

H atoms treated by a mixture of independent and constrained refinement

Extinction correction: none  
Scattering factors from  
*International Tables for Crystallography* (Vol. C)

*Acta Cryst.* (1998). C54, 342–345

(1,3-Butadiynyl-C<sup>1</sup>)(η<sup>5</sup>-cyclopentadienyl)(triphenylphosphine-P)nickel(II)

Table 1. Selected geometric parameters (Å, °)

Co1—N4	1.938 (3)	Co1—Cl1	2.2786 (10)
Co1—N2	1.941 (3)	Co1—Cl2	2.2826 (9)
Co1—N3	1.956 (3)	Cl3···O1	3.000 (3)
Co1—N1	2.054 (3)		
N4—Co1—N2	96.07 (12)	N3—Co1—Cl1	92.84 (9)
N4—Co1—N3	85.58 (11)	N1—Co1—Cl1	97.60 (8)
N2—Co1—N3	84.66 (11)	N4—Co1—Cl2	85.59 (8)
N4—Co1—N1	85.36 (11)	N2—Co1—Cl2	176.69 (9)
N2—Co1—N1	84.30 (11)	N3—Co1—Cl2	92.62 (8)
N3—Co1—N1	164.89 (11)	N1—Co1—Cl2	98.71 (8)
N4—Co1—Cl1	172.75 (8)	Cl1—Co1—Cl2	87.42 (4)
N2—Co1—Cl1	90.82 (9)		

The temperature of the crystal was controlled using the Oxford Cryosystems Cryostream Cooler (Cosier & Glazer, 1986). The data collection nominally covered over a hemisphere of reciprocal space, by a combination of three sets of exposures with different  $\varphi$  angles for the crystal; each 10 s exposure covered 0.3° in  $\omega$ . The crystal-to-detector distance was 5.0 cm. Coverage of the unique set was over 97% complete to at least 26° in  $\theta$ . Crystal decay was found to be negligible by repeating the initial frames at the end of data collection and analysing the duplicate reflections. H atoms were added at calculated positions and refined using a riding model. The H atom attached to O1 was included and refined freely. Although the H atoms on the lattice water were visible on difference maps, they were not included. Anisotropic displacement parameters were used for all non-H atoms; H atoms were given isotropic displacement parameters equal to 1.2*U*<sub>eq</sub> of the carrier atom.

Data collection: SMART (Siemens, 1995). Cell refinement: SAINT (Siemens, 1995). Data reduction: SAINT. Program(s) used to solve structure: SHELXTLPC (Siemens, 1990). Program(s) used to refine structure: SHELXL97 (Sheldrick, 1997). Molecular graphics: SHELXTLPC. Software used to prepare material for publication: SHELXTLPC.

EPSRC and Siemens plc generously supported the purchase of the SMART diffractometer. The Warwick-Kansas collaboration has been supported by NATO.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: MU1372). Services for accessing these data are described at the back of the journal.

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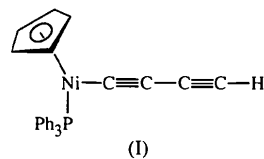
(Received 15 October 1997; accepted 12 November 1997)

## Abstract

The title compound, [Ni(Cp)(PPh<sub>3</sub>)(C≡C—C≡C—H)] or [Ni(C<sub>4</sub>H)(C<sub>5</sub>H<sub>5</sub>)(C<sub>18</sub>H<sub>15</sub>P)], has metal–ligand dimensions of Ni—P 2.1410 (4), Ni—C 1.8383 (15) Å and P—Ni—C 93.47 (5)°, and principal alkyne dimensions of C≡C 1.212 (2) and 1.187 (3) Å, and C≡C—C 177.94 (19) and 179.5 (2)°. Intra- and intermolecular C—H···C≡C interactions are present with the shortest C···C distance being 3.198 Å.

## Comment

Transition metal  $\sigma$ -acetylide polymers have attracted much interest in recent years due to their potential applications in liquid-crystal technology and non-linear optics (Long, 1995). Attention has focused on the acetylide ligand  $\pi$  system (which can provide a pathway for electron-density delocalization between the metal centre and ligand) to determine the extent of mixing of the ligand- and metal-based orbitals, extensive delocalization being necessary for a large non-linear response in conducting materials (McGrady *et al.*, 1997; Whittall *et al.*, 1997). In contrast to monoacetylide derivatives, few diacetylide organometallic complexes have been structurally characterized to date (Sun *et al.*, 1992; Worth *et al.*, 1992). We report herein on the structure of the title compound, (I), which incorporates a  $\sigma$ -bonded 1,3-butadiynyl ligand.



