Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

(η^5-Cyclopentadienyl)(3-hydroxy-3-methylbut-1-ynyl-κC^1)(triphenylphosphine-κP)nickel(II): novel O—H$\cdots\pi$ bonding in an organometallic molecule

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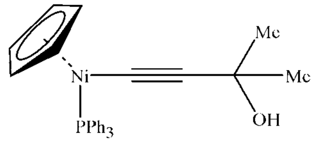
Received 9 May 2007
Accepted 31 May 2007
Online 23 June 2007

In the title compound, [Ni(C_5H_5)(C_5H_7O)($C_{18}H_{15}P$)], 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≡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 (η^5-C_5H_5)Ni(PPh_3)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 (η^5-C_5H_5)Ni(PPh_3)C≡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.



(I)

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 akynylene (Gallagher *et al.*, 2002) and a butadiynyl derivative (Gallagher *et al.*, 1998). In addition, a cluster system with $Co_2(CO)_6$ coordinated to the C≡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 $Co_2(CO)_6$ cluster. The C1≡C2 bond is similar to those in other nickel–alkynyl complexes [mean C≡C = 1.203 (11) Å]. These are somewhat longer than the mean value of the corresponding distance for the 25 recorded structures containing the $HOMe_2C$—C≡C fragment, for which the mean C≡C bond is 1.193 (10) Å. This has previously been attibuted to delocalization of the π system in the *M*—C≡C fragment (Gallagher *et al.*, 1998). Interestingly, only one other $HOMe_2C$—C≡C structure is of a metal–alkyne system, namely *cis*-($HOMe_2C$—C≡C)$_2$Pt-(PPh_3)$_2$, in which the mean C≡C distance is much shorter at 1.16 Å (Furlani *et al.*, 1984). The Ni1—C1≡C2 and C1≡C2—C3 angles each deviate somewhat from the mean Ni—C≡C angle [175.9 (17)°] in the other nickel complexes and the C≡C—C angle [177.2 (18)°] in the other $HOMe_2C$—C≡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

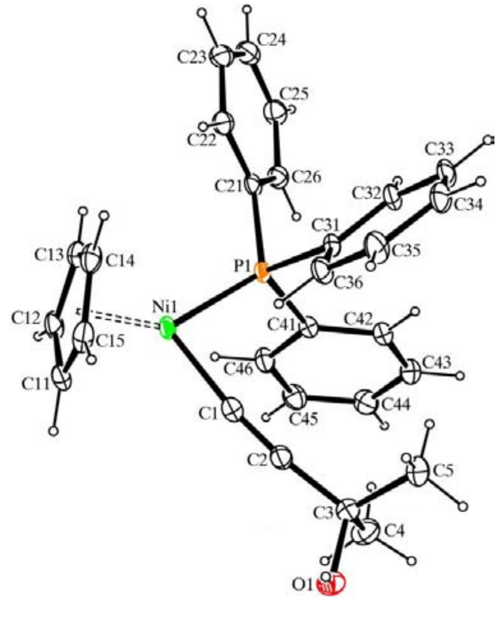


Figure 1
The molecular structure of (I), showing the atom labels and 50% probability displacement ellipsoids for non-H atoms.

