

$(\eta^5\text{-Cyclopentadienyl})(3\text{-hydroxy-3-methylbut-1-ynyl-}\kappa\text{C}^1)(\text{triphenylphosphine-}\kappa\text{P})\text{nickel(II)}$: novel O—H $\cdots\pi$ bonding in an organo-metallic molecule

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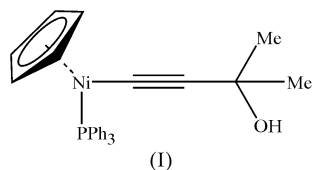
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In the title compound, $[\text{Ni}(\text{C}_5\text{H}_5)(\text{C}_5\text{H}_7\text{O})(\text{C}_{18}\text{H}_{15}\text{P})]$, the molecule adopts the expected half-sandwich structure with no unusual metal–ligand distances. No classical hydrogen bonds are found in the structure; instead, the OH group of the butynol unit is involved in an unusual O—H $\cdots\pi$ interaction with the C $\equiv$ C group of an adjacent molecule. The crystal structure is further stabilized by C—H $\cdots$ O and C—H $\cdots\pi$ interactions, leading to an extensive network of spiral columns.

Comment

The title compound, (I), was prepared by reaction of equimolar amounts of $(\eta^5\text{-C}_5\text{H}_5)\text{Ni}(\text{PPh}_3)\text{Br}$ (Barnett, 1974) and 2-methylbut-3-yn-2-ol in Et_3N at ambient temperature in the presence of a CuI catalyst as a possible precursor to the terminal alkyne complex $(\eta^5\text{-C}_5\text{H}_5)\text{Ni}(\text{PPh}_3)\text{C}\equiv\text{CH}$. Derivatives of 2-methylbut-3-yn-2-ol are often used as an alternative to alkylsilylacetylenes as precursors for the synthesis of terminal alkynes (Crisp & Jiang, 1998). However, (I) proved unstable under standard deprotection conditions, the butynol group proving more robust than the metal centre of the molecule, with only decomposition products isolated. We report here the structure of this compound, which provides a rare organometallic example of an O—H $\cdots\pi$ interaction in the crystal structure.



The molecule of (I) has the expected half-sandwich structure, with the 3-hydroxy-3-methylbutynyl ligand σ -bound to the Ni^{II} atom (Fig. 1). A search of the Cambridge Structural Database (CSD, Version 5.28 to January 2007; Allen, 2002)

reveals 15 other nickel–alkynyl complexes (for example, Whittall *et al.*, 1998; Butler *et al.*, 2005), together with an alkynylene (Gallagher *et al.*, 2002) and a butadiynyl derivative (Gallagher *et al.*, 1998). In addition, a cluster system with $\text{Co}_2(\text{CO})_6$ coordinated to the C $\equiv$ C group of a nickel–alkyne is also known (Gallagher *et al.*, 2002). Analysis of the principal metal–ligand dimensions in these compounds using VISTA (CCDC, 1994) shows that the Ni1—P1 and Ni1—C1 distances and the P1—Ni1—C1 angle (Table 1) compare reasonably well with the mean values [Ni—P = 2.139 (7) Å, Ni—C = 1.844 (10) Å and P—Ni—C = 92 (3)°] found in the previously reported complexes, excluding the $\text{Co}_2(\text{CO})_6$ cluster. The C1 $\equiv$ C2 bond is similar to those in other nickel–alkynyl complexes [mean C $\equiv$ C = 1.203 (11) Å]. These are somewhat longer than the mean value of the corresponding distance for the 25 recorded structures containing the $\text{HOME}_2\text{C—C}\equiv\text{C}$ fragment, for which the mean C $\equiv$ C bond is 1.193 (10) Å. This has previously been attributed to delocalization of the π system in the $M\text{—C}\equiv\text{C}$ fragment (Gallagher *et al.*, 1998). Interestingly, only one other $\text{HOME}_2\text{C—C}\equiv\text{C}$ structure is of a metal–alkyne system, namely *cis*-($\text{HOME}_2\text{C—C}\equiv\text{C}$) $_2\text{Pt}(\text{PPh}_3)_2$, in which the mean C $\equiv$ C distance is much shorter at 1.16 Å (Furlani *et al.*, 1984). The Ni1—C1 $\equiv$ C2 and C1 $\equiv$ C2—C3 angles each deviate somewhat from the mean Ni—C $\equiv$ C angle [175.9 (17)°] in the other nickel complexes and the C $\equiv$ C—C angle [177.2 (18)°] in the other $\text{HOME}_2\text{C—C}\equiv\text{C}$ structures. This is likely to be a consequence of the formation of inversion-related dimers involving an O—H $\cdots\pi$ interaction with the alkyne C atoms, as outlined below.