Molecule (I) has a half-sandwich structure and contains the  $\sigma$ -bonded 1,3-butadiynyl ligand. A view of the molecule with our numbering scheme is given in Fig. 1 and selected dimensions are given in Table 1. The principal metal–ligand dimensions are Ni1—P1 2.1410 (4), Ni1—C1 1.8383 (15) Å and P1—Ni1—C1 93.47 (5)°.

The terminal  $C\equiv C$  bond length of 1.187(3) Å is significantly shorter than the  $M-C\equiv C$  bond length of 1.212(2) Å resulting from a combination of increased librational motion along the 1,3-butadiynyl group from the metal centre and greater delocalization of the  $\pi$  system in the  $M-C\equiv C$  alkyne fragment; the  $C_{sp}-C_{sp}$  bond length is 1.370(2) Å. These bond lengths are in agreement with the expected values of 1.18(1) ( $C_{sp}\equiv C_{sp}$ ) and 1.38(1) Å ( $C_{sp}-C_{sp}$ ) (Orpen *et al.*, 1994). The angles in the  $Ni-C\equiv C-C\equiv CH$  group deviate slightly from linearity with  $Ni-C\equiv C$  177.61(14), and  $C\equiv C-C$  177.94(19) and 179.5(2)°.

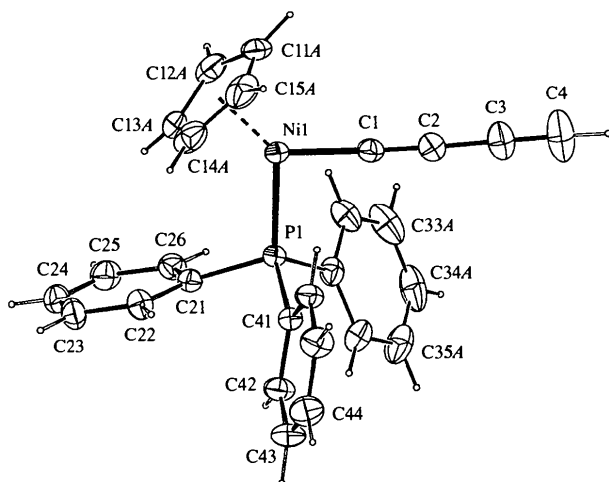


Fig. 1. A view of (I) with the atomic numbering scheme. Atom labels with the suffix 'A' are for the major conformations of the cyclopentadienyl and phenyl rings. Displacement ellipsoids are drawn at the 30% probability level.

In (I), the cyclopentadienyl ring (Cp) adopts two conformations [occupancies 0.59(3) and 0.41(3)] in the crystal (see details in the *Experimental* section). The  $Ni1-C_{Cp}$  distances are in the ranges 2.077(16)–2.15(2) and 2.06(3)–2.16(2) Å for the major and minor conformations, respectively. The ring centroid ( $Cg1$ ) of the major conformation is 1.7343(2) Å from  $Ni1$ ;  $Cg1-Ni1-P1$  and  $Cg1-Ni1-C1$  are 134.21(1) and 131.88(4)°, respectively, with the cyclopentadienyl ring plane at an angle of 83.4(6)° to the  $P1, Ni1, C4$  plane.

The  $C31-C36$  phenyl ring adopts two conformations [occupancies 0.612(17) and 0.388(17)] in the crystal (details in the *Experimental* section). The phosphorus atom  $P1$  lies 0.268(2) and 0.117(2) Å from the  $C21-C26$  and  $C41-C46$  phenyl-ring planes, respectively, with values of 0.086(8) and 0.045(12) Å for the disordered phenyl ring. In chloro(trimesitylphosphine)gold(I) (Alyea *et al.*, 1992), the  $P$  atom is 0.34 Å from the aromatic ring planes due to steric effects within the bulky phosphine mesityl groups.

The intramolecular  $C32B-H32B\cdots C1$  and intermolecular  $C35B-H35B\cdots C3^i$  interactions involve the 1,3-butadiynyl group [symmetry code: (i)  $-x, 1-y, 2-z$ ; details in Table 2]. A  $C-H\cdots\pi$ (arene) interaction is also present,  $C43-H43\cdots Cg2^{ii}$ , where  $Cg2^{ii}$  is the centroid of the  $C21-C26$  ring and symmetry code (ii) is  $(-x, -y, 2-z)$ . The intermolecular interactions can be viewed in Fig. 2. The butadiynyl  $H4$  atom only forms a weak contact with an arene ring:  $C-H\cdots Cg45^{iii}$ , where  $Cg45^{iii}$  is the midpoint of  $C44-C45$  and symmetry code (iii) is  $(x, 1+y, z)$ . Examination of the structure with *PLATON* (Spek, 1997a) showed that there are no solvent-accessible voids in the crystal lattice.