  DOI: 10.1107/S0108270107026522

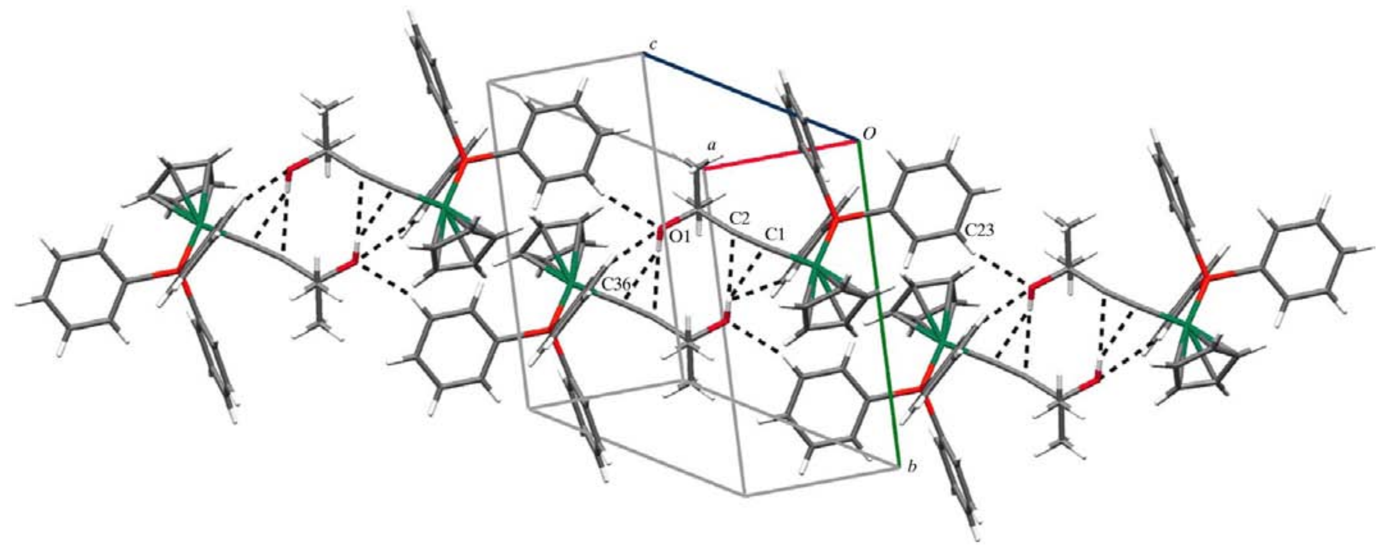


Figure 2
Inversion-related dimers formed through a combination of C—H···O and O—H···π interactions are linked into undulating chains by an additional C23—H23···O1[ii] interaction [symmetry code: (ii) $x - 1$, y, $z - 1$]. Hydrogen bonds and O—H···π interactions are shown as dashed lines.

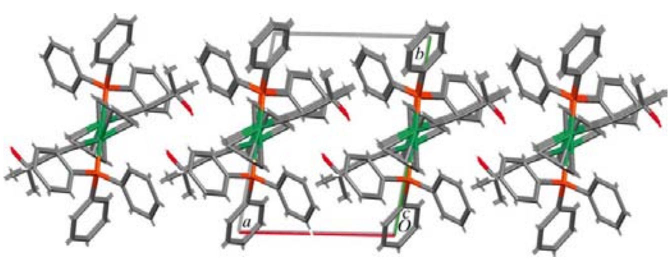


Figure 3
The crystal packing of (I), showing spiral columns down the *c* axis.

group in an unusual O—H···π interaction with the C1≡C2 group. The contact places atom H1 of the OH group almost equidistant from the C atoms of the C≡C bond [H1···C1^{i} = 2.49 (5) Å and H1···C2^{i} = 2.45 (4) Å; symmetry code: (i) $-x+1, -y+1, -z+1$]. This interaction is further stabilized by a C36—H36···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···π interactions with distances of less than 2.5 Å between the H atom and *Cg* (the mid-point of the C≡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···π 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···*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···*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···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···*Cg*1^{iii} interaction [*Cg*1 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···π interactions link adjacent columns in the crystal structure to form an extensive columnar network down *c* (Fig. 3).

Experimental

A solution of Ni(η^5-C_5H_5)(PPh_3)Br (0.466 g, 1 mmol), $HOMe_2C$—C≡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. ^{1}H 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 [ν(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* $TBAPF_6$, Pt, i_{red}/i_{ox} 0.3).

Crystal data

$[Ni(C_5H_5)(C_5H_7O)(C_{18}H_{15}P)]$	γ = 94.490 (3)°
M_r = 469.18	V = 1152.13 (18) Å^3
Triclinic, $P\overline{1}$	Z = 2
a = 8.9097 (8) Å	Mo $K\alpha$ radiation
b = 11.0904 (8) Å	μ = 0.93 mm^{-1}
c = 12.7489 (14) Å	T = 85 (2) K
α = 100.643 (5)°	0.28 × 0.19 × 0.10 mm
β = 109.694 (4)°	

Data collection

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

Refinement

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

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, °).

*Cg*1 is the centroid of the C21–C26 benzene ring.

D—H···A	D—H	H···A	D···A	D—H···A
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) = 1.2U_{eq}(C)] for aromatic and 0.98 Å [U_{iso}(H) = 1.5U_{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).

We thank the New Zealand Foundation for Research Science and Technology for a Postdoctoral Fellowship to CJM and the University of Otago for the purchase of the diffractometer.

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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