For Supporting Information

Addition Reactions of O-bound Cyclic Nickel Enolates to α,β-unsaturated Ketones

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Synthesis of complex $\overline{\mathrm{Ni(C_6H_4\text{-}\mathit{o}\text{-}C(=CHCH_3)O}}$)(dippe) (2).

To a solution of Ni(C_6H_4-*o*-C(O)Et)(Cl)(dippe) (490 mg, 1 mmol) in 80 mL of anhydrous THF at -78°C under N_2 was added KO^{t}Bu (123 mg, 1.1 mmol). After being stirred at room temperature for 1 hour, the solvent was removed in vacuum. The resulting yellow solid was extracted with toluene and this solution was centrifuged to separate the KCl. Recrystallization from THF provided 299 mg (66 %) of the enolate **2** as yellow crystals.

Anal. Calcd for $C_{23}H_{40}P_2ONi$: C, 61.0; H, 8.9. Found: C, 60.8; H, 8.9. IR (Nujol) 1610 cm^{-1}. ^{1}H NMR (C_6D_6, 20°C) δ 0.75 (dd, 6H, $^3J_{HP} = 11.8$ Hz, $^3J_{HH} = 7.0$ Hz, CH_3), 0.80 (m, 2H, CH_2), 0.94 (dd, 6H, $^3J_{HP} = 12.9$ Hz, $^3J_{HH} = 7.1$ Hz, CH_3), 1.05 (m, 2H, CH_2), 1.14 (dd, 6H, $^3J_{HP} = 17.1$ Hz, $^3J_{HH} = 7.3$ Hz, CH_3), 1.38 (dd, 6H, $^3J_{HP} = 15.4$ Hz, $^3J_{HH} = 7.2$ Hz, CH_3), 2.00 (m, 2H, C*H*), 2.10 (m, 2H, C*H*), 2.36 (d, 3H, $^3J_{HH} = 6.7$ Hz, CH_3), 5.27 (c, 1H, $^3J_{HH} = 6.7$ Hz, =C*H*), 7.17 (m, 2H, CH_{ar}), 7.37 (m, 1H, CH_{ar}), 7.73 (m, 1H, CH_{ar}); ^{31}P{^{1}H} NMR (C_6D_6, 20°C) AX spin system, $\delta_A = 65.4$, $\delta_X = 72.5$, $J_{AX} = 32$ Hz; ^{13}C{^{1}H} NMR (C_6D_6, 20°C) δ 11.4 (s, *C*H_3), 16.2 (dd, 1C, $^1J_{CP} = 19.5$ Hz, $^2J_{CP} = 10.5$ Hz, CH_2), 18.1 (d, 2C, $^2J_{CP} = 4.0$ Hz, CH_3), 18.2 (s, 2C, CH_3), 19.2 (d, 2C, $^2J_{CP} = 4.4$ Hz, CH_3), 21.1 (d, 2C, $^2J_{CP} = 6.0$ Hz, CH_3), 22.4 (t, 1C, $J_{CP} = 24.2$ Hz, CH_2), 24.0 (d, 2C, $^1J_{CP} = 16.6$ Hz, CH), 25.2 (d, 2C, $^1J_{CP} = 21.2$ Hz, CH), 86.1 (s, =*C*H), 121.3 (s, *C*H_{ar}), 123.3 (s, *C*H_{ar}), 123.9 (d, $J_{CP} = 7$ Hz, *C*H_{ar}), 137.5 (m, *C*H_{ar}), 156.5 (s, C_{ar}-C-O), 158.0 (dd, $^2J_{CP} = 27$ and 88 Hz, C_{ar}-Ni), 169.7 (d, $^3J_{CP} = 13$ Hz, *C*-O).

Reaction of complex 2 with methylvinylketone (MVK). Synthesis of complex $Ni(C_6H_4$-*o*-$C(CH(CH_3)CH_2CH=C(CH_3)O)O$(dippe) (3).

To a suspension of 117 mg (0.25 mmol) of complex **2** in 5 mL of THF at -78 °C, 21 µL (0.25 mmol) of MVK was added. The mixture was stirred for one hour at room temperature, after which time another half-equivalent (10.5 µl) of MVK was added. After 1h, the reaction was shown to be complete by $^{31}P\{^1H\}$ NMR. The solvent was removed to obtain an orange oil which was washed twice with 20 mL of petroleum ether. The complex was extracted with 20 mL of Et_2O and this solution was filtered. The volume was reduced and cooled to -30 °C to provide 106 mg (81%) of yellow needles.

