Supporting Information for:

Isocyanate and carbodiimide synthesis by nitrene-group-transfer from a nickel(II) imido complex

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Experimental Section

General Considerations. Unless otherwise stated, all operations were performed in a M. Braun Lab Master dry box under an atmosphere of purified nitrogen or using high-vacuum and standard Schlenk techniques under an argon atmosphere.[1] Hexanes, petroleum ether, and toluene were dried by passage through activated alumina and Q-5 columns.[2] All other solvents were dried and degassed by using standard high-vacuum and Schlenk techniques.[1,2] C_6D_6, and CD_2Cl_2 were purchased form Cambridge Isotope Laboratory (CIL), degassed, and dried over CaH_2 or activated 4Å molecular sieves. Celite, alumina, and 4Å molecular sieves were activated under vacuum overnight at a temperature above 180°C. ^{13}CO (99%) was purchased in a lecture bottle from CIL and used as received. (dtbpe)Ni{NH(2,6-$(CHMe_2)_2C_6H_3$)} (dtbpe = 1,2-bis(di-*tert*-butylphosphino)ethane),[3] [(dtbpe)Ni{NH(2,6-$(CHMe_2)_2C_6H_3$)}][PF_6] **(2a)**[3], (dtbpe)Ni{N{2,6-$(CHMe_2)_2C_6H_3$)} **(1)** [3], (dtbpe)Ni$(CO)_2$[4], FeCp*$_2$ (Cp* = C_5Me_5),[5] and [FeCp*$_2$][B(3,5-$(CF_3)_2C_6H_3)_4$][6] were prepared according to the literature. Infrared data (Fluorolube mulls, CaF_2 plates) were measured by using a Nicolet 20SXB instrument. Elemental analysis was performed by Desert Analytics (Tucson, AZ). ^1H, ^{13}C, ^{19}F and ^{31}P NMR spectra were recorded on a Bruker 500 and 400 MHz NMR spectrometers. ^1H and ^{13}C NMR are reported with reference to solvent resonances (residual C_6D_5H in C_6D_6, 7.16 ppm and 128.0 ppm; residual $CHDCl_2$ in CD_2Cl_2, 5.32 ppm and 53.8 ppm. ^{19}F NMR

spectra were reported with respect to external CCl_3F (0 ppm). ^{31}P NMR spectra were reported with respect to external 85% H_3PO_4 (0 ppm). X-ray diffraction data were collected on a Bruker Platform goniometer with a Charged Coupled Device (CCD) detector (Smart Apex). Structures were solved by direct or Patterson methods using the SHELXTL (version 5.1) program library (G. Sheldrick, Bruker Analytical X-ray Systems, Madison, WI).

Preparation of [(dtbpe)Ni{*C,N* : η^2-CONH(2,6-$(CHMe_2)_2C_6H_3$)}][PF_6] (3a). In a 200 mL round bottom flask was dissolved [(dtbpe)Ni{NH(2,6-$(CHMe_2)_2C_6H_3$)}][PF_6] **(2a)** [606 mg, 0.869 mmol] in 35 mL of THF and the purple solution cooled to –78°C. The solution was stirred under a CO atmosphere and allowed to warm. After 2 hours the golden yellow solution was filtered to remove small traces of a pale red solid. The solution was dried under vacuum and extracted with ca. 80 mL of toluene, filtered and the filtrate dried under vacuum to afford a pale yellow powder. The powder was dissolved in a minimum of THF, filtered, layered with Et_2O, and the solution cooled to –35°C for 2 days to afford small yellow crystals of **3a** [494 mg, 0.680 mmol, 79%] in one crop. The ^{13}C isotopomer [(dtbpe)Ni{*C,N* : η^2-CONH(2,6-$(CHMe_2)_2C_6H_3$)}][PF_6] **(3a)** (**3a-^{13}C**) was analogously prepared from ^{13}CO in similar yield.

^1H NMR for **3a** (500.1 MHz, 22°C, CD_2Cl_2): δ 8.14 (s, N*H*, 1H), 7.41 (t, *p*-aryl, 1 H), 7.24 (d, *m*-aryl, 2 H), 2.96 (sept., C*H*$(CH_3)_2$, 2 H), 2.07 (m, CH_2CH_2, 2H), 1.94 (m, CH_2CH_2, 2H), 1.46 (d, C(CH_3)$_3$, 18 H, J_{HP} = 15 Hz), 1.46 (d, C(CH_3)$_3$, 18 H, J_{HP} = 14 Hz), 1.20 (d, CH(CH_3)$_2$, 12 H). $^{13}C\{^1H\}$ NMR for **3a-^{13}C** (125.8 MHz, 22°C, CD_2Cl_2): δ 183.2 (dd, *C*ONH, J_{CPcis} = 10 Hz, $J_{CPtrans}$ = 65 Hz), 145.1 (aryl), 133.1 (aryl), 130.1 (aryl), 124.4 (aryl), 35.48 (m, *C*H_2*C*H_2), 30.31 (s, C(*C*H_3)$_3$), 30.15 (s, C(*C*H_3)$_3$), 29.62 (s, *C*H(CH$_3$)$_2$), 25.27 (m, *C*H_2*C*H_2), 23.48 (s, CH(*C*H_3)$_2$), 20.61 (bs, *C*(CH$_3$)$_3$), 20.41 (bs, *C*(CH$_3$)$_3$). $^{31}P\{^1H\}$ NMR for **3a** (202.4 MHz, 22°C, CD_2Cl_2): δ 112.1 (d, ^{t}Bu$_2$*P*CH$_2$CH$_2$*P*^{t}Bu$_2$, J_{PP} = 10 Hz), 90.63 (d, ^{t}Bu$_2$*P*CH$_2$CH$_2$*P*^{t}Bu$_2$, J_{PP} = 10 Hz), -143.8 (septet, J_{PF} = 711 Hz, *P*F$_6$).

$^{31}P\{^{1}H\}$ NMR for **3a-^{13}C**: δ 112.0 (t, $^{t}Bu_2PCH_2CH_2P^{t}Bu_2$, J_{PP} = 10 Hz), 90.60 (dd, $^{t}Bu_2PCH_2CH_2P^{t}Bu_2$, J_{PP} = 9.7 Hz, $J_{PCtrans}$ = 65 Hz), -143.8 (septet, J_{PF} = 711 Hz, PF_6). ^{19}F NMR (470.6 MHz, 22°C, CD_2Cl_2): δ -73.6 (d, J_{FP} = 711 Hz, PF_6). IR for **3a** (Fluorolube mull, CaF_2): 3351 (m), 2961 (m), 2867 (m), 1600 (m), 1577 (m), 1464 (m), 1392 (w) cm^{-1}. IR for **3a-^{13}C**: 1548 (m, ν_{13CO}). Anal. calcd. for $C_{31}H_{57}NNiF_6OP_3$ C, 51.26; H, 8.05; N, 1.93. Found: C, 51.02; H, 8.34; N, 1.91.

Preparation of [(dtbpe)Ni{*C,N*: η²-CONH(2,6-$(CHMe_2)_2C_6H_3$)}][B(3,5-$(CF_3)_2C_6H_3)_4$] (3b). In a vial was dissolved (dtbpe)Ni{NH(2,6-$(CHMe_2)_2C_6H_3$)} [34 mg, 0.061 mmol] in 8 mL of Et_2O and the solution cooled to –35°C. To the red solution was added a cold Et_2O (~3 mL) solution of $[FeCp^*_2][B(3,5\text{-}(CF_3)_2C_6H_3)_4]$[5] [73 mg, 0.061 mmol] causing a rapid change of color to purple. After 1 hr the mixture was filtered, dried under vacuum, and washed with petroleum ether until washing were clear. The dark residue was extracted with Et_2O, filtered and dried under vacuum to afford crude [(dtbpe)Ni{NH(2,6-$(CHMe_2)_2C_6H_3$)}][B(3,5-$(CF_3)_2C_6H_3)_4$] **(2b)** [87 mg, 0.062 mmol, 99% yield]. The solid was loaded into a Schlenk flask and dissolved in 10 mL of Et_2O. The solution was degassed, cooled to –78°C, and stirred under an atmosphere of CO for 15 min. Upon warming to 0°C the color gradually changed to a golden yellow. After 20 min, the solution was degassed, taken into the glove box, filtered, concentrated, and cooled to –35°C for 1 day to afford large yellow crystals of **(3b)** (suitable for single crystal X-ray diffraction) [45 mg, 0.031 mmol, 50% yield].

Anal. calcd. for $C_{63}H_{70}BNNiF_{24}OP_2$ C, 52.38; H, 4.88; N, 0.97. Found: C, 52.57; H, 4.74; N, 0.82.

Preparation of (dtbpe)Ni{*C,N*:η²-C(O)N(2,6-$(CHMe_2)_2C_6H_3$)} (4). In a vial was dissolved **(3a)** [208 mg, 0.286 mmol] in 20 mL of THF and the solution cooled to –35°C. To the orange solution was added dropwise a cold THF solution containing $NaN(SiMe_3)_2$ [53 mg, 0.289 mmol] causing a slight change in color to pale yellow. The

mixture was allowed to react for 3-4h upon which the solutions darkened slightly and volatiles were removed under reduced pressure. The yellow residue was extracted with 70 mL of toluene (stirred for 10 min to get all the solid into solution), filtered to remove a brown solid and dried under vacuum. The solids were then washed with hexanes (2x10 mL), filtered and dried under vacuum to afford pure **4** as a pale yellow powder [98 mg, 0.169 mmol, 59% yield]. The hexane washings were dried under vacuum, extracted with 15 mL of Et_2O, filtered and cooled to –35°C for 2 d to afford an additional 20 mg. Total collected of **4** was 118 mg, 71% yield. Analytically pure crystals of **4** can be obtained from a dilute Et_2O solution cooled for several days at –35°C. The ^{13}C isotopomer (dtbpe)Ni{*C*,*N*:η^2-^{13}C(O)N(2,6-$(CHMe_2)_2C_6H_3$)} **(4-^{13}C)** was analogously prepared from the deprotonation of ^{13}CO enriched **3a-^{13}C** in similar yield.

^1H NMR for **4** (500.1 MHz, 22°C, CD_2Cl_2): δ 7.08-7.02 (m, aryl, 3 H), 3.45 (sept, C*H*$(CH_3)_2$, 2 H), 1.77 (m, CH_2CH_2, 2 H), 1.69 (m, CH_2CH_2, 2 H), 1.43 (d, ^{t}Bu, 18 H, J_{HP} = 12 Hz), 1.43 (d, ^{i}Pr, 3 H), 1.24 (d, ^{t}Bu, 18 H, J_{HP} = 12 Hz), 1.23 (d, ^{i}Pr, 3 H), 1.21 (d, ^{i}Pr, 3 H), 1.18 (d, ^{i}Pr, 3 H). $^{13}C\{^1H\}$ NMR for **4** (125.8 MHz, 22°C, CD_2Cl_2): δ 160.2 (d, *C*O,$J_{CPtrans}$ = 59 Hz), 142.9 (aryl), 140.5 (aryl), 123.8 (aryl), 122.7 (aryl), 35.2 (bs, *C*$(CH_3)_3$), 35.1 (bs, *C*$(CH_3)_3$), 34.3 (s, *C*H$(CH_3)_2$), 34.2 (s, *C*H$(CH_3)_2$), 30.6 (d, C(*C*$H_3)_3$, J_{CP} = 5 Hz), 30.4 (d, C(*C*$H_3)_3$, J_{CP} < 2 Hz), 28.8 (s, CH(*C*$H_3)_2$), 26.1 (s, CH(*C*$H_3)_2$), 20.51 (t, *C*H_2CH_2, J_{CP} = 18.4 Hz), 22.4 (s, CH(*C*$H_3)_2$), 21.0 (t, *C*H_2CH_2, J_{CP} = 13 Hz). $^{13}C\{^1H\}$ NMR for **4-^{13}C** (125.8 MHz, 22°C, C_6D_6): δ 158.5 (dd, *C*O,$J_{CPtrans}$ = 59 Hz, J_{CPcis} = 5 Hz). $^{31}P\{^1H\}$ NMR for **4** (202.4 MHz, 22°C, CD_2Cl_2): δ 97.2 (d, ^{t}Bu$_2$*P*CH_2CH_2*P*^{t}Bu$_2$, J_{PP} = 51 Hz), 78.6 (d, ^{t}Bu$_2$*P*CH_2CH_2*P*^{t}Bu$_2$, J_{PP} = 51 Hz). $^{31}P\{^1H\}$ NMR for **4-^{13}C** (202.4 MHz, 22°C, C_6D_6): δ 96.1 (br d, ^{t}Bu$_2$*P*CH_2CH_2*P*^{t}Bu$_2$, $J_{PCtrans}$ = 57 Hz), 77.3 (m, ^{t}Bu$_2$*P*CH_2CH_2*P*^{t}Bu$_2$, $J_{PCtrans}$ = 57 Hz). IR for **4** (CH_2Cl_2, CaF_2): 2962 (s) 2902 (m), 2870 (m), 1718 (s), 1483 (m), 1467 (m), 1437 (m), 1373 (w), 1338 (m) cm^{-1}. For **4-^{13}C**: 1673 (s). Anal. calcd. for $C_{31}H_{56}NNiOP_2$ C, 64.15; H, 9.90; N, 2.41. Found: C, 63.92; H,

10.06; N, 2.32. Note: If the reaction is monitored by NMR or worked up after only 30-45 min the intermediate (dtbpe)Ni{*O,C*:η^2-OC=N(2,6-(CHMe$_2$)$_2$C$_6$H$_3$)} is observed by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy as a minor product along with **4** (1:3). The isotopomer (dtbpe)Ni{*O,C*:η^2-O^{13}C=N(2,6-(CHMe$_2$)$_2$C$_6$H$_3$)} could be prepared analogously.

^{1}H NMR of (dtbpe)Ni{*O,C*:η^2-OC=N(2,6-(CHMe$_2$)$_2$C$_6$H$_3$)} (500.1 MHz, 22°C, C_6D_6): δ 7.30-7.14 (m, aryl, 3 H), 3.76 (sept, C*H*(CH$_3$)$_2$, 2 H), 1.46 (d, ^{i}Pr, 3 H), 1.34 (d, ^{t}Bu, 18 H, J_{HP} = 13 Hz), 1.31 (m, C*H*$_2$C*H*$_2$, 2 H), 1.10 (m, C*H*$_2$C*H*$_2$, 2 H), 1.09 (d, ^{t}Bu, 18 H, J_{HP} = 12 Hz). ^{13}C{^{1}H} NMR for (dtbpe)Ni{*O,C*:η^2-O^{13}C=N(2,6-(CHMe$_2$)$_2$C$_6$H$_3$)} (125.8 MHz, 22°C, C_6D_6): δ 159.7 (dd, *C*O,$J_{CPtrans}$ = 61 Hz, J_{CPcis} = 5 Hz). ^{31}P{^{1}H} NMR for (dtbpe)Ni{*O,C*:η^2-OC=N(2,6-(CHMe$_2$)$_2$C$_6$H$_3$)} (202.4 MHz, 22°C, C_6D_6): δ 100.2 (d, ^{t}Bu$_2$*P*CH$_2$CH$_2$*P*^{t}Bu$_2$, J_{PP} = 55 Hz), 78.6 (d, ^{t}Bu$_2$*P*CH$_2$CH$_2$*P*^{t}Bu$_2$, J_{PP} = 52 Hz). ^{31}P{^{1}H} NMR for (dtbpe)Ni{*O,C*:η^2-O^{13}C=N(2,6-(CHMe$_2$)$_2$C$_6$H$_3$)} (202.4 MHz, 22°C, C_6D_6): δ 100.2 (dd, ^{t}Bu$_2$*P*CH$_2$CH$_2$*P*^{t}Bu$_2$, $J_{PCtrans}$ = 57 Hz, J_{PCcis} = 4 Hz), 77.7 (d, ^{t}Bu$_2$*P*CH$_2$CH$_2$*P*^{t}Bu$_2$, $J_{PCtrans}$ = 61 Hz). Stirring crude solutions of crude product after work-up for 3 h at room temperature afforded **4** quantitatively. Attempts to isolate (dtbpe)Ni{*O,C*:η^2-OC=N(2,6-(CHMe$_2$)$_2$C$_6$H$_3$)} were unsuccessful because of the thermal conversion to **4** (even at lower temperatures).