An obvious feature of the packing in this molecule is the complete absence of classical O—H $\cdots$ O hydrogen bonds, despite the presence of an OH group in the molecule. This is unusual, but not unprecedented (Steiner *et al.*, 1996), for alkynyl alcohols and stems from the involvement of the OH

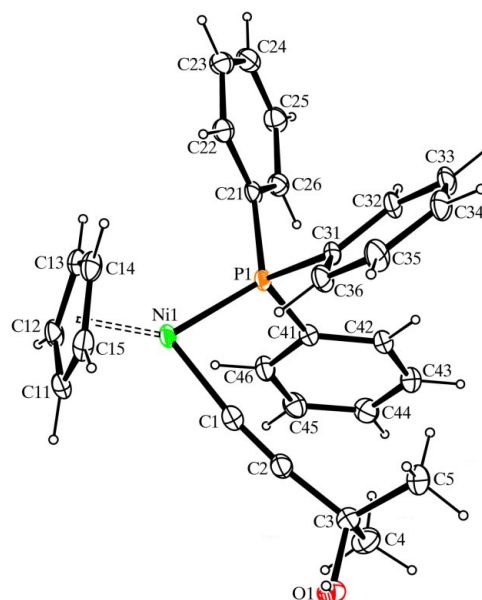
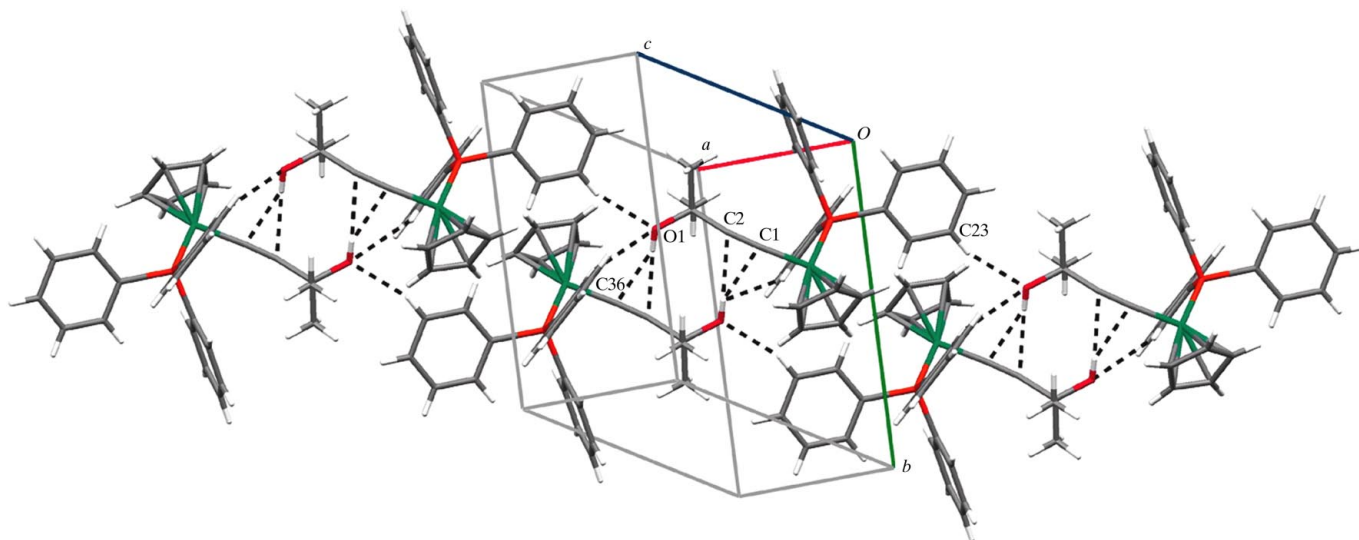
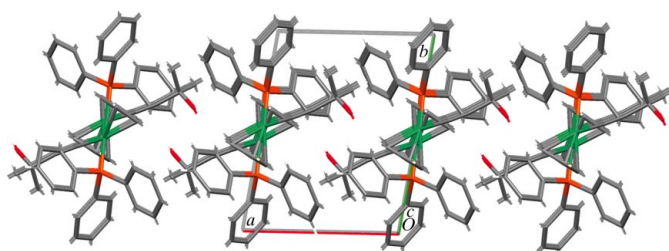


Figure 1
The molecular structure of (I), showing the atom labels and 50% probability displacement ellipsoids for non-H atoms.