Anal. Calcd for $C_{27}H_{46}P_2O_2Ni$: C, 62.0; H, 8.9. Found: C, 61.8; H, 8.9. IR (Nujol) 1680 cm^{-1}. ^1H NMR (C_6D_6, 20°C) δ 0.77 (dd, 3H, $^3J_{HP}$ = 11.7 Hz, $^3J_{HH}$ = 7.0 Hz, CH_3), 0.79 (m, 2H, CH_2), 0.82 (dd, 3H, $^3J_{HP}$ = 12.0 Hz, $^3J_{HH}$ = 7.0 Hz, CH_3), 0.93 (dd, 3H, $^3J_{HP}$ = 12.2 Hz, $^3J_{HH}$ = 7.1 Hz, CH_3), 1.07 (m, 6H, CH_3), 1.12 (m, 2H, CH_2), 1.14 (d, 3H, $^3J_{HH}$ = 6.3 Hz, CH_3), 1.22 (dd, 3H, $^3J_{HP}$ = 17.0 Hz, $^3J_{HH}$ = 7.3 Hz, CH_3), 1.38 (dd, 3H, $^3J_{HP}$ = 15.6 Hz, $^3J_{HH}$ = 7.2 Hz, CH_3), 1.46 (dd, 3H, $^3J_{HP}$ = 15.0 Hz, $^3J_{HH}$ = 7.1 Hz, CH_3), 1.93 (m, 2H, CH), 2.00 (m, 1H, CH), 1.98 (s, 3H, CH_3), 2.15 (m, 2H, CHH and CH), 2.49 (m, 1H, CHH), 2.57 (m, 1H, CH), 4.75 (d, 1H, $^3J_{HH}$ = 5.2 Hz, $=CH$), 7.18 (m, 2H, CH_{ar}), 7.29 (m, 1H, CH_{ar}), 7.35 (m, 1H, CH_{ar}); $^{31}P\{^1H\}$ NMR (C_6D_6, 20°C) AX spin system, δ_A = 73.7, δ_X = 76.7, J_{AX} = 23 Hz; $^{13}C\{^1H\}$ NMR (C_6D_6, 20°C) δ 16.1 (dd, $^1J_{CP}$ = 19 Hz, $^2J_{CP}$ = 11 Hz, CH_2), 17.8 (d, $^2J_{CP}$ = 6 Hz, CH_3), 17.9 (d, $^2J_{CP}$ = 5 Hz, CH_3), 18.4 (d, $^2J_{CP}$ = 3 Hz, CH_3), 18.6 (s, CH_3), 19.6 (d, $^2J_{CP}$ = 5 Hz, CH_3), 20.8 (d, $^2J_{CP}$ = 6 Hz, CH_3), 21.2 (d, $^2J_{CP}$ = 6 Hz, CH_3), 21.3 (s, CH_3), 22.6 (dd, $^1J_{CP}$ = 25 Hz, $^2J_{CP}$ = 24 Hz, CH_2), 23.2 (d, $^1J_{CP}$ = 16 Hz, CH), 24.5 (d, $^1J_{CP}$ = 18 Hz, CH), 25.1 (d, $^1J_{CP}$ = 21 Hz, CH), 25.1 (d, $^1J_{CP}$ = 21 Hz, CH), 28.3 (s, CH_2), 36.6 (s, CH), 93.8 (s, =*C*H), 117.3 (d, $^3J_{CP}$ = 13 Hz, O-*C*-O), 123.4 (s, *C*H$_{ar}$), 123.6 (s, *C*H$_{ar}$), 125.0 (d, J_{CP} = 7 Hz, *C*H$_{ar}$), 137.2 (m, *C*H$_{ar}$), 150.1 (s, =*C*-O), 159.0 (dd, $^2J_{CP}$ = 27 and 89 Hz, *C*$_{ar}$-Ni), 165.7 (s, *C*$_{ar}$-C-O).

Preparation of compound $C(O)(C_6H_4\text{-}o\text{-}C(CH(CH_3)CH_2CH{=}C(CH_3)O)O$ (4)

Through a solution of complex **3** (105 mg, 0.2 mmol) in tetrahydrofuran (15 mL) CO was bubbled for 5 minutes at room temperature. After this time the initial yellow solution turned pale yellow. The solvent was evaporated under vacuum and the resulting oil was extracted with 30 mL of petroleum ether and filtered. Compound **4** was separated from the complex Ni(dippe)(CO)$_2$ by spinning band chromatography, with an 4:1 mixture of ether petroleum/Et$_2$O as eluent (27 mg, 59 %).