Reaction of (dtbpe)Ni{N(2,6-(CHMe$_2$)$_2$C$_6$H$_3$)} (1) with excess CO. Synthesis of (dtbpe)Ni(CO)$_2$ (6) and O=C=N{2,6-(CHMe$_2$)$_2$C$_6$H$_3$} (5). In a Schlenk flask equipped with a stir bar was loaded **1** [213 mg, 0.386 mmol] and 20 mL of THF. The green-brown solution was cooled to 0°C and stirred over 1 atm of dry CO for 2 hrs. Upon warming the color changed immediately to red and then to a golden yellow. After stirring for an additional hour the volatiles were removed under reduced pressure. Examination of the crude reaction mixture by ^{1}H, ^{31}P NMR and GC mass spectroscopies revealed clean and quantitative formation of (dtbpe)Ni(CO)$_2$ (**6**) and O=C=N{2,6-

$(CHMe_2)_2C_6H_3$} (**5**) (compared with samples purchased from Aldrich). The solids were extracted with Et_2O, filtered and concentrated under reduced pressure. Cooling of the Et_2O extract for 3 days at –35°C afforded large crystals of pure **6** [98 mg, 226 mmol, 59% yield, two crops]. The formation of **6** was confirmed by ^1H and ^{31}P NMR spectroscopy and elemental analysis by comparison to authentic samples prepared independently.[4]

Reaction of (dtbpe)Ni{N(2,6-$(CHMe_2)_2C_6H_3$)} (1) with 1 equiv of CO. In a Schlenk flask equipped with a stir bar was loaded **1** [57 mg, 0.103 mmol] and 10 mL of toluene. The green-brown solution was cooled to –78°C and via syringe was added 1.05 equiv of CO [2.7 mL, 1 atm] for 1 hr. Upon allowing the reaction to reach slowly room temperature the color changed to red-brown and then to yellow-brown. The reaction mixture was allowed to stir for an additional hour and volatiles were then removed under reduced pressure. The brown-yellow residue was extracted with 20 mL of Et_2O, filtered and dried under vacuum to afford a pale yellow solid. Examination of the crude solids by ^1H and ^{31}P NMR spectroscopy revealed formation of **6**, **5**, and minor formation of **4b**. Attempts to separate any of the products formed in the reaction mixture proved unsuccessful.

Reaction of (dtbpe)Ni{*C,N*:η^2-C(O)N(2,6-$(CHMe_2)_2C_6H_3$)} (4) with excess CO. In a Schlenk flask equipped with a stir bar was loaded **4** [41 mg, 0.071 mmol] and 10 mL of Et_2O. The pale-yellow solution was stirred over 1 atm of dry CO for 2.5 h. The reaction mixture was filtered and the filtrate was dried under reduced pressure. Examination of the crude reaction mixture by ^1H and ^{31}P NMR spectroscopy revealed quantitative formation of **6** and **5**.

Preparation of (dtbpe)Ni{*C,N*:η^2-C(NCH_2Ph)N(2,6-$(CHMe_2)_2C_6H_3$)} (7). In a vial was dissolved **1** [132 mg, 0.239 mmol] in 10 mL of Et_2O and the solution cooled to –35°C. To the green solution was added dropwise 5 mL of cold Et_2O containing $CNCH_2Ph$ [28 mg, 0.239 mmol] causing an immediate color change to an orange-brown.

After 4 hours, the solution was filtered, dried under vacuum, extracted with hexanes, filtered, concentrated to 5 mL, and cooled to –35°C for 4 days. Pale yellow-pink crystals along with yellow powder forms over this time and the mother liquor is decanted to afford pure **7** [80 mg, 0.120 mmol, 50%] in one crop.

^{1}H NMR for **7** (500.1 MHz, 22°C, C_6D_6): δ 7.30 (d, aryl, 2 H), 7.24 (d, aryl, 2 H), 7.15 (m, aryl, 3 H), 7.06 (t, aryl, 1 H), 4.69 (d, CH_2Ph, 2 H, J_{HP} < 3 Hz), 3.79 (sept, CH(CH_3)$_2$, 2 H), 1.45 (d, CH(CH_3)$_2$, 12 H), 1.44 (d, CH(CH_3)$_2$, 12 H), 1.37 (d, ^{t}Bu, 18 H, J_{HP} = 13 Hz), 1.29 (m, CH_2CH_2, 2 H), 1.13 (m, CH_2CH_2, 2 H), 0.96 (d, ^{t}Bu, 18 H, J_{HP} = 12 Hz). ^{13}C{^{1}H} NMR for **7** (125.8 MHz, 22°C, C_6D_6): δ 149.7 (aryl), 149.6 (aryl), 148.8 (d, *C*NCH$_2$Ph,$J_{CPtrans}$ = 60 Hz), 142.7 (aryl), 140.3 (aryl), 126.3 (aryl), 122.2 (aryl), 121.0 (aryl), 52.8 (s, CN*C*H$_2$Ph), 35.1 (s, *C*H$_2$Ph), 34.7 (bs, *C*(CH_3)$_3$), 34.6 (bs, *C*(CH_3)$_3$), (bs, *C*H(CH_3)$_2$), 30.4 (s, C(*C*H$_3$)$_3$), 30.1 (s, C(*C*H$_3$)$_3$), 29.1 (s, CH(*C*H$_3$)$_2$), 24.1 (s, CH(*C*H$_3$)$_2$), 23.5 (t, *C*H$_2$*C*H$_2$, J_{CP} = 17 Hz), 23.0 (s, CH(*C*H$_3$)$_2$), 21.5 (t, *C*H$_2$*C*H$_2$, J_{CP} = 12 Hz). ^{31}P{^{1}H} NMR for **7** (202.4 MHz, 22°C, C_6D_6): δ 99.1 (d, ^{t}Bu$_2$*P*CH$_2$CH$_2$*P*^{t}Bu$_2$, J_{PP} = 46 Hz), 84.8 (d, ^{t}Bu$_2$*P*CH$_2$CH$_2$*P*^{t}Bu$_2$, J_{PP} = 45 Hz). IR for **7** (Fluorolube mull, CaF_2): 2961 (m), 2153 (ν_{CN}, s), 1671 (m), 1467 (w), 1422 (w), 1391 (w) cm^{-1}. Anal. calcd. for $C_{37}H_{64}N_2NiP_2$: C, 68.16; H, 9.63; N, 4.18. Found: C, 67.98; H, 9.64; N, 3.92.

Reaction of (dtbpe)Ni{*C*,*N*:η^2-C(NCH$_2$Ph)N(2,6-(CHMe$_2$)$_2$C$_6$H$_3$)} (7) with excess CO. In a NMR tube was dissolved **7** [26 mg, 0.039 mmol] in 1 mL of C_6D_6. The pale yellow solution was frozen, degassed, and placed under a 1 atm of CO at –42°C and allowed to warm to room temperature. The brown-yellow mixture was examined by ^{1}H and ^{31}P NMR spectroscopy after 3 hours. The NMR spectra of the reaction mixture revealed formation of **6** and PhCH$_2$N=C=N{2,6-(CHMe$_2$)$_2$C$_6$H$_3$} (**8**; 50% by integration) along with free benzyl isocyanide. GC-MS of the mixture identified the parent ion for **8** (292 (M^+)).

References

1. For a general description of the equipment and techniques used in carrying out this chemistry see: B. J. Burger, J. E. Bercaw. In *Experimental Organometallic Chemistry*; A. L. Wayda, M. Y. Darensbourg; ACS Symposium Series 357; American Chemical Society; Washington, DC, 1987; pp 79-98.

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CRYSTALLOGRAPHIC

SECTION

Crystallographic Experimental Section and Tables

Data Collection for the Crystal of 3b·2Et$_2$O.

A pale yellow block was selected under a stereo-microscope while immersed in Paratone oil to minimize possible reaction with air. The crystal was removed from the oil using a tapered fiber that also served to hold the crystal for data collection. The crystal was mounted and centered on a Bruker SMART APEX system. Rotation and still images showed diffractions to be sharp. Frames separated in reciprocal space were obtained and provided an orientation matrix and initial cell parameters. Final cell parameters were obtained from the full data set.

A “hemisphere" of data set was obtained of reciprocal space to a resolution of 0.84 Å using 0.3^o steps in ω using 30 second integration times for each frame. Data collection was made at 100 K. Integration of intensities and refinement of cell parameters were done using SAINT [1]. Absorption corrections were applied using SADABS [1] or psi-scans but corrections were small due to low absorption and equidimensional shape. Observation after 5.5 hours of data collection showed that the crystal was still clear suggesting no decomposition.

Structure solution and refinement

The space group was determined as P-1 based on systematic absences and intensity statistics. Direct methods was used to locate Ni, P, O, N, F, B, and C atoms from the E-map. With the exception of one disordered solvent molecule all other hydrogens were fixed at calculated positions and refined isotropically. All non-hydrogen atoms were refined anisotropic . Two Et$_2$O molecules were confined in the asymmetric unit, one of which was disordered and lying on an inversion center (O2S). To account for positional disorder at C6S and C7S, both atoms were refined at 0.5 occupancies. One

peripheral CF_3 group on the counter anion suffered from disorder but converged normally during refinement.

$R_{int} = \Sigma \mid F_o^2 - \langle F_o^2 \rangle \mid / \Sigma \mid F_o^2 \mid$

$R_1 = \Sigma \mid \mid F_o \mid - \mid F_c \mid \mid / \Sigma \mid F_o \mid$

$wR_2 = [\Sigma [w (F_o^2 - F_c^2)^2] / \Sigma [w (F_o^2)^2]]^{1/2}$

where: $w = q / \sigma^2 (F_o^2) + (aP)^2 + bP$;

$GoF = S = [\Sigma [w (F_o^2 - F_c^2)^2] / (n-p)^{1/2}$

n = number of independent reflections;

p = number of parameters refined.

References

[1] All software and sources of scattering factors are contained in the SHELXTL (version 5.1) program library (G. Sheldrick, Bruker Analytical X-ray Systems, Madison, WI).

Table 1. Crystal and structure refinement for **3b·2Et$_2$O**

Identification Code	danm59m	
Empirical formula	$C_{69}H_{80}BF_{24}NNiO_{2.5}P_2$	
Formula weight	1550.8	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space Group	P-1	
Unit cell dimensions	*a* = 12.495(3) Å	α = 98.050(2)°
	b = 16.167(4) Å	β = 91.659(4)°
	c = 18.487(4) Å	γ = 91.399(4)°
Volume	3694.7(14) Å^3	
Z	2	
Density (calculated)	1.394 mg/mm^3	
Absorption coefficient	0.410 mm^{-1}	
F(000)	1600	
Crystal size, color, habit	0.40 x 0.35 x 0.08 mm, pale yellow block, Et$_2$O	
Theta range for data collection	1.27 to 24.00°	
Index ranges	$-14 \le h \le 8$, $-18 \le k \le 18$, $-21 \le l \le 21$	
Completeness to theta = 24.00°, 98.8 %		
Reflections collected	17173	
Independent reflections	11460 (R_{int} = 0.0409)	

Absorption correction	semi empirical from psi-scans
Max. and min. transmission	0.9679 and 0.8531
Refinement method	Full-matrix least squares on F^2
Weighting scheme	$w = q\,[\sigma^2\,(F_o^2) + (aP)^2 + bP]^{-1}$ where:
	$P = (F_o^2 + 2\,F_c^2)/3$, a =, b =, q =1
Data / restraints / parameters	11460 / 0 / 917
Goodness-of-fit on F^2	1.069
Final R indices [I > 2 sigma(I)]	R1 = 0.0598, wR2 = 0.1503
R indices (all data)	R1 = 0.0713, wR2 = 0.1605
Largest diff. peak and hole	1.437 and -0.581 $eÅ^{-3}$

Table 2. Atomic coordinates [x 10^4] and equivalent isotropic displacement parameters [$Å^2$ x 10^3] for **3b·2Et₂O**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Ni	9513(1)	1556(1)	1817(1)	15(1)
P(2)	8945(1)	2634(1)	2501(1)	15(1)
P(1)	8316(1)	1688(1)	939(1)	18(1)
O	10326(2)	576(2)	1575(1)	21(1)
F(24)	-276(2)	3561(1)	6419(1)	29(1)
F(15)	3394(2)	207(1)	7092(1)	35(1)
F(23)	-471(2)	4121(2)	5437(1)	38(1)
F(22)	-63(2)	2833(1)	5369(1)	34(1)
F(18)	7495(2)	2327(2)	5932(1)	42(1)
F(12)	6360(2)	6951(1)	7498(2)	43(1)
F(6)	987(2)	4423(2)	9722(1)	47(1)
F(17)	6648(2)	1938(2)	4912(1)	42(1)
F(16)	7227(2)	1025(2)	5548(2)	46(1)
N	11234(2)	725(2)	2687(2)	18(1)
F(11)	4904(2)	6924(2)	8078(2)	46(1)
F(14)	2479(2)	372(2)	6135(2)	49(1)
F(13)	3901(2)	-354(2)	6041(1)	44(1)
C(111)	4844(3)	4201(2)	7280(2)	16(1)
F(5)	142(2)	3833(2)	8759(1)	44(1)
F(21)	4024(2)	4468(2)	4343(1)	54(1)
F(20)	3761(2)	5621(2)	4973(1)	55(1)
F(10)	4865(2)	6675(2)	6915(2)	47(1)
C(70)	10551(3)	963(2)	2209(2)	17(1)
C(121)	4355(3)	2620(2)	6647(2)	16(1)
C(101)	3296(3)	3387(2)	7787(2)	16(1)
C(63)	7182(3)	1932(2)	3083(2)	22(1)
C(138)	1966(3)	3597(2)	6338(2)	17(1)
F(9)	8054(2)	4816(2)	8757(2)	49(1)
C(60)	8240(3)	2399(2)	3341(2)	18(1)
C(71)	11835(3)	-27(2)	2550(2)	19(1)
C(131)	3071(3)	3800(2)	6393(2)	16(1)
C(2)	7915(3)	3096(2)	1946(2)	18(1)
F(4)	990(2)	4992(2)	8740(2)	54(1)
C(125)	5138(3)	1051(2)	6005(2)	22(1)
F(19)	2570(2)	5069(2)	4208(2)	70(1)
C(123)	4145(3)	1104(2)	6336(2)	20(1)
C(128)	5337(3)	2550(2)	6288(2)	17(1)
C(116)	5562(3)	5628(2)	7546(2)	18(1)
C(118)	4759(3)	5052(2)	7259(2)	18(1)
C(115)	6463(3)	5377(2)	7892(2)	21(1)
F(8)	7415(2)	3577(2)	8579(2)	75(1)
C(108)	2432(3)	3845(2)	8063(2)	18(1)
C(102)	3751(3)	2876(2)	8255(2)	21(1)
C(122)	3776(3)	1874(2)	6649(2)	18(1)
C(40)	7529(3)	679(2)	679(2)	23(1)
C(133)	2794(3)	4460(2)	5285(2)	18(1)

C(113)	6572(3)	4541(2)	7930(2)	21(1)
C(76)	12904(3)	47(2)	2353(2)	21(1)
C(126)	5727(3)	1790(2)	5981(2)	19(1)
C(1)	7359(3)	2443(2)	1362(2)	18(1)
C(132)	3461(3)	4226(2)	5836(2)	18(1)
C(30)	8833(3)	2098(3)	107(2)	28(1)
C(62)	7978(3)	3181(2)	3865(2)	25(1)
C(106)	2027(3)	3796(2)	8751(2)	21(1)
B	3874(3)	3503(3)	7014(2)	17(1)
C(137)	132(3)	3591(2)	5758(2)	22(1)
C(72)	11335(3)	-795(2)	2626(2)	22(1)
C(43)	7314(3)	336(2)	1399(2)	27(1)
C(61)	8915(3)	1806(2)	3739(2)	25(1)
C(73)	11963(3)	-1497(2)	2502(2)	27(1)
C(75)	13488(3)	-679(2)	2235(2)	26(1)
C(135)	1709(3)	4279(2)	5268(2)	19(1)
C(127)	6767(3)	1766(3)	5605(2)	28(1)
C(136)	1303(3)	3834(2)	5795(2)	17(1)
C(112)	5787(3)	3969(2)	7628(2)	19(1)
C(80)	13405(3)	889(2)	2237(2)	21(1)
C(53)	10675(3)	3513(3)	2065(2)	38(1)
F(7)	8315(2)	4038(3)	7758(2)	80(1)
C(50)	10008(3)	3481(2)	2748(2)	24(1)
C(105)	2494(3)	3288(2)	9206(2)	25(1)
C(117)	5426(3)	6529(2)	7509(2)	27(1)
C(103)	3377(3)	2830(2)	8953(2)	23(1)
C(134)	3279(3)	4906(3)	4710(2)	25(1)
C(124)	3487(3)	340(2)	6396(2)	26(1)
C(52)	9554(3)	4351(2)	2978(2)	34(1)
C(42)	8233(3)	57(2)	217(2)	29(1)
C(90)	10159(3)	-882(2)	2823(2)	25(1)
C(82)	13160(4)	1073(3)	1458(2)	38(1)
C(51)	10750(3)	3253(3)	3352(2)	38(1)
F(3)	4335(4)	1618(2)	9082(2)	100(1)
C(107)	1054(3)	4258(3)	8998(2)	31(1)
C(74)	13019(3)	-1438(2)	2311(2)	28(1)
C(104)	3939(4)	2313(3)	9441(2)	31(1)
C(41)	6445(3)	772(3)	285(2)	35(1)
C(114)	7584(3)	4241(3)	8257(2)	33(1)
C(33)	9924(4)	1692(3)	-76(2)	43(1)
C(81)	14602(3)	959(3)	2400(3)	43(1)
C(92)	9477(3)	-1254(3)	2146(2)	34(1)
F(2)	3292(3)	1945(3)	9839(3)	128(2)
C(32)	8076(4)	1937(3)	-566(2)	45(1)
F(1)	4670(5)	2658(2)	9820(3)	176(3)
C(31)	9025(4)	3034(3)	287(2)	44(1)
C(91)	10011(3)	-1409(3)	3438(2)	35(1)
O(1S)	7839(2)	-1598(2)	5939(1)	27(1)
C(4S)	8885(3)	-604(3)	5403(2)	36(1)
C(2S)	7123(3)	-2309(3)	5839(2)	31(1)
C(3S)	8038(4)	-1280(3)	5281(2)	41(1)
C(1S)	6000(4)	-2129(3)	5606(3)	46(1)
O(2S)	5000	5000	0	65(2)
C(5S)	6263(6)	4376(4)	703(4)	97(3)
C(6S)	5907(7)	4667(6)	72(5)	36(2)
C(7S)	5481(8)	4782(6)	635(5)	43(2)