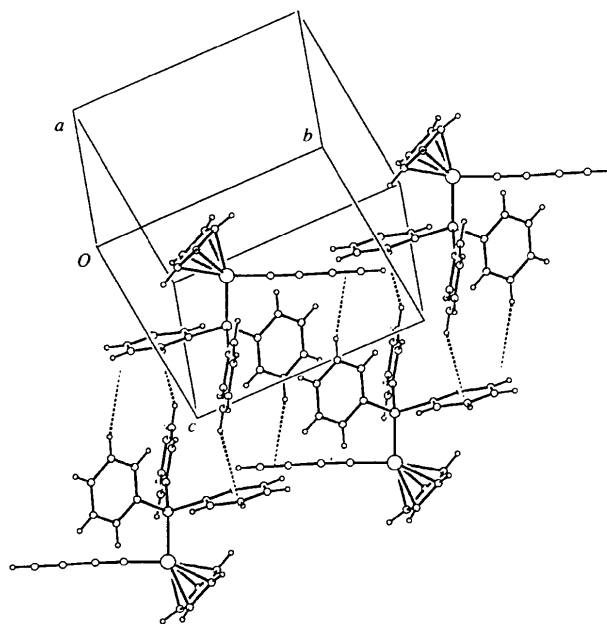


Fig. 2. A view of the intermolecular interactions in the crystal structure.

The 1,3-butadiynyl ligand in (I) can be compared with  $(CO)_2Ru(PEt_3)_2(C\equiv C-C\equiv C-SiMe_3)_2$  (Sun *et al.*, 1992), where the  $C-C$  bond lengths are 1.226(2), 1.370(2) and 1.209(2) Å along the  $Ru-C\equiv C-C\equiv C-Si$  chain, indicating  $\pi$  delocalization. In  $(CO)_9Co_3C-C\equiv C-C\equiv C-Si(Me)_3$  (Worth *et al.*, 1992), a similar trend of 1.212(8), 1.367(8) and 1.183(9) Å is observed in the carbon-carbon bond lengths of the dialkyne group, but is not significant. Further structural studies are in progress on related transition metal-acetylide complexes.

## Experimental

A mixture of  $CuI$  (5 mg),  $(Cp)Ni(PPh_3)Br$  (500 mg) and a fourfold excess of 1,3-butadiyne (as a 2 mol  $dm^{-3}$  THF solution) was added to  $Et_3N$  (50 ml) and stirred overnight

under N<sub>2</sub>. The solvent was removed under reduced pressure and the residue dissolved in Et<sub>2</sub>O and filtered. The preparation of a basic alumina column using a 1:1 benzene-hexane mixture and subsequent chromatography of the filtrate with Et<sub>2</sub>O eluted a green band, (Cp)Ni(PPh<sub>3</sub>)C≡C—C≡C—H (yield 76%). Crystals suitable for X-ray diffraction were grown from Et<sub>2</sub>O-hexane. <sup>1</sup>H NMR (δ, 270 MHz, CDCl<sub>3</sub>): 7.80–7.62 (m, 6H, Ph), 7.50–7.30 (m, 9H, Ph), 5.18 (s, 5H, Cp), 1.30 (s, 1H, C≡CH). <sup>13</sup>C NMR (δ, 67.8 MHz, CDCl<sub>3</sub>): 133.8 (d, <sup>2</sup>J<sub>CP</sub> = 12 Hz, *o*-Ph), 133.5 (d, <sup>1</sup>J<sub>CP</sub> = 49 Hz, *i*-Ph), 130.4 (s, *p*-Ph), 128.3 (d, <sup>3</sup>J<sub>CP</sub> = 12 Hz, *m*-Ph), 99.5 (s, NiC<sub>2</sub>—C), 93.1 (s, Cp), 85.9 (d, <sup>2</sup>J<sub>CP</sub> = 44 Hz, Ni—C), 71.5 (d, <sup>3</sup>J<sub>CP</sub> = 3 Hz, NiC≡C), 66.1 (s, ≡C—H). IR (ν<sub>C≡C</sub>, cm<sup>-1</sup>): 2138 (CH<sub>2</sub>Cl<sub>2</sub>); 2135 (KBr). Microanalysis: calculated for C<sub>27</sub>H<sub>21</sub>NiP: C 74.53, H 4.86%; found: C 74.12, H 4.79%.