HREIMS: m/*z* calcd. for $C_{14}H_{14}O_3$: 230.0943. Found: 230.0940. IR (Nujol) 1775, 1685 cm^{-1}. ^{1}H NMR (C_6D_6, 20°C) δ 0.41 (d, 3H, $^3J_{HH}$ = 6.0 Hz, C*H*$_3$), 1.61 (d, 3H, $^4J_{HH}$ = 0.8 Hz, C*H*$_3$), 1.81 (m, 1H, C*H*H), 2.06 (m, 2H, CH*H* and C*H*), 4.58 (d, 1H, $^3J_{HH}$ = 5.0 Hz, =C*H*), 6.90 (t, 1H, $^3J_{HH}$ = 6.8 Hz, C*H*$_{ar}$), 7.04 (m, 2H, C*H*$_{ar}$), 7.60 (d, 1H, $^3J_{HH}$ = 7.6 Hz, C*H*$_{ar}$); ^{13}C{^{1}H} NMR (C_6D_6, 20°C) δ 15.2 (s, *C*H$_3$ b), 19.2 (s, *C*H$_3$ g), 26.0 (s, *C*H$_2$ d), 32.7 (s, *C*H c), 97.4 (s, =*C*H e), 106.5 (s, O-*C*-O h), 121.8 (s, *C*H$_{ar}$), 125.1 (s, *C*H$_{ar}$), 127.7 (s, *C*$_{ar}$-C=O), 130.2 (s, *C*H$_{ar}$), 133.8 (s, *C*H$_{ar}$), 147.2 (s, *C*$_{ar}$-C-O), 148.4 (s, =*C*-O f), 167.6 (s, *C*=O i).

Reaction of complex 1 with methylpropenylketone (MPK). Synthesis of $Ni(C_6H_4\text{-}o\text{-}C({=}CHCH(CH_3)CH_2C(O)CH_3)O)(dippe)$ (6).

To a solution of 100 mg (0.2 mmol) of complex **1** in 5 mL of THF at -78 °C, 98 μL (1 mmol) of MPK was added. The reaction mixture was stirred for 24 hours at room temperature, after which time the solvent was evaporated under reduced pressure and the residue was extracted with 20 mL of $\mathrm{Et_2O}$. Concentration of the solution and cooling to -30 $^{\circ}$C provided 75 mg (72 %) of yellow crystals.

Anal. Calcd for $\mathrm{C_{27}H_{46}P_2O_2Ni}$: C, 62.0; H, 8.9. Found: C, 61.6; H, 8.9. IR (Nujol) 1710, 1605 cm^{-1}. ^{1}H NMR ($\mathrm{C_6D_6}$, 20°C) δ 0.73 (m, 6H, $\mathrm{C}\mathit{H}_3$), 0.77 (m, 2H, $\mathrm{C}\mathit{H}_2$), 0.93 (m, 6H, $\mathrm{C}\mathit{H}_3$), 1.06 (m, 2H, $\mathrm{C}\mathit{H}_2$), 1.10 (m, 6H, $\mathrm{C}\mathit{H}_3$), 1.35 (d, 3H, $^2J_{\mathrm{HH}}$ = 7 Hz, $\mathrm{C}\mathit{H}_3\mathrm{\text{-}CH}$), 1.38 (m, 6H, $\mathrm{C}\mathit{H}_3$), 1.95 (m, 2H, $\mathrm{C}\mathit{H}$), 1.97 (s, 3H, $\mathrm{C}\mathit{H}_3\mathrm{\text{-}C{=}O}$), 2.06 (m, 1H, $\mathrm{C}\mathit{H}$), 2.24 (m, 1H, $\mathrm{C}\mathit{H}$), 2.43 (dd, 1H, $^2J_{\mathrm{HH}}$ = 14.6 Hz, $^3J_{\mathrm{HH}}$ = 7.9 Hz, $\mathrm{C}\mathit{H}\mathrm{H}$), 2.73 (dd, 1H, $^2J_{\mathrm{HH}}$ = 14.6 Hz, $^3J_{\mathrm{HH}}$ = 6.3 Hz, $\mathrm{C}\mathit{H}\mathrm{H}$), 3.87 (m, 1H, $\mathrm{CH_3\text{-}C}\mathit{H}$), 4.92 (d, 1H, $^3J_{\mathrm{HH}}$ = 8.1 Hz, $\mathrm{{=}C}\mathit{H}$), 7.16 (m, 2H, $\mathrm{C}\mathit{H}_{\mathrm{ar}}$), 7.33 (m, 1H, $\mathrm{C}\mathit{H}_{\mathrm{ar}}$), 7.65 (m, 1H, $\mathrm{C}\mathit{H}_{\mathrm{ar}}$); ^{31}P{^{1}H} NMR ($\mathrm{C_6D_6}$, 20°C) AX spin system, $\delta_{\mathrm{A}} = 73.7$, $\delta_{\mathrm{X}} = 77.4$, $J_{\mathrm{AX}} = 22$ Hz; ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$, 20°C) δ 16.5 (dd, $^1J_{\mathrm{CP}}$= 20 Hz, $^2J_{\mathrm{CP}}$ = 10 Hz, $\mathit{C}\mathrm{H_2}$), 18.4 (s, $\mathit{C}\mathrm{H_3}$), 18.4 (d, $^2J_{\mathrm{CP}}$ = 5 Hz, $\mathit{C}\mathrm{H_3}$), 18.7 (d, $^2J_{\mathrm{CP}}$= 4 Hz, $\mathit{C}\mathrm{H_3}$), 18.9 (s, $\mathit{C}\mathrm{H_3}$), 19.5 (d, $^2J_{\mathrm{CP}}$= 4 Hz, $\mathit{C}\mathrm{H_3}$), 20.0 (d, $^2J_{\mathrm{CP}}$= 5 Hz, $\mathit{C}\mathrm{H_3}$), 21.5 (d, $^2J_{\mathrm{CP}}$= 5 Hz, $\mathit{C}\mathrm{H_3}$), 21.6 (d, $^2J_{\mathrm{CP}}$= 5 Hz, $\mathit{C}\mathrm{H_3}$), 22.9 (s, $\mathit{C}\mathrm{H_3\text{-}CH}$), 23.0 (dd, $^1J_{\mathrm{CP}}$= 26 Hz, $^2J_{\mathrm{CP}}$ = 23 Hz, $\mathit{C}\mathrm{H_2}$), 24.0 (d, $^1J_{\mathrm{CP}}$= 17 Hz, $\mathit{C}\mathrm{H}$), 24.7 (d, $^1J_{\mathrm{CP}}$= 17 Hz, $\mathit{C}\mathrm{H}$), 25.6 (d, $^1J_{\mathrm{CP}}$= 22 Hz, $\mathit{C}\mathrm{H}$), 25.8 (d, $^1J_{\mathrm{CP}}$= 22 Hz, $\mathit{C}\mathrm{H}$), 28.1 (s, $\mathrm{CH_3\text{-}}\mathit{C}\mathrm{H}$), 30.5 (s, $\mathit{C}\mathrm{H_3\text{-}C{=}O}$), 53.2 (s, $\mathit{C}\mathrm{H_2}$), 98.2 (s, $\mathrm{{=}}\mathit{C}\mathrm{H}$), 121.8 (s, $\mathit{C}\mathrm{H_{ar}}$), 123.6 (s, $\mathit{C}\mathrm{H_{ar}}$), 124.7 (d, J_{CP} = 7 Hz, $\mathit{C}\mathrm{H_{ar}}$), 138.1 (m, $\mathit{C}\mathrm{H_{ar}}$), 156.6 (s, $\mathit{C}_{\mathrm{ar}}\mathrm{\text{-}C\text{-}O}$), 158.9 (dd, $^2J_{\mathrm{CP}}$= 27 and 87 Hz, $\mathit{C}_{\mathrm{ar}}\mathrm{\text{-}Ni}$), 208.4 (s, $\mathit{C}\mathrm{{=}O}$).