Table 3. Bond lengths [Å] and angles [°] for **3b·2Et$_2$O.**

Ni-C(70)	1.823(4)
Ni-O	1.910(3)
Ni-P(2)	2.1530(11)
Ni-P(1)	2.2125(11)
P(2)-C(2)	1.858(4)
P(2)-C(50)	1.884(3)
P(2)-C(60)	1.887(3)
P(1)-C(1)	1.841(4)
P(1)-C(40)	1.879(4)
P(1)-C(30)	1.883(4)
O-C(70)	1.270(4)
F(24)-C(137)	1.343(4)
F(15)-C(124)	1.340(4)
F(23)-C(137)	1.341(4)
F(22)-C(137)	1.345(4)
F(18)-C(127)	1.338(4)
F(12)-C(117)	1.340(4)
F(6)-C(107)	1.333(4)
F(17)-C(127)	1.354(4)
F(16)-C(127)	1.333(5)
N-C(70)	1.314(4)
N-C(71)	1.440(5)
F(11)-C(117)	1.346(5)
F(14)-C(124)	1.341(4)
F(13)-C(124)	1.341(5)
C(111)-C(118)	1.388(5)
C(111)-C(112)	1.410(5)
C(111)-B	1.651(5)
F(5)-C(107)	1.347(5)
F(21)-C(134)	1.327(5)
F(20)-C(134)	1.315(5)
F(10)-C(117)	1.338(5)
C(121)-C(122)	1.392(5)
C(121)-C(128)	1.412(5)
C(121)-B	1.629(5)
C(101)-C(108)	1.392(5)
C(101)-C(102)	1.397(5)
C(101)-B	1.652(5)
C(63)-C(60)	1.536(5)
C(138)-C(136)	1.384(5)
C(138)-C(131)	1.409(5)
F(9)-C(114)	1.329(5)
C(60)-C(61)	1.540(5)
C(60)-C(62)	1.530(5)
C(71)-C(76)	1.401(5)
C(71)-C(72)	1.402(5)
C(131)-C(132)	1.408(5)
C(131)-B	1.633(5)
C(2)-C(1)	1.538(5)
F(4)-C(107)	1.342(5)
C(125)-C(123)	1.398(5)

C(125)-C(126)	1.394(5)
F(19)-C(134)	1.322(4)
C(123)-C(122)	1.392(5)
C(123)-C(124)	1.487(5)
C(128)-C(126)	1.385(5)
C(116)-C(115)	1.376(5)
C(116)-C(118)	1.394(5)
C(116)-C(117)	1.481(5)
C(115)-C(113)	1.373(5)
F(8)-C(114)	1.314(5)
C(108)-C(106)	1.396(5)
C(102)-C(103)	1.394(5)
C(40)-C(42)	1.536(5)
C(40)-C(41)	1.541(5)
C(40)-C(43)	1.539(5)
C(133)-C(135)	1.378(5)
C(133)-C(132)	1.396(5)
C(133)-C(134)	1.498(5)
C(113)-C(112)	1.381(5)
C(113)-C(114)	1.506(5)
C(76)-C(75)	1.393(5)
C(76)-C(80)	1.529(5)
C(126)-C(127)	1.490(5)
C(30)-C(31)	1.516(6)
C(30)-C(32)	1.529(6)
C(30)-C(33)	1.553(6)
C(106)-C(105)	1.382(5)
C(106)-C(107)	1.493(6)
C(137)-C(136)	1.503(5)
C(72)-C(73)	1.392(5)
C(72)-C(90)	1.532(5)
C(73)-C(74)	1.380(6)
C(75)-C(74)	1.374(5)
C(135)-C(136)	1.391(5)
C(80)-C(81)	1.516(5)
C(80)-C(82)	1.535(5)
C(53)-C(50)	1.539(6)
F(7)-C(114)	1.331(5)
C(50)-C(51)	1.522(6)
C(50)-C(52)	1.537(6)
C(105)-C(103)	1.400(6)
C(103)-C(104)	1.487(5)
C(90)-C(91)	1.526(5)
C(90)-C(92)	1.535(5)
F(3)-C(104)	1.335(5)
C(104)-F(1)	1.211(5)
C(104)-F(2)	1.297(5)
O(1S)-C(3S)	1.411(5)
O(1S)-C(2S)	1.427(5)
C(4S)-C(3S)	1.492(6)
C(2S)-C(1S)	1.504(6)
O(2S)-C(6S)	1.278(9)
O(2S)-C(6S)#1	1.278(9)
O(2S)-C(7S)#1	1.397(10)
O(2S)-C(7S)	1.397(10)
C(5S)-C(7S)	1.204(12)
C(5S)-C(6S)	1.383(10)

C(6S)-C(7S)	1.178(13)

C(70)-Ni-O	39.69(13)
C(70)-Ni-P(2)	117.04(12)
O-Ni-P(2)	156.65(8)
C(70)-Ni-P(1)	150.48(12)
O-Ni-P(1)	110.97(8)
P(2)-Ni-P(1)	92.08(4)
C(2)-P(2)-C(50)	105.37(17)
C(2)-P(2)-C(60)	105.32(16)
C(50)-P(2)-C(60)	110.80(16)
C(2)-P(2)-Ni	106.39(12)
C(50)-P(2)-Ni	113.14(13)
C(60)-P(2)-Ni	114.93(12)
C(1)-P(1)-C(40)	105.85(17)
C(1)-P(1)-C(30)	107.55(17)
C(40)-P(1)-C(30)	111.18(18)
C(1)-P(1)-Ni	105.07(11)
C(40)-P(1)-Ni	110.03(12)
C(30)-P(1)-Ni	116.42(14)
C(70)-O-Ni	66.5(2)
C(70)-N-C(71)	123.4(3)
C(118)-C(111)-C(112)	115.1(3)
C(118)-C(111)-B	123.9(3)
C(112)-C(111)-B	120.6(3)
O-C(70)-N	125.7(3)
O-C(70)-Ni	73.8(2)
N-C(70)-Ni	160.3(3)
C(122)-C(121)-C(128)	115.5(3)
C(122)-C(121)-B	120.5(3)
C(128)-C(121)-B	124.0(3)
C(108)-C(101)-C(102)	115.2(3)
C(108)-C(101)-B	124.4(3)
C(102)-C(101)-B	120.0(3)
C(136)-C(138)-C(131)	122.3(3)
C(61)-C(60)-C(62)	110.6(3)
C(61)-C(60)-C(63)	107.4(3)
C(62)-C(60)-C(63)	108.1(3)
C(61)-C(60)-P(2)	109.6(2)
C(62)-C(60)-P(2)	113.5(2)
C(63)-C(60)-P(2)	107.4(2)
C(76)-C(71)-C(72)	123.0(3)
C(76)-C(71)-N	118.0(3)
C(72)-C(71)-N	119.0(3)
C(138)-C(131)-C(132)	115.2(3)
C(138)-C(131)-B	123.1(3)
C(132)-C(131)-B	121.5(3)
C(1)-C(2)-P(2)	112.5(2)
C(123)-C(125)-C(126)	118.1(3)
C(122)-C(123)-C(125)	120.5(3)
C(122)-C(123)-C(124)	118.4(3)
C(125)-C(123)-C(124)	121.0(3)
C(126)-C(128)-C(121)	122.7(3)
C(115)-C(116)-C(118)	121.0(3)
C(115)-C(116)-C(117)	119.2(3)
C(118)-C(116)-C(117)	119.7(3)

C(111)-C(118)-C(116)	122.1(3)
C(116)-C(115)-C(113)	118.6(3)
C(101)-C(108)-C(106)	123.2(3)
C(103)-C(102)-C(101)	122.7(4)
C(123)-C(122)-C(121)	122.7(3)
C(42)-C(40)-C(41)	111.3(3)
C(42)-C(40)-C(43)	108.0(3)
C(41)-C(40)-C(43)	108.2(3)
C(42)-C(40)-P(1)	108.6(3)
C(41)-C(40)-P(1)	114.2(3)
C(43)-C(40)-P(1)	106.2(2)
C(135)-C(133)-C(132)	120.5(3)
C(135)-C(133)-C(134)	120.7(3)
C(132)-C(133)-C(134)	118.9(3)
C(115)-C(113)-C(112)	120.3(3)
C(115)-C(113)-C(114)	119.8(3)
C(112)-C(113)-C(114)	119.8(3)
C(75)-C(76)-C(71)	117.8(3)
C(75)-C(76)-C(80)	120.6(3)
C(71)-C(76)-C(80)	121.5(3)
C(128)-C(126)-C(125)	120.4(3)
C(128)-C(126)-C(127)	119.7(3)
C(125)-C(126)-C(127)	119.9(3)
C(2)-C(1)-P(1)	111.4(2)
C(133)-C(132)-C(131)	122.5(3)
C(31)-C(30)-C(32)	107.7(4)
C(31)-C(30)-C(33)	108.1(4)
C(32)-C(30)-C(33)	109.5(4)
C(31)-C(30)-P(1)	108.8(3)
C(32)-C(30)-P(1)	114.4(3)
C(33)-C(30)-P(1)	108.1(3)
C(105)-C(106)-C(108)	120.5(4)
C(105)-C(106)-C(107)	118.6(3)
C(108)-C(106)-C(107)	120.8(3)
C(131)-B-C(121)	106.1(3)
C(131)-B-C(111)	112.3(3)
C(121)-B-C(111)	111.1(3)
C(131)-B-C(101)	114.3(3)
C(121)-B-C(101)	110.2(3)
C(111)-B-C(101)	103.0(3)
F(23)-C(137)-F(22)	105.8(3)
F(23)-C(137)-F(24)	106.3(3)
F(22)-C(137)-F(24)	106.3(3)
F(23)-C(137)-C(136)	112.8(3)
F(22)-C(137)-C(136)	112.0(3)
F(24)-C(137)-C(136)	113.1(3)
C(73)-C(72)-C(71)	116.4(3)
C(73)-C(72)-C(90)	120.4(3)
C(71)-C(72)-C(90)	123.2(3)
C(74)-C(73)-C(72)	121.6(4)
C(74)-C(75)-C(76)	120.3(4)
C(133)-C(135)-C(136)	118.6(3)
F(16)-C(127)-F(18)	106.5(3)
F(16)-C(127)-F(17)	105.6(3)
F(18)-C(127)-F(17)	105.5(3)
F(16)-C(127)-C(126)	113.9(3)
F(18)-C(127)-C(126)	113.1(3)

F(17)-C(127)-C(126)	111.6(3)
C(138)-C(136)-C(135)	120.9(3)
C(138)-C(136)-C(137)	120.1(3)
C(135)-C(136)-C(137)	119.0(3)
C(113)-C(112)-C(111)	122.9(3)
C(81)-C(80)-C(82)	109.9(3)
C(81)-C(80)-C(76)	113.5(3)
C(82)-C(80)-C(76)	110.9(3)
C(51)-C(50)-C(52)	110.0(3)
C(51)-C(50)-C(53)	107.7(3)
C(52)-C(50)-C(53)	108.5(3)
C(51)-C(50)-P(2)	109.8(3)
C(52)-C(50)-P(2)	113.6(3)
C(53)-C(50)-P(2)	107.0(3)
C(106)-C(105)-C(103)	117.9(3)
F(10)-C(117)-F(12)	105.8(3)
F(10)-C(117)-F(11)	105.0(3)
F(12)-C(117)-F(11)	105.8(3)
F(10)-C(117)-C(116)	113.3(3)
F(12)-C(117)-C(116)	112.9(3)
F(11)-C(117)-C(116)	113.3(3)
C(102)-C(103)-C(105)	120.5(3)
C(102)-C(103)-C(104)	119.9(4)
C(105)-C(103)-C(104)	119.5(3)
F(20)-C(134)-F(19)	106.7(3)
F(20)-C(134)-F(21)	104.8(3)
F(19)-C(134)-F(21)	105.3(3)
F(20)-C(134)-C(133)	113.5(3)
F(19)-C(134)-C(133)	113.0(3)
F(21)-C(134)-C(133)	112.9(3)
F(14)-C(124)-F(13)	106.6(3)
F(14)-C(124)-F(15)	105.2(3)
F(13)-C(124)-F(15)	106.3(3)
F(14)-C(124)-C(123)	113.3(3)
F(13)-C(124)-C(123)	112.6(3)
F(15)-C(124)-C(123)	112.2(3)
C(91)-C(90)-C(72)	112.5(3)
C(91)-C(90)-C(92)	110.2(3)
C(72)-C(90)-C(92)	110.3(3)
F(6)-C(107)-F(4)	106.8(4)
F(6)-C(107)-F(5)	105.7(3)
F(4)-C(107)-F(5)	105.1(3)
F(6)-C(107)-C(106)	114.1(3)
F(4)-C(107)-C(106)	112.3(3)
F(5)-C(107)-C(106)	112.2(3)
C(73)-C(74)-C(75)	120.9(4)
F(1)-C(104)-F(2)	109.8(5)
F(1)-C(104)-F(3)	106.2(5)
F(2)-C(104)-F(3)	96.7(4)
F(1)-C(104)-C(103)	116.0(4)
F(2)-C(104)-C(103)	113.1(4)
F(3)-C(104)-C(103)	113.2(3)
F(8)-C(114)-F(9)	106.4(3)
F(8)-C(114)-F(7)	106.7(4)
F(9)-C(114)-F(7)	105.9(4)
F(8)-C(114)-C(113)	112.5(3)
F(9)-C(114)-C(113)	112.6(4)

F(7)-C(114)-C(113)	112.3(3)
C(3S)-O(1S)-C(2S)	112.9(3)
O(1S)-C(2S)-C(1S)	114.4(4)
O(1S)-C(3S)-C(4S)	110.5(3)
C(6S)-O(2S)-C(6S)#1	180.000(2)
C(6S)-O(2S)-C(7S)#1	128.0(6)
C(6S)#1-O(2S)-C(7S)#1	52.0(6)
C(6S)-O(2S)-C(7S)	52.0(6)
C(6S)#1-O(2S)-C(7S)	128.0(6)
C(7S)#1-O(2S)-C(7S)	180.0(8)
C(7S)-C(5S)-C(6S)	53.6(6)
C(7S)-C(6S)-O(2S)	69.2(8)
C(7S)-C(6S)-C(5S)	55.4(7)
O(2S)-C(6S)-C(5S)	123.9(9)
C(6S)-C(7S)-C(5S)	71.0(9)
C(6S)-C(7S)-O(2S)	58.8(6)
C(5S)-C(7S)-O(2S)	129.2(9)

