)	N(3)−Ni(1)−S(1)	91.89(13)

[Ni{$S_2P(OEt)_2$}$(CNXyl)_2$] (2). To a solution of **1** (0.214 g, 0.5 mmol)[6] in CH_2Cl_2 (20 mL) was added 2,6-dimethylphenyl isocyanide (CNXyl; 0.131 g, 1 mmol), and the mixture was stirred for 0.5 h at room temperature. The color changed from purple to deep red. The solvent was evaporated, and the residue was washed several times with hexane. The solid was dissolved in the minimum amount of CH_2Cl_2 and layered with hexane. Slow diffusion at −20 °C afforded compound **2** as green crystals. Yield: 0.048 g, 69%. Anal. Calcd for $C_{26}H_{38}N_2NiO_4P_2S_4$: C, 45.16; H, 5.54; N, 4.05. Found: C, 44.93; H, 5.28; N, 4.09. IR (CH_2Cl_2): ν(CN) 2181 cm^{-1}. ^1H NMR (Me_2CO-d_6; δ (ppm)): 8.12 (t(7), 2H, H^4 of Xyl), 6.71 (d(7), 4H, $H^3$and $H^5$of Xyl), 4.37 (m (br), 8H, $POCH_2$), 1.72 (m (br), 12H, $POCH_2CH_3$), 1.44 (s, 12H, CH_3 of Xyl). $^{31}P\{^1H\}$ NMR (δ (ppm)): 78 (v br).

[Ni{$S_2P(O)(OEt)$}(CNXyl)(PCy_3)] (3). (a) From 1. To a purple solution of **1** (0.214 g, 0.5 mmol)[6] in CH_2Cl_2 (20 mL) was added PCy_3 (0.28 g, 1 mmol), and the solution turned green. After the solution was stirred for 1 h, CNXyl (0.065 g, 0.5 mmol) was added and the solution turned red immediately. The mixture was stirred for 5 h, and then the solvent was evaporated in vacuo. The residue was washed with Et_2O to extract a small amount of starting **1**. The resulting solid was redissolved in CH_2Cl_2 and filtered. Addition of hexane followed by slow evaporation gave yellow crystals of **3**·CH_2Cl_2. Yield: 0.302 g, 85%. Anal. Calcd for $C_{29}H_{47}NNiO_2P_2S_2 \cdot CH_2Cl_2$: C, 50.65; H, 6.94; N, 1.97. Found: C, 50.33; H, 6.81; N, 1.83. IR

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(CH_2Cl_2): ν(CN) 2151 cm^{-1}. ^{1}H NMR ($CDCl_3$; δ (ppm)): 7.23 (t(7), 1H, H^4 of Xyl), 7.12 (d(7), 2H, $H^3$and $H^5$of Xyl), 4.08 (m (br), 2H, POCH_2), 2.42 (s, 6H, CH_3 of Xyl), 2.07 to 1.25 (m, 33H, Cy), 1.33 (m, 3H, POCH$_2$CH_3). ^{31}P{^{1}H} NMR δ 56.9 (d(12), S$_2$*P*O), 42.5 (d(12), *P*Cy$_3$).

(b) From 2. To a solution of **2** (0.346 g, 0.5 mmol) in CH_2Cl_2 (15 mL) was added PCy$_3$ (0.28 g, 1 mmol), and the mixture was stirred at room temperature for 30 h. The solvent was evaporated to dryness, and the residue was washed with Et$_2$O (2 × 5 mL). The solid was recrystallized from CH_2Cl_2/hexane. Yield: 0.26 g, 73%.

(c) From 4. To a solution of **4** (0.24 g, 0.5 mmol) (see below) in CH_2Cl_2 (15 mL) was added PCy$_3$ (0.28 g, 1 mmol), and the mixture was stirred at room temperature for 24 h. The solvent was evaporated to dryness, and the residue was washed with Et$_2$O (2 × 5 mL). The solid was recrystallized from CH_2Cl_2/hexane. Yield: 0.293 g, 80%.

[Ni{S$_2$P(O)(OEt)}(CNXyl)$_2$] (4). To a red solution of **2** (0.345 g, 0.5 mmol) in CH_2Cl_2 (20 mL) was added PCy$_3$ (0.14 g, 0.5 mmol), and the mixture was stirred at room temperature for 10 h. The color changed slowly to red-brown. The solvent was evaporated in vacuo, the residue was washed with hexane and redissolved in CH_2Cl_2/hexane (1/1, v/v), and the solution was chromatographed on silica. Elution with CH_2Cl_2/hexane (1/1, v/v) gave a purple band consisting of a small amount of purple **1**. Further elution with THF gave a red-orange band containing compound **4**. Addition of hexane and slow evaporation gave **4** as orange crystals. Yield: 0.174 g, 73%. Anal. Calcd for $C_{20}H_{23}N_2NiO_2PS_2$: C, 50.34; H, 4.86; N, 5.87. Found: C, 50.16; H, 5.03; N, 5.72. IR (CH_2Cl_2): ν(CN) 2192, 2175 cm^{-1}. ^{1}H NMR ($CDCl_3$; δ (ppm)): 7.28 (t(7), 2H, H^4 of Xyl), 7.14 (d(7), 4H, $H^3$and $H^5$of Xyl), 4.12 (m, 2H, POCH_2), 2.42 (s, 12H, CH_3 of Xyl), 1.35 (m, 3H, POCH$_2$CH_3). ^{31}P{^{1}H} NMR (δ (ppm)): 54.4.

[Ni{S$_2$P(OEt)$_2$}{2-pyCH=NC$_6$H$_4$-Me-4}$_2$][S$_2$P(OEt)$_2$] (5). To a solution of **1** (0.214 g, 0.5 mmol)[6] in CH_2Cl_2 (15 mL) was added 2-pyCH=NC$_6$H$_4$-Me-4 (0.196 g, 1 mmol). The mixture was stirred at room temperature for 2 h. The color of the solution changed from purple to red-brown. The solvent was evaporated to dryness, and the residue was washed with hexane (3 × 10 mL). The resulting solid was recrystallized from CH_2Cl_2/hexane to obtain orange crystals of **5**. Yield: 0.275, 67%. Anal. Calcd for $C_{34}H_{44}N_4NiO_4P_2S_4$: C, 49.70; H, 5.40; N, 6.82. Found: C, 49.63; H, 5.18; N, 6.51.

X-ray Diffraction Studies. Crystals were grown by slow diffusion of hexane into concentrated solutions of the complexes in CH_2Cl_2 at −20 °C. Relevant crystallographic details are given in Table 1. Intensity measurement was made with a Bruker AXS SMART 1000 diffractometer with graphite-monochromated Mo Kα X-radiation and a CCD area detector. A hemisphere of the reciprocal space was collected up to $2\theta = 48.6°$. Raw frame data were integrated with the SAINT[15] program. The structures were solved with SHELXTL.[16] A semiempirical absorption correction was applied with the program SADABS.[17] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were set in calculated positions and refined as riding atoms, with a common thermal parameter. All calculations and graphics were made with SHELXTL.

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Supporting Information Available: Complete tables of atomic coordinates, anisotropic thermal parameters, and bond lengths and angles for the structures of **2**−**5**; these data are also available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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