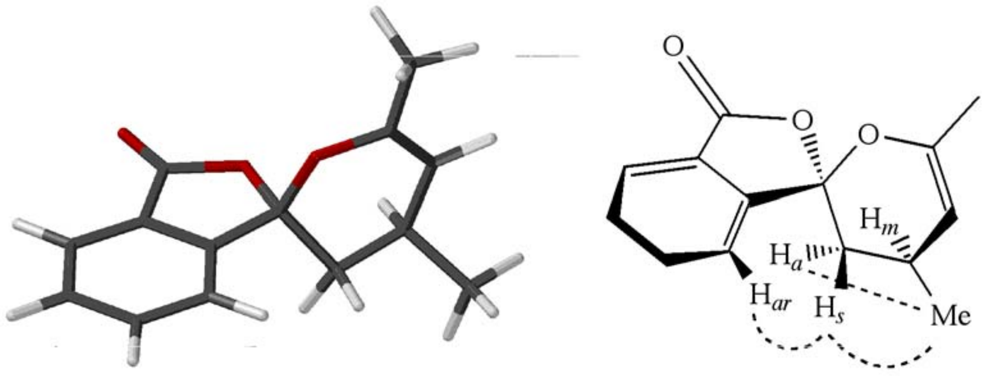
Preparation of compound $\overline{\mathrm{C(O)(C_6H_4\text{-}\mathit{o}\text{-}\underline{C(CH_2CH(CH_3)CH{=}C(CH_3)O})O}}$ (7)

A mixture of complex **1** (100 mg, 0.2 mmol) and MPK was stirred for 45 min at room temperature. ^{31}P{^{1}H} NMR showed that **5** was the major species. Through this solution, CO was bubbled for 5 minutes at room temperature and the solvent was removed under vacuum. The residue was extracted with 30 mL of petroleum ether, the resulting solution was taken to dryness and the residue subjected to spinning band chromatography. Elution with 3:2 petroleum ether/Et_2O gave compound **7** (24 mg, 53 %) as a white solid.