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

Table 4. Anisotropic displacement parameters [$Å^2$ x 10^3] for **3b·2Et$_2$O**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+ ... + 2hka^*b^*U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ni	15(1)	15(1)	15(1)	0(1)	1(1)	2(1)
P(2)	14(1)	13(1)	17(1)	1(1)	1(1)	0(1)
P(1)	20(1)	18(1)	15(1)	2(1)	1(1)	3(1)
O	23(1)	20(1)	19(1)	1(1)	-1(1)	5(1)
F(24)	19(1)	39(1)	28(1)	3(1)	2(1)	-4(1)
F(15)	53(2)	26(1)	29(1)	13(1)	5(1)	-6(1)
F(23)	21(1)	43(2)	54(2)	23(1)	-9(1)	-1(1)
F(22)	33(1)	31(1)	34(1)	-6(1)	-5(1)	-12(1)
F(18)	21(1)	54(2)	46(2)	-7(1)	8(1)	-3(1)
F(12)	24(1)	21(1)	86(2)	17(1)	5(1)	-5(1)
F(6)	43(2)	70(2)	26(1)	-1(1)	10(1)	17(1)
F(17)	39(2)	66(2)	22(1)	10(1)	11(1)	7(1)
F(16)	37(2)	39(2)	63(2)	4(1)	15(1)	19(1)
N	21(2)	14(2)	18(2)	1(1)	-1(1)	2(1)
F(11)	50(2)	22(1)	65(2)	-2(1)	22(1)	10(1)
F(14)	43(2)	34(2)	71(2)	25(1)	-23(1)	-17(1)
F(13)	68(2)	20(1)	43(2)	-3(1)	16(1)	-5(1)
C(111)	16(2)	18(2)	15(2)	4(2)	5(1)	2(1)
F(5)	20(1)	67(2)	46(2)	9(1)	1(1)	4(1)
F(21)	73(2)	50(2)	46(2)	22(1)	40(2)	20(1)
F(20)	90(2)	37(2)	41(2)	11(1)	20(2)	-23(2)
F(10)	60(2)	22(1)	60(2)	16(1)	-17(1)	6(1)
C(70)	18(2)	17(2)	17(2)	6(2)	5(2)	2(2)
C(121)	18(2)	18(2)	12(2)	6(1)	-3(1)	-1(2)
C(101)	15(2)	15(2)	17(2)	2(2)	-2(2)	-5(1)

C(63)	26(2)	22(2)	20(2)	5(2)	8(2)	-1(2)
C(138)	21(2)	16(2)	14(2)	1(2)	0(2)	1(2)
F(9)	46(2)	35(2)	63(2)	0(1)	-37(1)	-3(1)
C(60)	21(2)	20(2)	12(2)	2(2)	2(2)	-1(2)
C(71)	25(2)	17(2)	15(2)	2(2)	-1(2)	6(2)
C(131)	20(2)	13(2)	16(2)	1(1)	3(2)	2(1)
C(2)	22(2)	15(2)	18(2)	5(2)	3(2)	2(2)
F(4)	56(2)	43(2)	71(2)	26(2)	37(2)	25(1)
C(125)	30(2)	20(2)	15(2)	2(2)	-3(2)	5(2)
F(19)	32(2)	129(3)	65(2)	77(2)	-10(1)	-10(2)
C(123)	29(2)	19(2)	14(2)	7(2)	-5(2)	0(2)
C(128)	19(2)	19(2)	13(2)	5(2)	-5(2)	-4(2)
C(116)	14(2)	15(2)	26(2)	5(2)	6(2)	-1(1)
C(118)	14(2)	20(2)	20(2)	2(2)	4(2)	3(2)
C(115)	18(2)	20(2)	26(2)	2(2)	1(2)	-4(2)
F(8)	65(2)	41(2)	124(3)	44(2)	-58(2)	-16(2)
C(108)	18(2)	19(2)	18(2)	5(2)	-5(2)	-5(2)
C(102)	18(2)	20(2)	24(2)	4(2)	-1(2)	-1(2)
C(122)	16(2)	23(2)	16(2)	7(2)	2(2)	2(2)
C(40)	24(2)	20(2)	24(2)	-3(2)	-4(2)	2(2)
C(133)	22(2)	19(2)	15(2)	3(2)	0(2)	1(2)
C(113)	16(2)	22(2)	25(2)	6(2)	-2(2)	-1(2)
C(76)	22(2)	25(2)	15(2)	-1(2)	-3(2)	3(2)
C(126)	22(2)	22(2)	15(2)	3(2)	-2(2)	5(2)
C(1)	20(2)	19(2)	16(2)	5(2)	0(2)	4(2)
C(132)	17(2)	18(2)	18(2)	1(2)	2(2)	1(2)
C(30)	40(2)	29(2)	18(2)	9(2)	10(2)	7(2)
C(62)	30(2)	27(2)	19(2)	-1(2)	3(2)	3(2)
C(106)	17(2)	27(2)	18(2)	4(2)	6(2)	-7(2)
B	18(2)	17(2)	16(2)	4(2)	2(2)	-1(2)
C(137)	26(2)	20(2)	20(2)	2(2)	-4(2)	0(2)
C(72)	26(2)	24(2)	17(2)	5(2)	-1(2)	-1(2)
C(43)	28(2)	22(2)	30(2)	-1(2)	-1(2)	-7(2)
C(61)	29(2)	27(2)	20(2)	5(2)	-2(2)	3(2)
C(73)	42(3)	17(2)	22(2)	5(2)	1(2)	4(2)
C(75)	24(2)	28(2)	25(2)	-1(2)	-1(2)	5(2)
C(135)	22(2)	17(2)	16(2)	0(2)	-6(2)	6(2)
C(127)	29(2)	26(2)	28(2)	1(2)	0(2)	7(2)
C(136)	22(2)	15(2)	14(2)	0(2)	1(2)	-2(2)
C(112)	26(2)	14(2)	18(2)	6(2)	-1(2)	1(2)
C(80)	20(2)	20(2)	21(2)	-2(2)	-2(2)	-2(2)
C(53)	28(2)	32(3)	53(3)	2(2)	11(2)	-13(2)
F(7)	42(2)	134(3)	60(2)	-5(2)	-14(2)	48(2)
C(50)	17(2)	19(2)	33(2)	-2(2)	1(2)	-7(2)
C(105)	25(2)	30(2)	21(2)	8(2)	4(2)	-11(2)
C(117)	17(2)	23(2)	42(3)	7(2)	4(2)	0(2)
C(103)	27(2)	23(2)	21(2)	10(2)	0(2)	-3(2)
C(134)	25(2)	32(2)	20(2)	8(2)	-3(2)	2(2)
C(124)	37(2)	19(2)	22(2)	2(2)	-4(2)	-3(2)
C(52)	31(2)	20(2)	48(3)	1(2)	-1(2)	-8(2)
C(42)	35(2)	25(2)	25(2)	-6(2)	-5(2)	4(2)
C(90)	32(2)	18(2)	27(2)	4(2)	5(2)	-1(2)
C(82)	48(3)	31(3)	33(2)	3(2)	-3(2)	-14(2)
C(51)	27(2)	29(3)	52(3)	-4(2)	-14(2)	-9(2)
F(3)	163(4)	78(3)	64(2)	21(2)	-27(2)	61(3)
C(107)	30(2)	39(3)	25(2)	11(2)	7(2)	0(2)
C(74)	35(2)	22(2)	27(2)	3(2)	-3(2)	11(2)

C(104)	48(3)	27(2)	20(2)	10(2)	1(2)	1(2)
C(41)	32(2)	38(3)	32(2)	-5(2)	-9(2)	2(2)
C(114)	29(2)	26(2)	42(3)	5(2)	-14(2)	-2(2)
C(33)	47(3)	49(3)	36(3)	14(2)	19(2)	8(2)
C(81)	25(2)	29(3)	73(3)	4(2)	-8(2)	-4(2)
C(92)	35(2)	31(2)	35(2)	5(2)	0(2)	-4(2)
F(2)	94(3)	174(5)	153(4)	144(4)	26(3)	34(3)
C(32)	68(3)	45(3)	22(2)	11(2)	1(2)	13(2)
F(1)	242(6)	53(2)	231(5)	75(3)	-221(5)	-59(3)
C(31)	64(3)	35(3)	37(3)	14(2)	20(2)	-1(2)
C(91)	41(3)	33(3)	32(2)	9(2)	7(2)	-7(2)
O(1S)	33(2)	26(2)	20(1)	3(1)	-5(1)	-3(1)
C(4S)	38(3)	38(3)	32(2)	13(2)	-4(2)	0(2)
C(2S)	35(2)	26(2)	31(2)	2(2)	-2(2)	-1(2)
C(3S)	48(3)	51(3)	23(2)	6(2)	0(2)	-16(2)
C(1S)	34(3)	56(3)	49(3)	19(2)	-10(2)	-4(2)
O(2S)	99(5)	44(3)	51(3)	8(2)	-43(3)	10(3)
C(5S)	124(6)	38(4)	130(6)	36(4)	-95(5)	-18(4)
C(6S)	33(5)	34(5)	42(6)	14(4)	-15(4)	3(4)
C(7S)	55(6)	47(6)	28(5)	8(5)	2(5)	-6(5)

Table 5. Hydrogen coordinates [x 10^4] and isotropic displacement parameters [$Å^2$ x 10^3] for **3b·2Et$_2$O.**

	x	y	z	U(eq)
H(0A)	11328	1034	3103	21
H(63A)	6803	1802	3499	33
H(63B)	7330	1425	2771	33
H(63C)	6751	2279	2817	33
H(13A)	1671	3294	6679	21
H(2A)	7381	3356	2267	22
H(2B)	8252	3528	1708	22
H(12A)	5398	538	5805	26
H(12B)	5740	3035	6257	20
H(11A)	4146	5243	7045	21
H(11B)	6987	5766	8096	26
H(10A)	2109	4202	7774	22
H(10B)	4326	2552	8096	25
H(12C)	3115	1890	6869	21
H(1A)	7025	2724	988	22
H(1B)	6801	2147	1586	22
H(13B)	4190	4356	5835	21
H(62A)	7622	3021	4279	38
H(62B)	7519	3527	3617	38
H(62C)	8629	3488	4027	38
H(43A)	6903	-179	1296	41
H(43B)	6921	736	1713	41
H(43C)	7982	238	1637	41
H(61A)	8554	1686	4165	38

H(61B)	9602	2068	3882	38
H(61C)	9012	1296	3417	38
H(73A)	11663	-2018	2548	32
H(75A)	14200	-650	2104	31
H(13C)	1259	4450	4911	22
H(11C)	5885	3405	7656	23
H(80A)	13071	1322	2574	25
H(53A)	11228	3939	2170	57
H(53B)	10220	3638	1670	57
H(53C)	10994	2981	1929	57
H(10C)	2229	3252	9666	30
H(52A)	10134	4752	3096	50
H(52B)	9124	4338	3398	50
H(52C)	9123	4505	2583	50
H(42A)	7838	-460	76	44
H(42B)	8863	-43	498	44
H(42C)	8438	285	-213	44
H(90A)	9903	-322	2990	31
H(82A)	12400	1027	1358	57
H(82B)	13513	679	1114	57
H(82C)	13411	1629	1413	57
H(51A)	11292	3686	3474	57
H(51B)	11084	2735	3186	57
H(51C)	10345	3194	3776	57
H(74A)	13418	-1918	2233	34
H(41A)	6090	235	172	52
H(41B)	6562	1002	-158	52
H(41C)	6007	1139	597	52
H(33A)	10203	1894	-499	64
H(33B)	9824	1096	-173	64
H(33C)	10419	1835	332	64
H(81A)	14750	840	2887	64
H(81B)	14858	1515	2359	64
H(81C)	14958	565	2057	64
H(92A)	9570	-914	1765	51
H(92B)	8736	-1268	2269	51
H(92C)	9699	-1811	1981	51
H(32A)	8397	2159	-966	67
H(32B)	7411	2205	-458	67
H(32C)	7946	1347	-696	67
H(31A)	9297	3249	-133	66
H(31B)	9537	3152	687	66
H(31C)	8364	3296	419	66
H(91A)	10448	-1176	3857	52
H(91B)	10220	-1971	3278	52
H(91C)	9273	-1412	3568	52
H(4SA)	9006	-389	4953	53
H(4SB)	9537	-825	5573	53
H(4SC)	8658	-161	5763	53
H(2SA)	7100	-2542	6294	37
H(2SB)	7407	-2729	5473	37
H(3SA)	7384	-1060	5097	49
H(3SB)	8266	-1727	4917	49
H(1SA)	5569	-2635	5552	69
H(1SB)	6010	-1913	5148	69
H(1SC)	5703	-1724	5970	69

Table 6. Torsion angles [°] for **3b·2Et$_2$O**.

C(70)-Ni-P(2)-C(2)	179.54(16)
O-Ni-P(2)-C(2)	-176.4(2)
P(1)-Ni-P(2)-C(2)	-5.44(12)
C(70)-Ni-P(2)-C(50)	64.31(18)
O-Ni-P(2)-C(50)	68.4(2)
P(1)-Ni-P(2)-C(50)	-120.66(14)
C(70)-Ni-P(2)-C(60)	-64.33(17)
O-Ni-P(2)-C(60)	-60.2(2)
P(1)-Ni-P(2)-C(60)	110.69(12)
C(70)-Ni-P(1)-C(1)	158.1(2)
O-Ni-P(1)-C(1)	163.26(14)
P(2)-Ni-P(1)-C(1)	-12.90(12)
C(70)-Ni-P(1)-C(40)	44.6(3)
O-Ni-P(1)-C(40)	49.73(16)
P(2)-Ni-P(1)-C(40)	-126.42(13)
C(70)-Ni-P(1)-C(30)	-83.1(3)
O-Ni-P(1)-C(30)	-77.90(17)
P(2)-Ni-P(1)-C(30)	105.95(15)
P(2)-Ni-O-C(70)	-5.7(3)
P(1)-Ni-O-C(70)	-176.01(18)
Ni-O-C(70)-N	177.2(4)
C(71)-N-C(70)-O	0.1(5)
C(71)-N-C(70)-Ni	172.1(7)
P(2)-Ni-C(70)-O	177.45(14)
P(1)-Ni-C(70)-O	7.6(3)
O-Ni-C(70)-N	-173.3(9)
P(2)-Ni-C(70)-N	4.2(9)
P(1)-Ni-C(70)-N	-165.7(7)
C(2)-P(2)-C(60)-C(61)	165.0(2)
C(50)-P(2)-C(60)-C(61)	-81.6(3)
Ni-P(2)-C(60)-C(61)	48.2(3)
C(2)-P(2)-C(60)-C(62)	-70.9(3)
C(50)-P(2)-C(60)-C(62)	42.6(3)
Ni-P(2)-C(60)-C(62)	172.4(2)
C(2)-P(2)-C(60)-C(63)	48.6(3)
C(50)-P(2)-C(60)-C(63)	162.0(2)
Ni-P(2)-C(60)-C(63)	-68.2(3)
C(70)-N-C(71)-C(76)	100.5(4)
C(70)-N-C(71)-C(72)	-80.1(4)
C(136)-C(138)-C(131)-C(132)	-2.9(5)
C(136)-C(138)-C(131)-B	-178.1(3)
C(50)-P(2)-C(2)-C(1)	147.9(3)
C(60)-P(2)-C(2)-C(1)	-94.9(3)
Ni-P(2)-C(2)-C(1)	27.5(3)
C(126)-C(125)-C(123)-C(122)	-1.7(5)
C(126)-C(125)-C(123)-C(124)	-178.4(3)
C(122)-C(121)-C(128)-C(126)	-2.4(5)
B-C(121)-C(128)-C(126)	180.0(3)
C(112)-C(111)-C(118)-C(116)	1.5(5)
B-C(111)-C(118)-C(116)	174.4(3)
C(115)-C(116)-C(118)-C(111)	-2.6(5)
C(117)-C(116)-C(118)-C(111)	-179.9(3)