**Figure 2**

Inversion-related dimers formed through a combination of $C-H \cdots O$ and $O-H \cdots \pi$ interactions are linked into undulating chains by an additional $C23-H23 \cdots O1^{ii}$ interaction [symmetry code: (ii) $x - 1, y, z - 1$]. Hydrogen bonds and $O-H \cdots \pi$ interactions are shown as dashed lines.

**Figure 3**

The crystal packing of (I), showing spiral columns down the c axis.

group in an unusual $O-H \cdots \pi$ interaction with the $C1 \equiv C2$ group. The contact places atom H1 of the OH group almost equidistant from the C atoms of the $C \equiv C$ bond [$H1 \cdots C1^i = 2.49$ (5) Å and $H1 \cdots C2^i = 2.45$ (4) Å; symmetry code: (i) $-x + 1, -y + 1, -z + 1$]. This interaction is further stabilized by a $C36-H36 \cdots O1^i$ hydrogen bond involving a phenyl ring of the triphenylphosphine ligand, giving a bifurcated arrangement (Table 2) (Desiraju & Steiner, 1999). Complementary bifurcated interactions involving two adjacent molecules generate inversion-related dimers (Fig. 2).

A search of the CSD for $O-H \cdots \pi$ interactions with distances of less than 2.5 Å between the H atom and Cg (the mid-point of the $C \equiv C$ bond) gave 15 examples. Three of these involved organometallic compounds (Furlani *et al.*, 1984; Akita *et al.*, 1997; Campbell *et al.*, 2003) and another a zinc-porphyrin coordination complex (Chen *et al.*, 2005). However, in each case, the OH group involved in similar interactions with the alkyne came from either water or methanol solvent molecules. This would appear, therefore, to be the first example of this type of intermolecular interaction between two organometallic systems. $O-H \cdots \pi$ interactions of this type were first reported by Lin *et al.* (1982) and were subsequently confirmed by a neutron study (Allen *et al.*, 1996). They are discussed in more detail by Desiraju & Steiner (1999). The

remaining structures from the CSD search showing similar interactions involved organic alkynyl alcohols and in all cases with the $H \cdots Cg$ contact limited to 2.5 Å the H atom is found to be approximately equidistant from each C atom of the alkyne. Extending the search to include contacts up to 3.0 Å revealed a further 42 hits but, as the $H \cdots Cg$ distance increased, there was a trend towards close contact with only one of the two alkyne C atoms (see, for example, Mondal *et al.*, 2004; Das *et al.*, 2003).

In the crystal structure, the dimers (Fig. 2) are further linked by a $C23-H23 \cdots O1^{ii}$ interaction [symmetry code: (ii) $x - 1, y, z - 1$] to form chains along c (Table 2). The crystal packing is completed by a $C34-H34 \cdots Cg1^{iii}$ interaction [Cg1 is the centroid of the $C21-C26$ benzene ring; symmetry code: (iii) $x + 1, y, z$], which adds two additional molecules to the inversion-related packing synthon. The $C-H \cdots \pi$ interactions link adjacent columns in the crystal structure to form an extensive columnar network down c (Fig. 3).