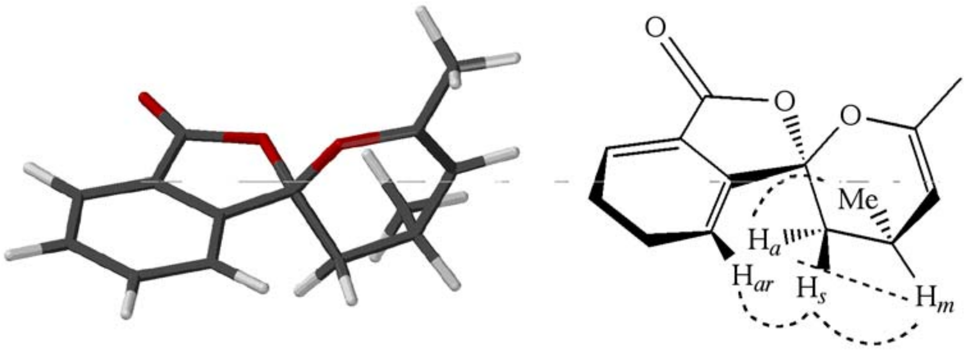
HREIMS: m/*z* calcd. for $C_{14}H_{14}O_3$: 230.0943. Found: 230.0940. IR (Nujol) 1775, 1685 cm^{-1}. ^1H NMR (C_6D_6, 20°C) δ 0.81 (d, 3H, $^3J_{HH}$ = 7.0 Hz, CH_3), 1.39 (dd, 1H, $^2J_{HH}$ = 13.4 Hz, $^3J_{HH}$ = 6.0, C*H*H), 1.46 (dd, 1H, $^2J_{HH}$ = 13.2 Hz, $^3J_{HH}$ = 12.0 Hz, CH*H*), 1.61 (m, 3H, CH_3), 2.57 (m, 1H, C*H*), 4.45 (m, 1H, =C*H*), 6.86 (t, 1H, $^3J_{HH}$ = 7.3 Hz, CH_{ar}), 6.98 (m, 2H, CH_{ar}), 7.63 (d, 1H, $^3J_{HH}$ = 7.3 Hz, CH_{ar}); $^{13}C\{^1H\}$ NMR (C_6D_6, 20°C) δ 19.2 (s, *C*H_3), 20.5 (s, *C*H_3), 23.6 (s, *C*H), 37.8 (s, *C*H_2), 104.0 (s, =*C*H), 104.2 (s, O-*C*-O), 121.9 (s, *C*H_{ar}), 125.2 (s, *C*H_{ar}), 127.0 (s, C_{ar}-C=O), 130.3 (s, *C*H_{ar}), 133.6 (s, *C*H_{ar}), 147.9 (s, C_{ar}-C-O), 148.3 (s, =*C*-O), 167.2 (s, O-*C*=O).

Stereochemistry of complex **7**

As observed in the reaction of **2** + MVK, compound **5** is formed as a single diastereomer pair. Its precise stereochemistry has been established on the basis of the 2D ^1H NOESY spectrum of complex **7**, which allows establishing the spatial relationships shown in Figure 1. Thus, the diastereotopic protons labeled H_a and H_s, can be assigned to two close but well defined multiplets at δ 1.39 and 1.46 ppm, respectively, on the basis of the selective NOE crosspeak that links the latter with an aromatic resonance at δ 6.98. The methyne proton H_m is correlated to H_a, but not to H_s, and this allows assigning the *meso* configuration (*rs*+*sr*) to **7** (and **5**). To obtain further support, we have modeled the two possible diastereomers, optimized their structures with the DFT method pBP86/DN* included in the program *Spartan*,[1] and compared the observed NOE relationships with the calculated positions of the hydrogen atoms.[2] As it can be readily seen in Figure 1, the non-selective NOE found between the Me substituent and H_s and H_a is due to the staggered disposition adopted by these in the *meso* diastereomer, and it is not expected to be found in the opposite diastereomer pair.



Observed (*sr* + *rs*)



Not Observed (*ss* + *rr*)

Figure 1. NOE relationships in the two possible configurations of compound **7**

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[1] Mac Spartan Pro fro the Macintosh, version 1.0.4. Wavefunction, inc. 2000.

[2] The values of the dihedral angles H_aCCH_m y H_sCCH_m for the *meso* diastereomer (48 and 167°, respectively) show an excellent agreement with the values deduced from the experimental coupling constants J_{HaHm} and J_{HsHm} with the Karplus equation (41 and 169°).

X-ray Crystal Structure Determination of 3.

$C_{27}H_{46}NiP_2O_2$, monoclinic, $P2_1/c$, a = 10.364 (4), b = 14.185 (4), c = 19.437(5) Å, β = 98.64(3)°, V = 2825(1) Å^3, Z = 4, D_{calcd}= 1.230 Mg m^{-3}, F(000) = 1128, λ = 0.71073 Å, μMoKα = 8.20 cm^{-1}.