C(118)-C(116)-C(115)-C(113)	1.9(5)
C(117)-C(116)-C(115)-C(113)	179.2(4)
C(102)-C(101)-C(108)-C(106)	-1.0(5)
B-C(101)-C(108)-C(106)	-173.3(3)
C(108)-C(101)-C(102)-C(103)	-0.6(5)
B-C(101)-C(102)-C(103)	172.1(3)
C(125)-C(123)-C(122)-C(121)	0.5(5)
C(124)-C(123)-C(122)-C(121)	177.3(3)
C(128)-C(121)-C(122)-C(123)	1.5(5)
B-C(121)-C(122)-C(123)	179.2(3)
C(1)-P(1)-C(40)-C(42)	171.4(2)
C(30)-P(1)-C(40)-C(42)	54.9(3)
Ni-P(1)-C(40)-C(42)	-75.6(3)
C(1)-P(1)-C(40)-C(41)	46.6(3)
C(30)-P(1)-C(40)-C(41)	-69.9(3)
Ni-P(1)-C(40)-C(41)	159.6(2)
C(1)-P(1)-C(40)-C(43)	-72.6(3)
C(30)-P(1)-C(40)-C(43)	170.9(3)
Ni-P(1)-C(40)-C(43)	40.4(3)
C(116)-C(115)-C(113)-C(112)	-0.3(6)
C(116)-C(115)-C(113)-C(114)	175.6(3)
C(72)-C(71)-C(76)-C(75)	-0.6(5)
N-C(71)-C(76)-C(75)	178.8(3)
C(72)-C(71)-C(76)-C(80)	176.8(3)
N-C(71)-C(76)-C(80)	-3.9(5)
C(121)-C(128)-C(126)-C(125)	1.2(5)
C(121)-C(128)-C(126)-C(127)	179.4(3)
C(123)-C(125)-C(126)-C(128)	0.9(5)
C(123)-C(125)-C(126)-C(127)	-177.3(3)
P(2)-C(2)-C(1)-P(1)	-39.5(3)
C(40)-P(1)-C(1)-C(2)	149.3(2)
C(30)-P(1)-C(1)-C(2)	-91.8(3)
Ni-P(1)-C(1)-C(2)	32.8(3)
C(135)-C(133)-C(132)-C(131)	0.0(5)
C(134)-C(133)-C(132)-C(131)	-179.5(3)
C(138)-C(131)-C(132)-C(133)	2.4(5)
B-C(131)-C(132)-C(133)	177.7(3)
C(1)-P(1)-C(30)-C(31)	40.6(3)
C(40)-P(1)-C(30)-C(31)	156.0(3)
Ni-P(1)-C(30)-C(31)	-76.9(3)
C(1)-P(1)-C(30)-C(32)	-79.9(3)
C(40)-P(1)-C(30)-C(32)	35.6(4)
Ni-P(1)-C(30)-C(32)	162.6(3)
C(1)-P(1)-C(30)-C(33)	157.8(3)
C(40)-P(1)-C(30)-C(33)	-86.7(3)
Ni-P(1)-C(30)-C(33)	40.3(3)
C(101)-C(108)-C(106)-C(105)	1.3(5)
C(101)-C(108)-C(106)-C(107)	-175.8(3)
C(138)-C(131)-B-C(121)	92.0(4)
C(132)-C(131)-B-C(121)	-82.9(4)
C(138)-C(131)-B-C(111)	-146.4(3)
C(132)-C(131)-B-C(111)	38.7(5)
C(138)-C(131)-B-C(101)	-29.6(5)
C(132)-C(131)-B-C(101)	155.5(3)
C(122)-C(121)-B-C(131)	-83.2(4)
C(128)-C(121)-B-C(131)	94.3(4)
C(122)-C(121)-B-C(111)	154.4(3)

C(128)-C(121)-B-C(111)	-28.0(4)
C(122)-C(121)-B-C(101)	41.0(4)
C(128)-C(121)-B-C(101)	-141.5(3)
C(118)-C(111)-B-C(131)	27.2(5)
C(112)-C(111)-B-C(131)	-160.2(3)
C(118)-C(111)-B-C(121)	145.9(3)
C(112)-C(111)-B-C(121)	-41.6(4)
C(118)-C(111)-B-C(101)	-96.2(4)
C(112)-C(111)-B-C(101)	76.4(4)
C(108)-C(101)-B-C(131)	-30.3(5)
C(102)-C(101)-B-C(131)	157.7(3)
C(108)-C(101)-B-C(121)	-149.6(3)
C(102)-C(101)-B-C(121)	38.4(4)
C(108)-C(101)-B-C(111)	91.8(4)
C(102)-C(101)-B-C(111)	-80.2(4)
C(76)-C(71)-C(72)-C(73)	0.7(5)
N-C(71)-C(72)-C(73)	-178.7(3)
C(76)-C(71)-C(72)-C(90)	-178.5(3)
N-C(71)-C(72)-C(90)	2.1(5)
C(71)-C(72)-C(73)-C(74)	-0.3(5)
C(90)-C(72)-C(73)-C(74)	178.9(3)
C(71)-C(76)-C(75)-C(74)	0.1(5)
C(80)-C(76)-C(75)-C(74)	-177.3(3)
C(132)-C(133)-C(135)-C(136)	-2.2(5)
C(134)-C(133)-C(135)-C(136)	177.4(3)
C(128)-C(126)-C(127)-F(16)	159.0(3)
C(125)-C(126)-C(127)-F(16)	-22.8(5)
C(128)-C(126)-C(127)-F(18)	37.3(5)
C(125)-C(126)-C(127)-F(18)	-144.6(3)
C(128)-C(126)-C(127)-F(17)	-81.6(4)
C(125)-C(126)-C(127)-F(17)	96.6(4)
C(131)-C(138)-C(136)-C(135)	0.9(5)
C(131)-C(138)-C(136)-C(137)	179.3(3)
C(133)-C(135)-C(136)-C(138)	1.8(5)
C(133)-C(135)-C(136)-C(137)	-176.7(3)
F(23)-C(137)-C(136)-C(138)	153.6(3)
F(22)-C(137)-C(136)-C(138)	-87.1(4)
F(24)-C(137)-C(136)-C(138)	33.0(5)
F(23)-C(137)-C(136)-C(135)	-27.9(5)
F(22)-C(137)-C(136)-C(135)	91.3(4)
F(24)-C(137)-C(136)-C(135)	-148.6(3)
C(115)-C(113)-C(112)-C(111)	-0.8(6)
C(114)-C(113)-C(112)-C(111)	-176.7(3)
C(118)-C(111)-C(112)-C(113)	0.2(5)
B-C(111)-C(112)-C(113)	-173.0(3)
C(75)-C(76)-C(80)-C(81)	-31.5(5)
C(71)-C(76)-C(80)-C(81)	151.2(4)
C(75)-C(76)-C(80)-C(82)	92.8(4)
C(71)-C(76)-C(80)-C(82)	-84.5(4)
C(2)-P(2)-C(50)-C(51)	166.2(3)
C(60)-P(2)-C(50)-C(51)	52.8(3)
Ni-P(2)-C(50)-C(51)	-78.0(3)
C(2)-P(2)-C(50)-C(52)	42.6(3)
C(60)-P(2)-C(50)-C(52)	-70.8(3)
Ni-P(2)-C(50)-C(52)	158.4(2)
C(2)-P(2)-C(50)-C(53)	-77.1(3)
C(60)-P(2)-C(50)-C(53)	169.5(3)

Ni-P(2)-C(50)-C(53)	38.7(3)
C(108)-C(106)-C(105)-C(103)	0.0(5)
C(107)-C(106)-C(105)-C(103)	177.2(3)
C(115)-C(116)-C(117)-F(10)	150.2(3)
C(118)-C(116)-C(117)-F(10)	-32.5(5)
C(115)-C(116)-C(117)-F(12)	30.0(5)
C(118)-C(116)-C(117)-F(12)	-152.7(3)
C(115)-C(116)-C(117)-F(11)	-90.3(4)
C(118)-C(116)-C(117)-F(11)	87.1(4)
C(101)-C(102)-C(103)-C(105)	1.8(5)
C(101)-C(102)-C(103)-C(104)	-176.3(3)
C(106)-C(105)-C(103)-C(102)	-1.5(5)
C(106)-C(105)-C(103)-C(104)	176.6(3)
C(135)-C(133)-C(134)-F(20)	120.0(4)
C(132)-C(133)-C(134)-F(20)	-60.4(5)
C(135)-C(133)-C(134)-F(19)	-1.6(5)
C(132)-C(133)-C(134)-F(19)	178.0(3)
C(135)-C(133)-C(134)-F(21)	-120.9(4)
C(132)-C(133)-C(134)-F(21)	58.7(5)
C(122)-C(123)-C(124)-F(14)	55.6(4)
C(125)-C(123)-C(124)-F(14)	-127.6(4)
C(122)-C(123)-C(124)-F(13)	176.7(3)
C(125)-C(123)-C(124)-F(13)	-6.5(5)
C(122)-C(123)-C(124)-F(15)	-63.3(4)
C(125)-C(123)-C(124)-F(15)	113.5(4)
C(73)-C(72)-C(90)-C(91)	49.1(5)
C(71)-C(72)-C(90)-C(91)	-131.7(4)
C(73)-C(72)-C(90)-C(92)	-74.3(4)
C(71)-C(72)-C(90)-C(92)	104.8(4)
C(105)-C(106)-C(107)-F(6)	27.1(5)
C(108)-C(106)-C(107)-F(6)	-155.7(3)
C(105)-C(106)-C(107)-F(4)	148.8(4)
C(108)-C(106)-C(107)-F(4)	-34.0(5)
C(105)-C(106)-C(107)-F(5)	-93.1(4)
C(108)-C(106)-C(107)-F(5)	84.1(4)
C(72)-C(73)-C(74)-C(75)	-0.2(6)
C(76)-C(75)-C(74)-C(73)	0.3(6)
C(102)-C(103)-C(104)-F(1)	88.1(6)
C(105)-C(103)-C(104)-F(1)	-90.0(6)
C(102)-C(103)-C(104)-F(2)	-143.8(4)
C(105)-C(103)-C(104)-F(2)	38.1(6)
C(102)-C(103)-C(104)-F(3)	-35.1(6)
C(105)-C(103)-C(104)-F(3)	146.8(4)
C(115)-C(113)-C(114)-F(8)	148.8(4)
C(112)-C(113)-C(114)-F(8)	-35.2(5)
C(115)-C(113)-C(114)-F(9)	28.6(5)
C(112)-C(113)-C(114)-F(9)	-155.4(4)
C(115)-C(113)-C(114)-F(7)	-90.8(5)
C(112)-C(113)-C(114)-F(7)	85.2(5)
C(3S)-O(1S)-C(2S)-C(1S)	-66.3(5)
C(2S)-O(1S)-C(3S)-C(4S)	-173.4(4)
C(6S)#1-O(2S)-C(6S)-C(7S)	105(100)
C(7S)#1-O(2S)-C(6S)-C(7S)	180.000(1)
C(6S)#1-O(2S)-C(6S)-C(5S)	114(100)
C(7S)#1-O(2S)-C(6S)-C(5S)	-171.5(7)
C(7S)-O(2S)-C(6S)-C(5S)	8.5(7)
C(7S)-C(5S)-C(6S)-O(2S)	-9.6(8)

O(2S)-C(6S)-C(7S)-C(5S)	171.5(7)
C(5S)-C(6S)-C(7S)-O(2S)	-171.5(7)
C(6S)-C(5S)-C(7S)-O(2S)	9.4(8)
C(6S)#1-O(2S)-C(7S)-C(6S)	180.000(1)
C(7S)#1-O(2S)-C(7S)-C(6S)	-128(100)
C(6S)-O(2S)-C(7S)-C(5S)	-10.4(9)
C(6S)#1-O(2S)-C(7S)-C(5S)	169.6(9)
C(7S)#1-O(2S)-C(7S)-C(5S)	-139(100)

Data Collection for the Crystal of 4.

A pale yellow block was selected under a stereo-microscope while immersed in Paratone oil to avoid possible reaction with air. The crystal was removed from the oil using a tapered fiber that also served to hold the crystal for data collection. The crystal was mounted and centered on a Bruker SMART APEX system. Rotation and still images showed diffractions to be weak at high 2Θ angles while frames separated in reciprocal space were obtained and provided an orientation matrix and initial cell parameters. Final cell parameters were obtained from the full data set.

A "hemisphere" data set was obtained which samples approximately 1.2 hemispheres of reciprocal space to a resolution of 0.84 Å using 0.3 degree steps in ω and using 30 sec integration times with each frame. Absorption corrections were applied using SADABS [1] or semi-empirical from psi-scans.

The space group was determined as $P2_1/n$ based on systematic absences and intensity statistics. Direct methods was used to locate Ni, P, O, N and C atoms from the E-map. All other hydrogens were fixed at calculated positions and refined isotropically. All non-hydrogen atoms were refined anisotropic with the exception of C42. The peripheral atoms of the molecule were highly disordered. The space group was checked for any missing symmetry using the Platon program.

$R_{int} = \Sigma \mid F_o^2 - \langle F_o^2 \rangle \mid / \Sigma \mid F_o^2 \mid$ $\qquad$ $R_1 = \Sigma \; \big| \, |F_o| - |F_c| \, \big| / \Sigma |F_o|$

$wR_2 = [\Sigma [w (F_o^2 - F_c^2)^2] / \Sigma [w (F_o^2)^2]]^{1/2}$ $\qquad$ where: $w = q / \sigma^2 (F_o^2) + (aP)^2 + bP$;

GoF = $S = [\Sigma [w (F_o^{2} - F_c^{2})^{2}] / (n-p)^{1/2}$ n = number of independent reflections;

p = number of parameters refined.

References

[1] All software and sources of scattering factors are contained in the SHELXTL (version 5.1) program library (G. Sheldrick, Bruker Analytical X-ray Systems, Madison, WI).

Structure solution and refinement

Table 7. Crystal and structure refinement for **4**

Identification Code	danm23m	
Empirical formula	$C_{31}H_{57}NNiOP_2$	
Formula weight	580.43	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space Group	$P2_1/n$	
Unit cell dimensions	*a* = 12.0638(11) Å	α = 90°
	b = 17.8563(17) Å	β = 103.291(2)°
	c = 15.7736(15) Å	γ = 90°
Volume	3306.9(5) $Å^3$	
Z	4	
Density (calculated)	1.166 mg/mm^3	
Absorption coefficient	0.706 mm^{-1}	
F(000)	1264	
Crystal size, color, habit	0.10 x 0.08 x 0.07 mm, pale yellow block, Et_2O	
Theta range for data collection	1.75 to 28.29°	
Index ranges	$-13 \le h \le 15$, $-23 \le k \le 22$, $-16 \le l \le 20$	
Completeness to theta = 28.29°, 95.2 %		
Reflections collected	20138	
Independent reflections	7814 (R_{int} = 0.0478)	
Absorption correction	semi empirical from psi-scans	
Max. and min. transmission	0.9523 and 0.9328	
Refinement method	Full-matrix least squares on F^2	
Weighting scheme	$w = q [\sigma^2 (F_o^2) + (aP)^2 + bP]^{-1}$ where:	
	$P = (F_o^2 + 2 F_c^2)/3$, a =, b =, q =1	
Data / restraints / parameters	7814 / 0 / 321	

Goodness-of-fit on F^2	1.204
Final R indices [I > 2 sigma(I)]	R1 = 0.1782, wR2 = 0.3668
R indices (all data)	R1 = 0.1828, wR2 = 0.3692
Largest diff. peak and hole	2.635 and -1.822 $eÅ^{-3}$

Table 8. 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	7496(1)	1329(1)	2691(1)	11(1)
P(2)	8386(2)	1814(1)	1801(2)	18(1)
P(1)	6924(4)	2440(2)	3063(3)	49(1)
N	7074(6)	474(4)	3191(6)	15(2)
C(76)	5268(8)	-165(5)	3224(6)	18(2)
C(71)	6405(8)	9(5)	3629(7)	17(2)
C(5)	9976(9)	1686(7)	2028(9)	33(3)
C(9)	4748(9)	128(6)	2318(7)	23(2)
C(6)	7747(10)	1533(6)	626(6)	25(2)
C(75)	4655(9)	-622(6)	3652(7)	23(2)
C(82)	8264(10)	212(7)	5843(7)	28(2)
C(72)	6899(8)	-258(6)	4474(6)	18(2)
C(10)	7782(12)	306(6)	2721(11)	44(4)
C(74)	5129(9)	-893(6)	4477(7)	24(2)
C(8)	8135(8)	-71(6)	4918(6)	18(2)
C(92)	5021(11)	-379(7)	1626(8)	35(3)
C(73)	6254(9)	-711(6)	4887(7)	24(2)
C(91)	3487(10)	277(8)	2152(8)	35(3)
C(1)	7570(30)	3101(8)	2410(20)	149(15)
O(1)	8261(17)	-234(5)	2532(14)	138(9)
C(81)	8887(10)	-735(7)	4880(11)	50(4)
C(2)	8164(12)	2848(5)	1843(8)	33(3)
C(53)	10436(14)	1990(20)	2920(20)	220(30)
C(63)	8130(30)	1967(15)	-50(12)	160(17)
C(52)	10286(11)	882(8)	2043(16)	80(7)
C(62)	7886(17)	704(8)	493(10)	68(6)
C(61)	6482(17)	1671(17)	468(11)	135(14)
C(3)	7587(18)	2657(8)	4244(13)	72(7)
C(51)	10561(16)	2067(13)	1410(20)	142(15)
C(32)	7166(10)	2119(7)	4812(9)	35(3)
C(43)	4739(11)	2145(6)	3271(8)	35(3)
C(4)	5405(18)	2708(10)	2864(13)	90(9)
C(42)	4920(40)	2640(30)	1880(30)	210(20)
C(31)	7530(40)	3423(10)	4576(16)	230(30)
C(41)	5080(30)	3477(12)	3080(40)	290(40)
C(33)	8840(20)	2500(30)	4349(19)	260(30)

Table 9. Bond lengths [Å] and angles [^{o}] for **4**.