Experimental

A solution of $Ni(\eta^5-C_5H_5)(PPh_3)Br$ (0.466 g, 1 mmol), $HOMe_2C-C \equiv C-H$ (0.084 g, 1 mmol) and a catalytic amount of CuI (0.010 g, 5 mol%) in triethylamine (30 ml) was stirred in the absence of light for 4 h. The solvent was removed under reduced pressure and the diethyl ether soluble portion purified using column chromatography (SiO_2/CH_2Cl_2). Green blocks of (I) suitable for X-ray diffraction were obtained by slow evaporation from CH_2Cl_2 layered with hexane. 1H NMR (300 MHz, $CDCl_3$): δ 7.7 (*m*, 6H, phenyl), 7.4 (*m*, 9H, phenyl), 5.18 (*s*, 5H, cyclopentadiene), 0.94 (*s*, 6H, $-CMe_2-$). ^{13}C NMR (126 MHz, $CDCl_3$): δ 134.3 (phenyl *ipso*), 134.0, 128.2 (phenyl *o, m*), 130.2 (phenyl *p*), 124.2 (C2), 92.4 (cyclopentadiene), 73.9 (*d*, $J = 50$ Hz, C1), 66.4 (C3), 31.9 (Me). ^{31}P NMR (121 MHz, $CDCl_3$): δ 42.4. IR [$\nu(CC)$, cm^{-1}]: 2107 (CH_2Cl_2). Microanalysis calculated for $C_{28}H_{27}NiOP$: C 71.68, H 5.80, P 6.60%; found: C 71.60, H 5.95, P 6.32%. E_p^{ox} 0.78 V (CH_2Cl_2 , 0.1 M TBAPF₆, Pt, i_{red}/i_{ox} 0.3).

Crystal data

[Ni(C₅H₅)(C₅H₇O)(C₁₈H₁₅P)]
M_r = 469.18
 Triclinic, *P* $\bar{1}$
a = 8.9097 (8) Å
b = 11.0904 (8) Å
c = 12.7489 (14) Å
 α = 100.643 (5)°
 β = 109.694 (4)°
 γ = 94.490 (3)°
V = 1152.13 (18) Å³
Z = 2
 Mo *K*α radiation
 μ = 0.93 mm^{−1}
T = 85 (2) K
 0.28 × 0.19 × 0.10 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
 Absorption correction: multi-scan (*SADABS*; Bruker, 2004)
T_{min} = 0.715, *T_{max}* = 0.911
 28022 measured reflections
 7726 independent reflections
 6277 reflections with *I* > 2σ(*I*)
R_{int} = 0.046

Refinement

R [*F*² > 2σ(*F*²)] = 0.060
wR (*F*²) = 0.186
S = 1.06
 7726 reflections
 286 parameters
 H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}}$ = 2.45 e Å^{−3}
 $\Delta\rho_{\text{min}}$ = −1.73 e Å^{−3}

Table 1

Selected geometric parameters (Å, °).

Ni1—C1	1.855 (2)	C3—O1	1.440 (3)
Ni1—P1	2.1253 (6)	C3—C4	1.533 (3)
C1—C2	1.208 (3)	C3—C5	1.531 (3)
C2—C3	1.485 (3)	O1—H1	0.77 (4)
C1—Ni1—P1	86.12 (6)	C1—C2—C3	172.3 (2)
C2—C1—Ni1	172.94 (18)		

Table 2

Hydrogen-bond geometry (Å, °).

Cg1 is the centroid of the C21–C26 benzene ring.

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C36—H36...O1 ⁱ	0.95	2.59	3.389 (3)	142
C23—H23...O1 ⁱⁱ	0.95	2.56	3.475 (3)	161
C34—H34...Cg1 ⁱⁱⁱ	0.95	2.63	3.460 (3)	147

Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $x - 1, y, z - 1$; (iii) $x + 1, y, z$.

The hydroxyl H atom, H1, was located in a difference Fourier map and refined freely with an isotropic displacement parameter. Other H atoms were refined using a riding model, with C—H distances of 0.95 Å [*U*_{iso}(H) = 1.2*U*_{eq}(C)] for aromatic and 0.98 Å [*U*_{iso}(H) = 1.5*U*_{eq}(C)] for methyl H atoms. A rotating group model was used for the methyl groups. A number of high peaks were found in the final difference map, located less than 1.0 Å from atom Ni1, but no chemical significance could be attached to them.

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine

structure: *SHELXL97* (Sheldrick, 1997) and *TITAN2000* (Hunter & Simpson, 1999); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *Mercury* (Bruno *et al.*, 2002); software used to prepare material for publication: *SHELXL97*, *enCIFer* (Allen *et al.*, 2004), *PLATON* (Spek, 2003) and *PARST* (Nardelli, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GA3055). Services for accessing these data are described at the back of the journal.

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