Intensity data were collected at r.t. on a Philips PW1100 single-crystal diffractometer using a graphite monochromated MoKα radiation; 8633 reflections were measured (with θ in the range 3.04-30.01°) of which 8236 were independent and included in the structure refinement. A correction for absorption was applied [max. and min. values for the transmission coefficient were 1.000 and 0.804].[1] The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares procedures (based on F_o^2), with anisotropic thermal parameters in the last cycles of refinement for all non-hydrogen atoms. The hydrogen atoms were introduced into the geometrically calculated positions and refined riding on the corresponding parent atoms. The refinement converged at $wR2$ = 0.0959 for all data and 304 variables [$R1$ = 0.0371 for 5385 reflections with $I > 2\sigma(I)$. The SHELX-97 system of computer programs was used.[2]

[1] (a) Walker N.; Stuart D., *Acta Crystallogr.*, 1983, *A39*, 158. (b) Ugozzoli F., *Comput. Chem*. 1987, *11*, 109.

[2] SHELX-97. Programs for Crystal Structure Analysis (Release 97-2). Sheldrick, G.M., Institüt für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany, 1998

Table 1	Crystal data and structure refinement of **3**
Table 2	Atomic coordinates of non-H atoms of **3**
Table 3	Anisotropic coefficients of non-H atoms of **3**
Table 4	Atomic coordinates of H atoms of **3**
Table 5	List of bond lengths (Å) and angles (deg) of **3**

Table 1. Crystal data and structure refinement for **3**.

Identification code	**3**
Empirical formula	C27 H46 Ni O2 P2
Formula weight	523.29
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	monoclinic, $P2_1/c$
Unit cell dimensions	*a* = 10.364(4) Å α = 90 deg. *b* = 14.185(4) Å β = 98.64(3) deg. *c* = 19.437(5) Å γ = 90 deg.
Volume	2825.1(15) Å^3
Z, Calculated density	4, 1.230 Mg/m^3
Absorption coefficient	0.820 mm^{-1}
F(000)	1128
θ range for data collection	3.04 to 30.01 deg.
Index ranges	0=*h*=14, 0=*k*=19, -27=*l*=26
Reflections collected / unique	8633 / 8236 [R(int) = 0.0218]
Completeness to 2θ = 30.01	99.7%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8236 / 0 / 304
Goodness-of-fit on F^2	0.930
Final R indices [*I*>2σ(*I*)]	R1 = 0.0371, wR2 = 0.0865
R indices (all data)	R1 = 0.0695, wR2 = 0.0959
Largest diff. peak and hole	0.476 and -0.484 e.Å^{-3}

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

Atom	*x*	*y*	*z*	*U*(eq)
Ni(1)	1364(1)	1638(1)	8361(1)	24(1)
P(1)	25(1)	670(1)	7768(1)	28(1)
P(2)	2987(1)	733(1)	8144(1)	32(1)
O(1)	2658(1)	2364(1)	8859(1)	33(1)
O(2)	2823(1)	3982(1)	8999(1)	37(1)
C(1)	147(2)	2506(1)	8682(1)	26(1)
C(2)	819(2)	3211(1)	9092(1)	27(1)
C(3)	181(2)	3927(1)	9389(1)	38(1)
C(4)	-1170(2)	3948(2)	9307(1)	42(1)
C(5)	-1868(2)	3250(2)	8924(1)	40(1)
C(6)	-1216(2)	2554(1)	8613(1)	35(1)
C(7)	2283(2)	3101(1)	9234(1)	27(1)
C(8)	2810(2)	2982(1)	10013(1)	32(1)
C(9)	4290(2)	2881(2)	10098(1)	41(1)
C(10)	4850(2)	3633(2)	9699(1)	43(1)
C(11)	4142(2)	4113(2)	9198(1)	39(1)
C(12)	2184(2)	2144(2)	10326(1)	46(1)
C(13)	4635(3)	4881(2)	8781(1)	67(1)
C(14)	940(2)	-401(1)	7591(1)	39(1)
C(15)	2364(2)	-200(2)	7534(1)	42(1)
C(16)	-1318(2)	161(2)	8179(1)	38(1)
C(17)	-894(3)	17(2)	8959(1)	60(1)
C(18)	-1897(2)	-742(2)	7832(1)	49(1)
C(19)	-789(2)	1023(2)	6890(1)	40(1)
C(20)	206(3)	1366(2)	6444(1)	62(1)
C(21)	-1838(3)	1764(2)	6897(1)	64(1)
C(22)	3822(2)	138(2)	8934(1)	52(1)
C(23)	2879(3)	-400(2)	9304(1)	72(1)
C(24)	4965(3)	-484(2)	8810(2)	93(1)
C(25)	4324(2)	1274(2)	7754(1)	43(1)
C(26)	3781(3)	1857(2)	7123(2)	67(1)
C(27)	5230(2)	1879(2)	8267(2)	74(1)