Ni-N	1.844(8)
Ni-C(10)	1.859(11)
Ni-P(2)	2.136(3)

Ni-P(1)	2.223(3)
P(2)-C(2)	1.868(10)
P(2)-C(5)	1.882(12)
P(2)-C(6)	1.903(11)
P(1)-C(1)	1.849(14)
P(1)-C(4)	1.849(18)
P(1)-C(3)	1.89(2)
N-C(10)	1.289(14)
N-C(71)	1.440(12)
C(76)-C(75)	1.378(13)
C(76)-C(71)	1.408(14)
C(76)-C(9)	1.515(14)
C(71)-C(72)	1.412(14)
C(5)-C(52)	1.481(19)
C(5)-C(53)	1.50(2)
C(5)-C(51)	1.49(2)
C(9)-C(91)	1.507(15)
C(9)-C(92)	1.512(15)
C(6)-C(63)	1.48(2)
C(6)-C(62)	1.509(16)
C(6)-C(61)	1.51(2)
C(75)-C(74)	1.383(16)
C(82)-C(8)	1.518(14)
C(72)-C(73)	1.384(13)
C(72)-C(8)	1.532(13)
C(10)-O(1)	1.196(15)
C(74)-C(73)	1.401(15)
C(8)-C(81)	1.503(15)
C(1)-C(2)	1.350(18)
C(3)-C(31)	1.47(2)
C(3)-C(32)	1.481(18)
C(3)-C(33)	1.51(3)
C(43)-C(4)	1.52(2)
C(4)-C(41)	1.49(3)
C(4)-C(42)	1.54(5)

N-Ni-C(10)	40.7(4)
N-Ni-P(2)	147.8(2)
C(10)-Ni-P(2)	107.3(4)
N-Ni-P(1)	119.5(2)
C(10)-Ni-P(1)	159.7(4)
P(2)-Ni-P(1)	92.62(11)
C(2)-P(2)-C(5)	105.1(6)
C(2)-P(2)-C(6)	105.4(5)
C(5)-P(2)-C(6)	108.7(5)
C(2)-P(2)-Ni	106.2(3)
C(5)-P(2)-Ni	118.0(4)
C(6)-P(2)-Ni	112.4(4)
C(1)-P(1)-C(4)	105.7(10)
C(1)-P(1)-C(3)	106.1(12)
C(4)-P(1)-C(3)	107.0(9)
C(1)-P(1)-Ni	103.1(5)
C(4)-P(1)-Ni	122.8(8)
C(3)-P(1)-Ni	110.9(6)
C(10)-N-C(71)	131.3(8)
C(10)-N-Ni	70.2(6)
C(71)-N-Ni	157.4(6)

C(75)-C(76)-C(71)	119.0(10)
C(75)-C(76)-C(9)	121.0(9)
C(71)-C(76)-C(9)	120.0(9)
C(76)-C(71)-C(72)	120.6(9)
C(76)-C(71)-N	120.3(9)
C(72)-C(71)-N	119.1(8)
C(52)-C(5)-C(53)	107(2)
C(52)-C(5)-C(51)	107.4(14)
C(53)-C(5)-C(51)	109(2)
C(52)-C(5)-P(2)	111.3(8)
C(53)-C(5)-P(2)	106.0(9)
C(51)-C(5)-P(2)	115.9(11)
C(91)-C(9)-C(92)	111.0(10)
C(91)-C(9)-C(76)	114.0(9)
C(92)-C(9)-C(76)	111.3(9)
C(63)-C(6)-C(62)	110.5(15)
C(63)-C(6)-C(61)	106(2)
C(62)-C(6)-C(61)	106.1(16)
C(63)-C(6)-P(2)	116.1(11)
C(62)-C(6)-P(2)	111.1(8)
C(61)-C(6)-P(2)	106.6(8)
C(76)-C(75)-C(74)	121.1(10)
C(73)-C(72)-C(71)	118.8(9)
C(73)-C(72)-C(8)	120.3(9)
C(71)-C(72)-C(8)	120.9(8)
O(1)-C(10)-N	138.9(11)
O(1)-C(10)-Ni	152.1(10)
N-C(10)-Ni	69.0(6)
C(75)-C(74)-C(73)	120.0(9)
C(81)-C(8)-C(82)	111.8(10)
C(81)-C(8)-C(72)	110.0(8)
C(82)-C(8)-C(72)	112.7(8)
C(72)-C(73)-C(74)	120.5(10)
C(2)-C(1)-P(1)	120.8(10)
C(1)-C(2)-P(2)	117.2(8)
C(31)-C(3)-C(32)	109.7(13)
C(31)-C(3)-C(33)	105(3)
C(32)-C(3)-C(33)	107(2)
C(31)-C(3)-P(1)	120(2)
C(32)-C(3)-P(1)	109.7(10)
C(33)-C(3)-P(1)	104.8(10)
C(41)-C(4)-C(43)	109.0(12)
C(41)-C(4)-C(42)	104(3)
C(43)-C(4)-C(42)	105(3)
C(41)-C(4)-P(1)	120(2)
C(43)-C(4)-P(1)	110.9(9)
C(42)-C(4)-P(1)	106.3(19)

Symmetry transformations used to generate equivalent atoms:

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

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ni	13(1)	11(1)	11(1)	2(1)	3(1)	0(1)
P(2)	22(1)	13(1)	22(1)	-2(1)	12(1)	-4(1)
P(1)	87(3)	13(1)	72(3)	22(2)	70(3)	22(2)
N	1(3)	9(3)	34(5)	-5(3)	4(3)	0(3)
C(76)	19(5)	18(5)	20(5)	0(4)	8(4)	3(4)
C(71)	17(4)	12(4)	24(5)	-7(4)	10(4)	-1(3)
C(5)	18(5)	38(7)	47(7)	-14(6)	16(5)	-10(5)
C(9)	25(5)	17(5)	25(5)	-4(4)	3(4)	-5(4)
C(6)	43(6)	20(5)	12(4)	-1(4)	9(4)	10(4)
C(75)	23(5)	19(5)	28(5)	-6(4)	11(4)	-7(4)
C(82)	35(6)	28(6)	18(5)	3(4)	0(4)	-3(5)
C(72)	17(4)	20(5)	16(4)	1(4)	7(4)	-2(4)
C(10)	54(8)	7(5)	91(11)	-3(6)	57(9)	-7(5)
C(74)	25(5)	23(5)	29(5)	-3(4)	15(4)	-8(4)
C(8)	18(5)	20(5)	15(4)	-1(4)	1(4)	-2(4)
C(92)	40(7)	34(6)	29(6)	4(5)	3(5)	17(5)
C(73)	30(5)	21(5)	24(5)	2(4)	13(4)	0(4)
C(91)	21(6)	45(7)	34(6)	-1(6)	-4(5)	-2(5)
C(1)	270(30)	14(6)	250(30)	54(12)	250(30)	50(12)
O(1)	217(18)	5(4)	280(20)	-1(8)	231(19)	-1(7)
C(81)	15(5)	30(7)	98(12)	-35(7)	-2(6)	-1(5)
C(2)	67(9)	5(4)	39(6)	4(4)	39(6)	-6(5)
C(53)	6(7)	440(60)	200(30)	-240(40)	-4(12)	4(17)
C(63)	330(50)	130(20)	31(10)	-26(12)	61(18)	-160(30)
C(52)	9(6)	37(8)	180(20)	37(11)	3(9)	-1(5)
C(62)	108(15)	24(7)	47(9)	-17(6)	-32(9)	22(8)
C(61)	84(14)	260(30)	36(9)	-62(14)	-39(9)	126(19)
C(3)	124(16)	33(7)	92(13)	-38(8)	95(13)	-43(9)
C(51)	61(12)	123(19)	280(40)	160(20)	118(19)	73(13)
C(32)	31(6)	24(6)	43(7)	5(5)	-5(5)	-12(5)
C(43)	44(7)	19(5)	37(7)	-3(5)	-1(6)	0(5)
C(4)	121(16)	80(12)	108(14)	90(12)	108(14)	91(12)
C(31)	650(90)	20(8)	99(18)	-17(10)	230(40)	-40(20)
C(41)	250(40)	49(13)	720(100)	140(30)	400(60)	95(19)
C(33)	86(17)	580(80)	160(30)	-280(40)	95(18)	-200(30)

Table 11. Hydrogen coordinates [x 10^4] and isotropic displacement parameters [$Å^2$ x 10^3] for 4.

H(9A)	5114	610	2265	28
H(75A)	3910	-751	3382	27
H(82A)	9050	324	6090	42
H(82B)	8008	-167	6186	42
H(82C)	7815	656	5838	42
H(74A)	4700	-1196	4760	29
H(8A)	8381	333	4582	22
H(92A)	4686	-179	1060	53

H(92B)	4718	-870	1679	53
H(92C)	5832	-411	1699	53
H(73A)	6571	-896	5441	28
H(91A)	3219	465	1571	53
H(91B)	3343	640	2562	53
H(91C)	3096	-180	2217	53
H(1A)	6965	3415	2091	178
H(1B)	8079	3424	2823	178
H(81A)	9660	-613	5159	75
H(81B)	8844	-865	4282	75
H(81C)	8638	-1152	5173	75
H(2A)	8907	3086	1979	39
H(2B)	7775	3013	1266	39
H(53A)	11251	1951	3067	330
H(53B)	10133	1705	3336	330
H(53C)	10218	2504	2944	330
H(63A)	7777	1774	-615	239
H(63B)	8945	1926	40	239
H(63C)	7928	2484	-14	239
H(52A)	11099	834	2159	119
H(52B)	9952	660	1489	119
H(52C)	10007	632	2491	119
H(62A)	7557	577	-103	102
H(62B)	7510	429	868	102
H(62C)	8682	580	630	102
H(61A)	6122	1535	-119	203
H(61B)	6347	2191	559	203
H(61C)	6172	1374	865	203
H(51A)	11364	1970	1586	213
H(51B)	10429	2597	1426	213
H(51C)	10268	1881	836	213
H(32A)	7504	2231	5411	52
H(32B)	7369	1619	4681	52
H(32C)	6352	2158	4713	52
H(43A)	3955	2296	3160	53
H(43B)	5050	2124	3888	53
H(43C)	4792	1660	3021	53
H(42A)	4136	2786	1737	318
H(42B)	4988	2131	1698	318
H(42C)	5345	2960	1575	318
H(31A)	7910	3440	5181	352
H(31B)	6746	3565	4510	352
H(31C)	7893	3762	4253	352
H(41A)	4269	3523	2935	438
H(41B)	5403	3835	2745	438
H(41C)	5372	3570	3687	438
H(33A)	9238	2627	4930	393
H(33B)	9125	2794	3938	393
H(33C)	8944	1978	4247	393

Table 12. Torsion angles [°] for 4.

N-Ni-P(2)-C(2)	179.0(7)
C(10)-Ni-P(2)-C(2)	-176.2(7)
P(1)-Ni-P(2)-C(2)	-0.5(5)
N-Ni-P(2)-C(5)	-63.4(7)
C(10)-Ni-P(2)-C(5)	-58.6(7)
P(1)-Ni-P(2)-C(5)	117.1(5)
N-Ni-P(2)-C(6)	64.2(6)
C(10)-Ni-P(2)-C(6)	69.0(7)
P(1)-Ni-P(2)-C(6)	-115.3(4)
N-Ni-P(1)-C(1)	179.1(13)
C(10)-Ni-P(1)-C(1)	166.9(19)
P(2)-Ni-P(1)-C(1)	-1.2(13)
N-Ni-P(1)-C(4)	-62.2(6)
C(10)-Ni-P(1)-C(4)	-74.4(16)
P(2)-Ni-P(1)-C(4)	117.5(5)
N-Ni-P(1)-C(3)	65.9(6)
C(10)-Ni-P(1)-C(3)	53.7(16)
P(2)-Ni-P(1)-C(3)	-114.4(5)
P(2)-Ni-N-C(10)	7.1(11)
P(1)-Ni-N-C(10)	-173.6(9)
C(10)-Ni-N-C(71)	-164(2)
P(2)-Ni-N-C(71)	-157.2(15)
P(1)-Ni-N-C(71)	22.2(19)
C(75)-C(76)-C(71)-C(72)	-2.3(14)
C(9)-C(76)-C(71)-C(72)	179.8(9)
C(75)-C(76)-C(71)-N	178.9(8)
C(9)-C(76)-C(71)-N	1.0(13)
C(10)-N-C(71)-C(76)	-95.4(15)
Ni-N-C(71)-C(76)	65(2)
C(10)-N-C(71)-C(72)	85.8(16)
Ni-N-C(71)-C(72)	-114.1(17)
C(2)-P(2)-C(5)-C(52)	178.2(13)
C(6)-P(2)-C(5)-C(52)	-69.3(14)
Ni-P(2)-C(5)-C(52)	60.1(13)
C(2)-P(2)-C(5)-C(53)	62(2)
C(6)-P(2)-C(5)-C(53)	174(2)
Ni-P(2)-C(5)-C(53)	-56(2)
C(2)-P(2)-C(5)-C(51)	-58.8(17)
C(6)-P(2)-C(5)-C(51)	53.7(17)
Ni-P(2)-C(5)-C(51)	-176.9(15)
C(75)-C(76)-C(9)-C(91)	33.4(14)
C(71)-C(76)-C(9)-C(91)	-148.7(10)
C(75)-C(76)-C(9)-C(92)	-93.1(12)
C(71)-C(76)-C(9)-C(92)	84.8(12)
C(2)-P(2)-C(6)-C(63)	51.6(19)
C(5)-P(2)-C(6)-C(63)	-60.7(19)
Ni-P(2)-C(6)-C(63)	166.8(18)
C(2)-P(2)-C(6)-C(62)	179.0(12)
C(5)-P(2)-C(6)-C(62)	66.7(12)
Ni-P(2)-C(6)-C(62)	-65.8(12)
C(2)-P(2)-C(6)-C(61)	-65.8(15)
C(5)-P(2)-C(6)-C(61)	-178.1(15)
Ni-P(2)-C(6)-C(61)	49.5(15)
C(71)-C(76)-C(75)-C(74)	1.8(15)
C(9)-C(76)-C(75)-C(74)	179.7(9)
C(76)-C(71)-C(72)-C(73)	1.8(14)
N-C(71)-C(72)-C(73)	-179.4(8)

C(76)-C(71)-C(72)-C(8)	-179.9(9)
N-C(71)-C(72)-C(8)	-1.1(13)
C(71)-N-C(10)-O(1)	-10(4)
Ni-N-C(10)-O(1)	178(3)
C(71)-N-C(10)-Ni	172.0(11)
N-Ni-C(10)-O(1)	-177(4)
P(2)-Ni-C(10)-O(1)	7(4)
P(1)-Ni-C(10)-O(1)	-161(3)
P(2)-Ni-C(10)-N	-176.1(6)
P(1)-Ni-C(10)-N	16(2)
C(76)-C(75)-C(74)-C(73)	-0.8(16)
C(73)-C(72)-C(8)-C(81)	75.3(13)
C(71)-C(72)-C(8)-C(81)	-103.0(12)
C(73)-C(72)-C(8)-C(82)	-50.2(13)
C(71)-C(72)-C(8)-C(82)	131.5(10)
C(71)-C(72)-C(73)-C(74)	-0.7(15)
C(8)-C(72)-C(73)-C(74)	-179.1(9)
C(75)-C(74)-C(73)-C(72)	0.3(16)
C(4)-P(1)-C(1)-C(2)	-126(3)
C(3)-P(1)-C(1)-C(2)	120(3)
Ni-P(1)-C(1)-C(2)	4(3)
P(1)-C(1)-C(2)-P(2)	-4(3)
C(5)-P(2)-C(2)-C(1)	-123(2)
C(6)-P(2)-C(2)-C(1)	122(2)
Ni-P(2)-C(2)-C(1)	3(2)
C(1)-P(1)-C(3)-C(31)	55(2)
C(4)-P(1)-C(3)-C(31)	-57(2)
Ni-P(1)-C(3)-C(31)	167(2)
C(1)-P(1)-C(3)-C(32)	-176.4(12)
C(4)-P(1)-C(3)-C(32)	71.1(14)
Ni-P(1)-C(3)-C(32)	-65.2(13)
C(1)-P(1)-C(3)-C(33)	-62(2)
C(4)-P(1)-C(3)-C(33)	-175(2)
Ni-P(1)-C(3)-C(33)	49(2)
C(1)-P(1)-C(4)-C(41)	-59(2)
C(3)-P(1)-C(4)-C(41)	54(2)
Ni-P(1)-C(4)-C(41)	-176(2)
C(1)-P(1)-C(4)-C(43)	172.8(15)
C(3)-P(1)-C(4)-C(43)	-74.4(16)
Ni-P(1)-C(4)-C(43)	55.4(16)
C(1)-P(1)-C(4)-C(42)	59(2)
C(3)-P(1)-C(4)-C(42)	172(2)
Ni-P(1)-C(4)-C(42)	-58(2)

Data Collection for the Crystal of 7

A pink block was selected under a stereo-microscope while immersed in mineral oil to avoid possible reaction with air. The crystal was removed from the oil using a tapered fiber that also served to hold the crystal for data collection. The crystal was mounted and centered on a Bruker SMART APEX system. Rotation and still images showed

diffractions to be sharp while frames separated in reciprocal space were obtained and provided an orientation matrix and initial cell parameters. Final cell parameters were obtained from the full data set.

A "hemisphere" data set was obtained which samples approximately 1.2 hemispheres of reciprocal space to a resolution of 0.84A using 0.3 degree steps in ω using 10 sec integration times for each frame. Absorption corrections were applied using semi-empirical from psi-scans or SADABS [1].

Structure solution and refinement

The space group was determined as $P2_1/n$ based on systematic absences and intensity statistics. Direct methods was used to locate the heavy atoms of Ni, P and heteroatoms from the E-map.

Prior to location of H, all atoms were converted to and refined anisotropically. H atoms were refined isotropically and fixed at calculated positions. No anomalous bond lengths or thermal parameters were noted.

$R_{int} = \Sigma \mid F_o^2 - \langle F_o^2 \rangle \mid / \Sigma \mid F_o^2 \mid$

$R_1 = \Sigma \mid \mid F_o \mid - \mid F_c \mid \mid / \Sigma \mid F_o \mid$

$wR_2 = [\Sigma [w (F_o^2 - F_c^2)^2] / \Sigma [w (F_o^2)^2]]^{1/2}$

where: $w = q / \sigma^2 (F_o^2) + (aP)^2 + bP$;

$GoF = S = [\Sigma [w (F_o^2 - F_c^2)^2] / (n-p)^{1/2}$

n = number of independent reflections;

p = number of parameters refined.

References

[1] All software and sources of scattering factors are contained in the SHELXTL (version 5.1) program library (G. Sheldrick, Bruker Analytical X-ray Systems, Madison, WI).

Table 13. Crystal and structure refinement for 7

Identification Code	danm26m
Empirical formula	$C_{38}H_{64}F_6N_2NiP_2$

Formula weight	669.56
Temperature	100 K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space Group	$P2_1/n$
Unit cell dimensions	a = 10.8143(7) Å α = 90 ° b = 17.9376(12) Å β = 100.1160(10) ° c = 19.3299(14) Å γ = 90 °
Volume	3691.4(4) $Å^3$
Z	4
Density (calculated)	1.205 Mg/mm^3
Absorption coefficient	0.640 mm^{-1}
F(000)	1456
Crystal size	0.60 x 0.40 x 0.40 mm, pink prism
Theta range for data collection	2.02 to 28.27
Index ranges	$-14 \le h \le 13, -23 \le k \le 22 -18 \le l \le 25$
Reflections collected	22171
Independent reflections	8619 (R_{int} = 0.0481)
Completeness to theta = 28.27°	94.2%
Absorption correction	semi-empirical from psi-scans
Max. and min. transmission	0.7839 and 0.7000
Refinement method	Full-matrix least squares on F^2
Data / restraints / parameters	8619 / 0 / 389
Goodness-of-fit on F^2	1.114
Final R indices [I > 2 sigma(I)]	R_1 = 0.0502, wR_2 = 0.1202
R indices (all data)	R_1 = 0.0569, wR_2 = 0.1239

Largest diff. peak and hole	1.323 and -0.328 eÅ^{-3}

Table 14. Atomic coordinates [x 10^4] and equivalent isotropic displacement parameters [$Å^2$ x 10^3] for 7. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ni	3799(1)	2544(1)	1819(1)	14(1)
P(2)	3820(1)	1812(1)	939(1)	14(1)
P(1)	1936(1)	3030(1)	1350(1)	18(1)
N(1)	4766(2)	2955(1)	2633(1)	17(1)
C(10)	5315(2)	2366(1)	2413(1)	21(1)
C(75)	3806(2)	3191(1)	4370(1)	18(1)
C(6)	5255(2)	1869(1)	503(1)	18(1)
C(2)	2544(2)	2142(1)	234(1)	19(1)
C(71)	4654(2)	3241(1)	3299(1)	15(1)
C(5)	3461(2)	806(1)	1095(1)	17(1)
C(63)	4999(2)	1649(1)	-279(1)	22(1)
C(73)	5071(2)	4230(1)	4155(1)	18(1)
C(101)	7239(2)	2065(1)	3155(1)	26(1)
C(4)	2106(2)	4031(1)	1079(1)	25(1)
C(72)	5214(2)	3938(1)	3505(1)	16(1)
C(76)	3946(2)	2864(1)	3739(1)	16(1)
C(9)	5977(2)	4351(1)	3040(1)	19(1)
C(53)	4334(2)	524(1)	1756(1)	23(1)
C(74)	4364(2)	3868(1)	4583(1)	19(1)
N(2)	6269(2)	1936(1)	2529(1)	27(1)
C(102)	7818(2)	1332(1)	3445(1)	24(1)
C(3)	494(2)	2940(1)	1780(2)	28(1)
C(62)	6339(2)	1389(1)	891(1)	23(1)
C(61)	5691(2)	2685(1)	562(1)	22(1)
C(51)	2121(2)	776(1)	1247(1)	23(1)
C(43)	2801(2)	4470(1)	1715(1)	27(1)
C(52)	3522(2)	282(1)	476(1)	23(1)
C(42)	891(3)	4438(2)	764(2)	41(1)
C(92)	5683(3)	5179(1)	2984(2)	32(1)
C(103)	9017(2)	1328(1)	3817(1)	27(1)
C(8)	3380(2)	2104(1)	3531(1)	21(1)
C(106)	7702(3)	1(2)	3605(2)	32(1)
C(1)	1444(2)	2509(1)	519(1)	22(1)
C(105)	8898(3)	12(2)	3985(2)	32(1)
C(91)	7385(2)	4227(2)	3282(1)	27(1)
C(41)	2949(3)	4015(1)	525(2)	33(1)
C(33)	620(3)	3474(2)	2408(2)	36(1)
C(107)	7161(3)	667(2)	3332(1)	28(1)
C(82)	2163(3)	1945(2)	3805(2)	37(1)
C(104)	9568(3)	659(2)	4100(2)	34(1)
C(32)	464(3)	2141(2)	2054(2)	32(1)
C(81)	4317(3)	1485(1)	3769(2)	34(1)
C(31)	-766(3)	3072(2)	1290(2)	41(1)

Symmetry transformations to generate equivalent atoms:

Table 15. Bond lengths [Å] and angles [°] for 7.

Ni-C(10)	1.857(2)
Ni-N(1)	1.8790(18)
Ni-P(2)	2.1517(6)
Ni-P(1)	2.2360(6)
P(2)-C(2)	1.858(2)
P(2)-C(5)	1.882(2)
P(2)-C(6)	1.895(2)
P(1)-C(1)	1.853(2)
P(1)-C(4)	1.888(2)
P(1)-C(3)	1.898(3)
N(1)-C(10)	1.318(3)
N(1)-C(71)	1.411(3)
C(10)-N(2)	1.275(3)
C(75)-C(74)	1.386(3)
C(75)-C(76)	1.387(3)
C(6)-C(61)	1.535(3)
C(6)-C(62)	1.539(3)
C(6)-C(63)	1.539(3)
C(2)-C(1)	1.543(3)
C(71)-C(76)	1.413(3)
C(71)-C(72)	1.415(3)
C(5)-C(51)	1.529(3)
C(5)-C(52)	1.533(3)
C(5)-C(53)	1.535(3)
C(73)-C(74)	1.382(3)
C(73)-C(72)	1.394(3)
C(101)-N(2)	1.474(3)
C(101)-C(102)	1.522(3)
C(4)-C(41)	1.524(4)
C(4)-C(42)	1.533(3)
C(4)-C(43)	1.540(3)
C(72)-C(9)	1.516(3)
C(76)-C(8)	1.520(3)
C(9)-C(92)	1.519(3)
C(9)-C(91)	1.530(3)
C(102)-C(103)	1.368(3)
C(102)-C(107)	1.385(4)
C(3)-C(32)	1.530(4)
C(3)-C(33)	1.535(3)
C(3)-C(31)	1.535(4)
C(103)-C(104)	1.406(4)
C(8)-C(81)	1.519(4)
C(8)-C(82)	1.529(4)
C(106)-C(105)	1.371(4)
C(106)-C(107)	1.393(4)
C(105)-C(104)	1.366(4)
C(10)-Ni-N(1)	41.32(9)
C(10)-Ni-P(2)	104.63(8)
N(1)-Ni-P(2)	144.97(6)

C(10)-Ni-P(1)	162.35(8)
N(1)-Ni-P(1)	121.07(6)
P(2)-Ni-P(1)	92.93(2)
C(2)-P(2)-C(5)	105.98(10)
C(2)-P(2)-C(6)	102.52(11)
C(5)-P(2)-C(6)	109.35(10)
C(2)-P(2)-Ni	106.01(7)
C(5)-P(2)-Ni	115.29(7)
C(6)-P(2)-Ni	116.27(7)
C(1)-P(1)-C(4)	105.47(11)
C(1)-P(1)-C(3)	101.74(12)
C(4)-P(1)-C(3)	109.26(12)
C(1)-P(1)-Ni	104.84(8)
C(4)-P(1)-Ni	111.00(8)
C(3)-P(1)-Ni	122.67(9)
C(10)-N(1)-C(71)	134.52(19)
C(10)-N(1)-Ni	68.46(13)
C(71)-N(1)-Ni	141.48(16)
N(2)-C(10)-N(1)	145.5(2)
N(2)-C(10)-Ni	144.3(2)
N(1)-C(10)-Ni	70.22(13)
C(74)-C(75)-C(76)	121.5(2)
C(61)-C(6)-C(62)	107.42(19)
C(61)-C(6)-C(63)	108.52(19)
C(62)-C(6)-C(63)	109.03(19)
C(61)-C(6)-P(2)	106.43(16)
C(62)-C(6)-P(2)	111.42(16)
C(63)-C(6)-P(2)	113.77(16)
C(1)-C(2)-P(2)	113.18(16)
N(1)-C(71)-C(76)	121.09(19)
N(1)-C(71)-C(72)	118.6(2)
C(76)-C(71)-C(72)	120.3(2)
C(51)-C(5)-C(52)	107.53(19)
C(51)-C(5)-C(53)	107.08(19)
C(52)-C(5)-C(53)	110.07(19)
C(51)-C(5)-P(2)	107.12(15)
C(52)-C(5)-P(2)	115.11(16)
C(53)-C(5)-P(2)	109.58(15)
C(74)-C(73)-C(72)	121.5(2)
N(2)-C(101)-C(102)	110.7(2)
C(41)-C(4)-C(42)	107.8(2)
C(41)-C(4)-C(43)	107.6(2)
C(42)-C(4)-C(43)	109.7(2)
C(41)-C(4)-P(1)	106.07(16)
C(42)-C(4)-P(1)	116.43(19)
C(43)-C(4)-P(1)	108.85(17)
C(73)-C(72)-C(71)	118.4(2)
C(73)-C(72)-C(9)	120.6(2)
C(71)-C(72)-C(9)	121.0(2)
C(75)-C(76)-C(71)	118.8(2)
C(75)-C(76)-C(8)	120.8(2)
C(71)-C(76)-C(8)	120.44(19)
C(72)-C(9)-C(92)	113.1(2)
C(72)-C(9)-C(91)	111.29(19)
C(92)-C(9)-C(91)	110.4(2)
C(73)-C(74)-C(75)	119.5(2)
C(10)-N(2)-C(101)	119.1(2)

C(103)-C(102)-C(107)	119.4(2)
C(103)-C(102)-C(101)	119.3(2)
C(107)-C(102)-C(101)	121.3(2)
C(32)-C(3)-C(33)	108.4(2)
C(32)-C(3)-C(31)	106.7(2)
C(33)-C(3)-C(31)	109.7(2)
C(32)-C(3)-P(1)	107.46(17)
C(33)-C(3)-P(1)	109.12(18)
C(31)-C(3)-P(1)	115.2(2)
C(102)-C(103)-C(104)	120.5(2)
C(81)-C(8)-C(76)	111.1(2)
C(81)-C(8)-C(82)	109.2(2)
C(76)-C(8)-C(82)	114.0(2)
C(105)-C(106)-C(107)	119.0(3)
C(2)-C(1)-P(1)	113.72(16)
C(104)-C(105)-C(106)	121.6(3)
C(102)-C(107)-C(106)	120.6(2)
C(105)-C(104)-C(103)	119.0(2)

Table 16. Anisotropic displacement parameters [$Å^2$ x 10^3] for 7. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11}+ ... + 2hka^*b^*U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ni	12(1)	12(1)	17(1)	-2(1)	-2(1)	0(1)
P(2)	13(1)	11(1)	17(1)	-2(1)	0(1)	1(1)
P(1)	14(1)	15(1)	24(1)	-7(1)	-4(1)	3(1)
N(1)	17(1)	18(1)	15(1)	-3(1)	1(1)	2(1)
C(10)	21(1)	22(1)	19(1)	1(1)	2(1)	-2(1)
C(75)	16(1)	21(1)	16(1)	2(1)	3(1)	2(1)
C(6)	17(1)	18(1)	20(1)	1(1)	4(1)	0(1)
C(2)	18(1)	16(1)	19(1)	-3(1)	-4(1)	2(1)
C(71)	15(1)	15(1)	14(1)	-1(1)	0(1)	4(1)
C(5)	19(1)	12(1)	19(1)	-2(1)	4(1)	0(1)
C(63)	25(1)	19(1)	23(1)	1(1)	9(1)	-1(1)
C(73)	19(1)	14(1)	20(1)	-3(1)	-3(1)	2(1)
C(101)	28(1)	24(1)	25(1)	-2(1)	1(1)	2(1)
C(4)	26(1)	13(1)	30(1)	-5(1)	-8(1)	5(1)
C(72)	14(1)	16(1)	16(1)	2(1)	-1(1)	2(1)
C(76)	15(1)	15(1)	18(1)	0(1)	-1(1)	2(1)
C(9)	19(1)	19(1)	19(1)	0(1)	4(1)	-1(1)
C(53)	25(1)	19(1)	24(1)	5(1)	4(1)	1(1)
C(74)	22(1)	19(1)	13(1)	-5(1)	0(1)	6(1)
N(2)	27(1)	30(1)	23(1)	-4(1)	-2(1)	6(1)
C(102)	22(1)	31(1)	19(1)	-4(1)	3(1)	2(1)
C(3)	15(1)	28(1)	42(2)	-17(1)	5(1)	1(1)
C(62)	17(1)	27(1)	28(1)	3(1)	6(1)	4(1)
C(61)	22(1)	21(1)	24(1)	1(1)	3(1)	-5(1)
C(51)	20(1)	20(1)	30(1)	-3(1)	8(1)	-3(1)
C(43)	27(1)	17(1)	32(1)	-6(1)	-9(1)	1(1)
C(52)	31(1)	15(1)	25(1)	-4(1)	9(1)	0(1)
C(42)	40(2)	21(1)	51(2)	-8(1)	-21(1)	13(1)

C(92)	36(2)	22(1)	42(2)	9(1)	14(1)	4(1)
C(103)	20(1)	25(1)	36(1)	-7(1)	6(1)	-2(1)
C(8)	28(1)	17(1)	19(1)	-4(1)	5(1)	-5(1)
C(106)	30(2)	29(1)	37(2)	0(1)	6(1)	-2(1)
C(1)	18(1)	17(1)	26(1)	-9(1)	-7(1)	4(1)
C(105)	30(2)	33(1)	32(1)	4(1)	4(1)	5(1)
C(91)	18(1)	28(1)	35(1)	5(1)	2(1)	-2(1)
C(41)	49(2)	14(1)	33(2)	1(1)	2(1)	0(1)
C(33)	25(1)	37(2)	47(2)	-23(1)	10(1)	-2(1)
C(107)	23(1)	30(1)	31(1)	-2(1)	2(1)	2(1)
C(82)	44(2)	33(2)	38(2)	-11(1)	18(1)	-19(1)
C(104)	26(1)	37(2)	34(2)	1(1)	-5(1)	6(1)
C(32)	22(1)	32(1)	43(2)	-15(1)	12(1)	-4(1)
C(81)	44(2)	19(1)	36(2)	0(1)	1(1)	0(1)
C(31)	16(1)	39(2)	63(2)	-23(2)	-4(1)	7(1)

Table 17. Hydrogen coordinates [x 10^4] and isotropic displacement parameters [$Å^2$ x 10^3] for 7.