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

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ni(1)	24(1)	24(1)	25(1)	-5(1)	4(1)	-1(1)
P(1)	29(1)	25(1)	30(1)	-5(1)	4(1)	-5(1)
P(2)	29(1)	32(1)	34(1)	-8(1)	4(1)	4(1)
O(1)	24(1)	36(1)	38(1)	-14(1)	3(1)	-3(1)
O(2)	38(1)	35(1)	36(1)	4(1)	1(1)	-11(1)
C(1)	27(1)	24(1)	29(1)	-2(1)	7(1)	-2(1)
C(2)	28(1)	27(1)	26(1)	-1(1)	4(1)	0(1)
C(3)	39(1)	33(1)	41(1)	-13(1)	2(1)	1(1)
C(4)	39(1)	40(1)	48(1)	-15(1)	8(1)	9(1)
C(5)	29(1)	40(1)	51(1)	-8(1)	9(1)	3(1)
C(6)	28(1)	32(1)	44(1)	-10(1)	5(1)	-4(1)
C(7)	28(1)	26(1)	28(1)	-4(1)	5(1)	-5(1)
C(8)	36(1)	31(1)	28(1)	-2(1)	4(1)	-2(1)
C(9)	37(1)	48(1)	35(1)	0(1)	-4(1)	-1(1)
C(10)	32(1)	53(1)	43(1)	-7(1)	2(1)	-13(1)
C(11)	38(1)	41(1)	38(1)	-4(1)	7(1)	-17(1)
C(12)	53(1)	45(1)	42(1)	11(1)	9(1)	-6(1)
C(13)	69(2)	68(2)	65(2)	15(1)	12(1)	-35(2)
C(14)	41(1)	29(1)	46(1)	-12(1)	5(1)	-1(1)
C(15)	42(1)	36(1)	48(1)	-16(1)	8(1)	2(1)
C(16)	37(1)	35(1)	44(1)	-3(1)	12(1)	-8(1)
C(17)	73(2)	63(2)	46(1)	2(1)	18(1)	-24(2)
C(18)	47(1)	40(1)	62(2)	-7(1)	13(1)	-19(1)
C(19)	41(1)	42(1)	34(1)	-3(1)	-1(1)	-6(1)
C(20)	63(2)	82(2)	41(1)	13(1)	7(1)	-12(2)
C(21)	68(2)	67(2)	54(2)	4(1)	-6(1)	17(2)
C(22)	47(1)	59(2)	46(1)	0(1)	-5(1)	16(1)
C(23)	84(2)	73(2)	56(2)	19(2)	1(2)	9(2)
C(24)	81(2)	105(3)	89(2)	16(2)	3(2)	57(2)
C(25)	31(1)	51(1)	50(1)	-15(1)	14(1)	1(1)
C(26)	59(2)	67(2)	81(2)	16(2)	26(2)	-6(1)
C(27)	42(1)	101(2)	84(2)	-43(2)	25(1)	-27(2)

Table 4. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for compound **3**.

Atom	*x*	*y*	*z*	*U*(eq)
H(3)	662	4395	9646	55(3)
H(4)	-1599	4428	9507	55(3)
H(5)	-2774	3246	8874	55(3)
H(6)	-1705	2098	8347	55(3)
H(8)	2604	3554	10258	30(5)
H(9A)	4654	2928	10587	51(5)
H(9B)	4514	2267	9931	51(5)
H(10)	5735	3770	9807	57(7)
H(12A)	2526	2093	10812	62(4)
H(12B)	2374	1577	10091	62(4)
H(12C)	1256	2234	10272	62(4)
H(13A)	3928	5124	8453	282(17)
H(13B)	5300	4635	8536	282(17)
H(13C)	4994	5378	9086	282(17)
H(14A)	903	-853	7962	59(4)
H(14B)	523	-684	7160	59(4)
H(15A)	2438	-7	7062	59(4)
H(15B)	2878	-768	7637	59(4)
H(16)	-2021	630	8129	40(6)
H(17A)	-542	595	9165	61(3)
H(17B)	-241	-467	9032	61(3)
H(17C)	-1634	-168	9171	61(3)
H(18A)	-2161	-631	7344	61(3)
H(18B)	-2642	-929	8039	61(3)
H(18C)	-1254	-1233	7894	61(3)
H(19)	-1208	459	6666	42(6)
H(20A)	872	896	6439	91(4)
H(20B)	595	1942	6634	91(4)
H(20C)	-221	1475	5978	91(4)
H(21A)	-2472	1546	7174	91(4)
H(21B)	-2258	1879	6430	91(4)
H(21C)	-1450	2338	7092	91(4)
H(22)	4187	639	9253	59(7)
H(23A)	2178	8	9385	105(5)
H(23B)	3324	-629	9741	105(5)
H(23C)	2533	-924	9022	105(5)
H(24A)	5564	-122	8585	105(5)
H(24B)	4647	-1007	8520	105(5)
H(24C)	5405	-714	9248	105(5)
H(25)	4846	763	7597	42(6)
H(26A)	3222	1471	6799	110(5)
H(26B)	4488	2092	6904	110(5)
H(26C)	3291	2377	7266	110(5)
H(27A)	5582	1505	8662	110(5)
H(27B)	4748	2399	8418	110(5)
H(27C)	5930	2115	8044	110(5)

Table 5. Bond lengths [Å] and angles [deg] for compound **3**.