	x	y	z	U(eq)
H(75A)	3327	2950	4658	22
H(2A)	2889	2500	-57	22
H(2B)	2226	1723	-61	22
H(63A)	5761	1689	-467	33
H(63B)	4376	1976	-533	33
H(63C)	4700	1145	-326	33
H(73A)	5460	4679	4304	22
H(10B)	6866	2316	3514	31
H(10C)	7889	2386	3032	31
H(9A)	5755	4140	2567	23
H(53A)	4150	10	1835	34
H(53B)	4207	816	2154	34
H(53C)	5192	569	1693	34
H(74A)	4263	4078	5009	22
H(62A)	7051	1430	659	35
H(62B)	6076	878	890	35
H(62C)	6566	1561	1367	35
H(61A)	6421	2741	347	33
H(61B)	5893	2823	1048	33
H(61C)	5031	3000	327	33
H(51A)	1903	268	1329	34
H(51B)	1549	970	852	34
H(51C)	2069	1070	1656	34
H(43A)	2893	4980	1583	41
H(43B)	3616	4255	1868	41
H(43C)	2327	4449	2091	41
H(52A)	3327	-217	600	35
H(52B)	4353	294	364	35
H(52C)	2927	441	75	35
H(42A)	1086	4939	645	61
H(42B)	337	4449	1101	61
H(42C)	491	4182	349	61

H(92A)	4797	5248	2829	49
H(92B)	6134	5403	2652	49
H(92C)	5932	5409	3435	49
H(10D)	9471	1770	3884	32
H(8A)	3184	2088	3017	25
H(10E)	7257	-444	3532	39
H(1A)	852	2125	596	26
H(1B)	1012	2848	166	26
H(10F)	9262	-432	4168	38
H(91A)	7557	3701	3313	41
H(91B)	7645	4451	3735	41
H(91C)	7839	4449	2950	41
H(41A)	3066	4514	368	49
H(41B)	2563	3717	134	49
H(41C)	3749	3805	724	49
H(33A)	-108	3432	2627	54
H(33B)	691	3977	2249	54
H(33C)	1357	3349	2742	54
H(10G)	6353	665	3070	34
H(82A)	1567	2334	3654	56
H(82B)	2335	1925	4309	56
H(82C)	1824	1476	3623	56
H(10H)	10377	658	4362	40
H(32A)	-257	2078	2275	47
H(32B)	1213	2046	2389	47
H(32C)	418	1798	1669	47
H(81A)	5083	1582	3598	51
H(81B)	3974	1017	3586	51
H(81C)	4488	1465	4273	51
H(31A)	-1440	3017	1550	61
H(31B)	-866	2715	914	61
H(31C)	-782	3567	1099	61

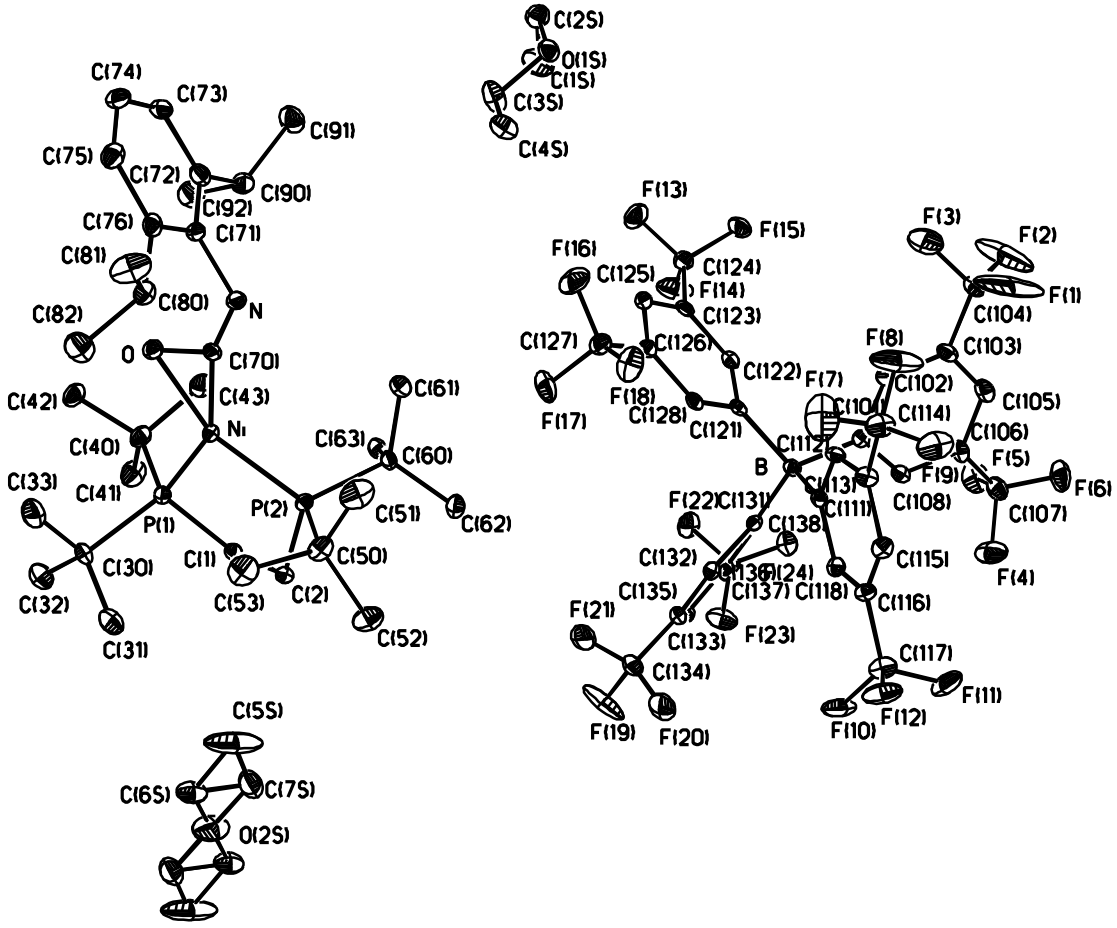
Table 18. Torsion angles [°] for 7.

C(10)-Ni-P(2)-C(2)	-165.45(11)
N(1)-Ni-P(2)-C(2)	-153.94(13)
P(1)-Ni-P(2)-C(2)	12.77(8)
C(10)-Ni-P(2)-C(5)	77.65(11)
N(1)-Ni-P(2)-C(5)	89.16(13)
P(1)-Ni-P(2)-C(5)	-104.13(8)
C(10)-Ni-P(2)-C(6)	-52.30(11)
N(1)-Ni-P(2)-C(6)	-40.78(14)
P(1)-Ni-P(2)-C(6)	125.93(8)
C(10)-Ni-P(1)-C(1)	177.2(3)
N(1)-Ni-P(1)-C(1)	173.97(11)
P(2)-Ni-P(1)-C(1)	2.84(9)
C(10)-Ni-P(1)-C(4)	63.7(3)
N(1)-Ni-P(1)-C(4)	60.56(12)
P(2)-Ni-P(1)-C(4)	-110.58(9)
C(10)-Ni-P(1)-C(3)	-68.0(3)
N(1)-Ni-P(1)-C(3)	-71.19(12)

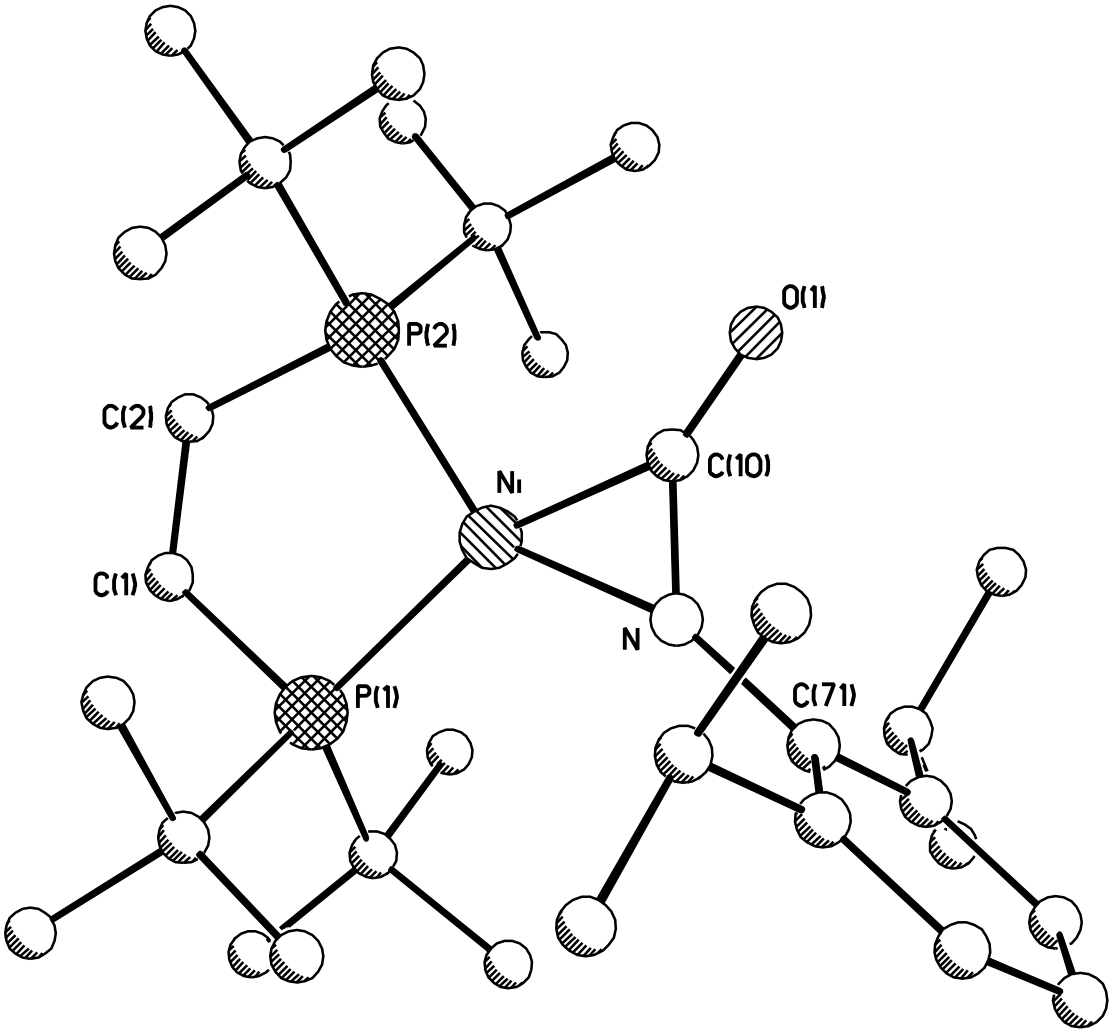
P(2)-Ni-P(1)-C(3)	117.67(9)
P(2)-Ni-N(1)-C(10)	-17.01(19)
P(1)-Ni-N(1)-C(10)	178.54(12)
C(10)-Ni-N(1)-C(71)	-135.6(3)
P(2)-Ni-N(1)-C(71)	-152.61(19)
P(1)-Ni-N(1)-C(71)	42.9(3)
C(71)-N(1)-C(10)-N(2)	-37.0(6)
Ni-N(1)-C(10)-N(2)	-179.3(4)
C(71)-N(1)-C(10)-Ni	142.3(3)
N(1)-Ni-C(10)-N(2)	179.4(4)
P(2)-Ni-C(10)-N(2)	-10.6(4)
P(1)-Ni-C(10)-N(2)	175.2(2)
P(2)-Ni-C(10)-N(1)	170.01(11)
P(1)-Ni-C(10)-N(1)	-4.1(3)
C(2)-P(2)-C(6)-C(61)	81.91(16)
C(5)-P(2)-C(6)-C(61)	-165.94(15)
Ni-P(2)-C(6)-C(61)	-33.22(17)
C(2)-P(2)-C(6)-C(62)	-161.28(16)
C(5)-P(2)-C(6)-C(62)	-49.14(19)
Ni-P(2)-C(6)-C(62)	83.58(16)
C(2)-P(2)-C(6)-C(63)	-37.53(18)
C(5)-P(2)-C(6)-C(63)	74.61(18)
Ni-P(2)-C(6)-C(63)	-152.67(14)
C(5)-P(2)-C(2)-C(1)	93.21(17)
C(6)-P(2)-C(2)-C(1)	-152.16(16)
Ni-P(2)-C(2)-C(1)	-29.79(18)
C(10)-N(1)-C(71)-C(76)	-67.9(3)
Ni-N(1)-C(71)-C(76)	46.2(3)
C(10)-N(1)-C(71)-C(72)	115.3(3)
Ni-N(1)-C(71)-C(72)	-130.5(2)
C(2)-P(2)-C(5)-C(51)	-54.37(18)
C(6)-P(2)-C(5)-C(51)	-164.22(15)
Ni-P(2)-C(5)-C(51)	62.55(16)
C(2)-P(2)-C(5)-C(52)	65.14(19)
C(6)-P(2)-C(5)-C(52)	-44.7(2)
Ni-P(2)-C(5)-C(52)	-177.94(14)
C(2)-P(2)-C(5)-C(53)	-170.19(16)
C(6)-P(2)-C(5)-C(53)	79.95(17)
Ni-P(2)-C(5)-C(53)	-53.27(17)
C(1)-P(1)-C(4)-C(41)	-51.53(19)
C(3)-P(1)-C(4)-C(41)	-160.22(17)
Ni-P(1)-C(4)-C(41)	61.48(18)
C(1)-P(1)-C(4)-C(42)	68.4(2)
C(3)-P(1)-C(4)-C(42)	-40.3(2)
Ni-P(1)-C(4)-C(42)	-178.62(18)
C(1)-P(1)-C(4)-C(43)	-167.05(18)
C(3)-P(1)-C(4)-C(43)	84.3(2)
Ni-P(1)-C(4)-C(43)	-54.04(19)
C(74)-C(73)-C(72)-C(71)	-2.3(3)
C(74)-C(73)-C(72)-C(9)	179.0(2)
N(1)-C(71)-C(72)-C(73)	178.10(19)
C(76)-C(71)-C(72)-C(73)	1.4(3)
N(1)-C(71)-C(72)-C(9)	-3.2(3)
C(76)-C(71)-C(72)-C(9)	-179.9(2)
C(74)-C(75)-C(76)-C(71)	-1.2(3)
C(74)-C(75)-C(76)-C(8)	177.0(2)
N(1)-C(71)-C(76)-C(75)	-176.3(2)

C(72)-C(71)-C(76)-C(75)	0.4(3)
N(1)-C(71)-C(76)-C(8)	5.4(3)
C(72)-C(71)-C(76)-C(8)	-177.9(2)
C(73)-C(72)-C(9)-C(92)	-45.3(3)
C(71)-C(72)-C(9)-C(92)	136.0(2)
C(73)-C(72)-C(9)-C(91)	79.7(3)
C(71)-C(72)-C(9)-C(91)	-99.0(2)
C(72)-C(73)-C(74)-C(75)	1.5(3)
C(76)-C(75)-C(74)-C(73)	0.3(3)
N(1)-C(10)-N(2)-C(101)	1.8(6)
Ni-C(10)-N(2)-C(101)	-177.2(2)
C(102)-C(101)-N(2)-C(10)	146.8(2)
N(2)-C(101)-C(102)-C(103)	153.5(2)
N(2)-C(101)-C(102)-C(107)	-25.7(3)
C(1)-P(1)-C(3)-C(32)	74.25(19)
C(4)-P(1)-C(3)-C(32)	-174.58(17)
Ni-P(1)-C(3)-C(32)	-42.1(2)
C(1)-P(1)-C(3)-C(33)	-168.45(19)
C(4)-P(1)-C(3)-C(33)	-57.3(2)
Ni-P(1)-C(3)-C(33)	75.2(2)
C(1)-P(1)-C(3)-C(31)	-44.5(2)
C(4)-P(1)-C(3)-C(31)	66.6(2)
Ni-P(1)-C(3)-C(31)	-160.90(15)
C(107)-C(102)-C(103)-C(104)	-1.8(4)
C(101)-C(102)-C(103)-C(104)	179.0(2)
C(75)-C(76)-C(8)-C(81)	-92.1(3)
C(71)-C(76)-C(8)-C(81)	86.2(3)
C(75)-C(76)-C(8)-C(82)	31.8(3)
C(71)-C(76)-C(8)-C(82)	-150.0(2)
P(2)-C(2)-C(1)-P(1)	34.1(2)
C(4)-P(1)-C(1)-C(2)	95.23(19)
C(3)-P(1)-C(1)-C(2)	-150.76(18)
Ni-P(1)-C(1)-C(2)	-22.04(19)
C(107)-C(106)-C(105)-C(104)	0.1(4)
C(103)-C(102)-C(107)-C(106)	1.4(4)
C(101)-C(102)-C(107)-C(106)	-179.4(3)
C(105)-C(106)-C(107)-C(102)	-0.5(4)
C(106)-C(105)-C(104)-C(103)	-0.5(4)
C(102)-C(103)-C(104)-C(105)	1.4(4)

Perspective view of **3b·2Et$_2$O** with thermal ellipsoids at the 35% probability level.



Perspective PLUTO view of **4**.



Perspective view of **7** with thermal ellipsoids at the 35% probability level.