Ni(1)-O(1)	1.8460(13)
Ni(1)-C(1)	1.9322(18)
Ni(1)-P(1)	2.1580(8)
Ni(1)-P(2)	2.2071(8)
P(1)-C(14)	1.850(2)
P(1)-C(16)	1.852(2)
P(1)-C(19)	1.855(2)
P(2)-C(15)	1.829(2)
P(2)-C(25)	1.843(2)
P(2)-C(22)	1.849(2)
O(1)-C(7)	1.365(2)
O(2)-C(11)	1.377(2)
O(2)-C(7)	1.469(2)
C(1)-C(2)	1.396(2)
C(1)-C(6)	1.400(3)
C(2)-C(3)	1.385(3)
C(2)-C(7)	1.509(3)
C(3)-C(4)	1.385(3)
C(4)-C(5)	1.376(3)
C(5)-C(6)	1.386(3)
C(7)-C(8)	1.539(3)
C(8)-C(12)	1.525(3)
C(8)-C(9)	1.524(3)
C(9)-C(10)	1.488(3)
C(10)-C(11)	1.317(3)
C(11)-C(13)	1.493(3)
C(14)-C(15)	1.523(3)
C(16)-C(17)	1.528(3)
C(16)-C(18)	1.528(3)
C(19)-C(21)	1.515(3)
C(19)-C(20)	1.523(3)
C(22)-C(23)	1.505(4)
C(22)-C(24)	1.526(3)
C(25)-C(26)	1.516(3)
C(25)-C(27)	1.527(3)

O(1)-Ni(1)-C(1)	86.16(7)
O(1)-Ni(1)-P(1)	173.33(4)
C(1)-Ni(1)-P(1)	100.36(6)
O(1)-Ni(1)-P(2)	84.84(5)
C(1)-Ni(1)-P(2)	170.38(6)
P(1)-Ni(1)-P(2)	88.56(3)
C(14)-P(1)-C(16)	101.54(10)
C(14)-P(1)-C(19)	103.01(10)
C(16)-P(1)-C(19)	103.56(10)
C(14)-P(1)-Ni(1)	108.37(7)
C(16)-P(1)-Ni(1)	118.84(7)
C(19)-P(1)-Ni(1)	119.11(8)
C(15)-P(2)-C(25)	104.40(10)
C(15)-P(2)-C(22)	106.52(12)
C(25)-P(2)-C(22)	104.13(11)
C(15)-P(2)-Ni(1)	109.90(7)
C(25)-P(2)-Ni(1)	118.56(8)
C(22)-P(2)-Ni(1)	112.40(8)
C(7)-O(1)-Ni(1)	117.70(11)
C(11)-O(2)-C(7)	115.85(15)
C(2)-C(1)-C(6)	115.44(17)
C(2)-C(1)-Ni(1)	110.29(13)
C(6)-C(1)-Ni(1)	134.23(14)
C(3)-C(2)-C(1)	122.31(17)
C(3)-C(2)-C(7)	121.92(17)
C(1)-C(2)-C(7)	115.62(16)
C(4)-C(3)-C(2)	120.34(19)
C(5)-C(4)-C(3)	119.14(19)
C(4)-C(5)-C(6)	119.81(19)
C(5)-C(6)-C(1)	122.91(18)
O(1)-C(7)-O(2)	109.45(14)
O(1)-C(7)-C(2)	109.89(15)
O(2)-C(7)-C(2)	105.95(15)
O(1)-C(7)-C(8)	110.72(15)
O(2)-C(7)-C(8)	107.67(14)
C(2)-C(7)-C(8)	112.99(16)
C(12)-C(8)-C(9)	111.41(17)
C(12)-C(8)-C(7)	111.59(16)
C(9)-C(8)-C(7)	108.65(16)
C(10)-C(9)-C(8)	109.92(18)
C(11)-C(10)-C(9)	122.60(19)
C(10)-C(11)-O(2)	123.86(19)
C(10)-C(11)-C(13)	125.5(2)
O(2)-C(11)-C(13)	110.65(19)
C(15)-C(14)-P(1)	112.96(14)
C(14)-C(15)-P(2)	109.79(14)
C(17)-C(16)-C(18)	111.18(19)

C(17)-C(16)-P(1)	110.95(15)
C(18)-C(16)-P(1)	114.02(15)
C(21)-C(19)-C(20)	109.4(2)
C(21)-C(19)-P(1)	114.01(16)
C(20)-C(19)-P(1)	110.89(15)
C(23)-C(22)-C(24)	110.9(2)
C(23)-C(22)-P(2)	111.83(17)
C(24)-C(22)-P(2)	114.21(19)
C(26)-C(25)-C(27)	109.8(2)
C(26)-C(25)-P(2)	110.43(16)
C(27)-C(25)-P(2)	113.13(16)