### Crystal data

[Ni(C<sub>4</sub>H)(C<sub>5</sub>H<sub>5</sub>)(C<sub>18</sub>H<sub>15</sub>P)]

*M<sub>r</sub>* = 435.12

Triclinic

P1

*a* = 9.9029 (7) Å

*b* = 10.1259 (6) Å

*c* = 11.6523 (11) Å

α = 79.919 (6)°

β = 76.972 (6)°

γ = 75.994 (5)°

*V* = 1095.52 (14) Å<sup>3</sup>

*Z* = 2

*D<sub>x</sub>* = 1.319 Mg m<sup>-3</sup>

*D<sub>m</sub>* not measured

### Data collection

Enraf-Nonius CAD-4 diffractometer

ω–2θ scans

Absorption correction:

empirical via 4 ψ scans at 4° steps (North *et al.*, 1968)

*T<sub>min</sub>* = 0.773, *T<sub>max</sub>* = 0.873

5005 measured reflections

5005 independent reflections

### Refinement

Refinement on *F*<sup>2</sup>

*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.024

*wR* (*F*<sup>2</sup>) = 0.066

*S* = 1.047

5005 reflections

342 parameters

H atoms treated by a

mixture of independent and constrained refinement

Mo Kα radiation

λ = 0.7107 Å

Cell parameters from 25 reflections

θ = 9.65–21.16°

μ = 0.968 mm<sup>-1</sup>

*T* = 294 (1) K

Plate

0.39 × 0.32 × 0.14 mm

Green

4085 reflections with

*I* > 2σ(*I*)

θ<sub>max</sub> = 27.4°

*h* = –12 → 12

*k* = 0 → 13

*l* = –14 → 15

3 standard reflections

frequency: 120 min

intensity variation: 1%

*w* = 1/[σ<sup>2</sup>(*F<sub>o</sub>*<sup>2</sup>) + (0.037*P*)<sup>2</sup>

+ 0.1432*P*]

where *P* = (*F<sub>o</sub>*<sup>2</sup> + 2*F<sub>c</sub>*<sup>2</sup>)/3

(Δ/σ)<sub>max</sub> = 0.001

Δρ<sub>max</sub> = 0.248 e Å<sup>-3</sup>

Δρ<sub>min</sub> = –0.220 e Å<sup>-3</sup>

Extinction correction: none

Scattering factors from

*International Tables for Crystallography* (Vol. C)

Ni1—P1—C21	112.47 (5)	P1—Ni1—C1	93.47 (5)
Ni1—P1—C31A	114.31 (16)	Ni1—C1—C2	177.61 (14)
Ni1—P1—C31B	117.5 (2)	C1—C2—C3	177.94 (19)
Ni1—P1—C41	112.43 (5)	C2—C3—C4	179.5 (2)

Table 2. *Hydrogen-bonding geometry* (Å, °)

<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>
C32B—H32B...C1	0.93	2.58	3.198 (7)	124
C35B—H35B...C3'	0.93	2.69	3.586 (7)	162
C43—H43...Cg2 <sup>†</sup>	0.93	2.81	3.685 (2)	156
C4—H4...Cg45 <sup>‡</sup>	0.96	3.04	3.94	158

Symmetry codes: (i) –*x*, 1 – *y*, 2 – *z*; (ii) –*x*, –*y*, 2 – *z*; (iii) *x*, 1 + *y*, *z*.

<sup>†</sup> Cg2 is the centroid of the C21–C26 ring and Cg45 is the midpoint of the C44–C45 bond.

H atoms were allowed for riding atoms with C—H 0.93 Å and the coordinates of the diacetylide C≡C—H H atom were refined to 0.96 Å. It was evident during the penultimate stage of refinement {when *R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] was 0.035} that there were minor components of disorder associated with the cyclopentadienyl ring and one of the phenyl rings. Coordinates for the minor components of both rings were generated and for the final refinement cycles, a combination of *DFIX* with *DELU/ISOR* controls was used in the *SHELXL97* (Sheldrick, 1997b) calculations. The relevant part of the *SHELXL97* instruction file (with details of the constraints and restraints used) is included in the CIF for this structure. The atoms of the major and minor conformations of the cyclopentadienyl ring were refined with anisotropic displacement parameters to final site occupancies of 0.59 (3) and 0.41 (3), respectively. The atoms of the major and minor conformations of the phenyl ring were constrained as rigid hexagons (C—C 1.390 Å and C—C—C 120°) with anisotropic displacement parameters. The final refined site occupancies were 0.612 (17) and 0.388 (17), respectively, with the rings oriented at 23.8 (8)° to one another. The main intermolecular interactions involve the minor phenyl ring conformation (C31B–C36B). A view showing both major and minor cyclopentadienyl and phenyl conformations has been deposited.

Data collection: *CAD-4-PC Software* (Enraf–Nonius, 1992). Cell refinement: *SET4* and *CELDIM* in *CAD-4-PC Software*. Data reduction: *DATRD2* in *NRCVAX96* (Gabe *et al.*, 1989). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997a). Program(s) used to refine structure: *NRCVAX96* and *SHELXL97*. Molecular graphics: *NRCVAX96*, *ORTEPII* (Johnson, 1976), *PLATON* (Spek, 1997a) and *PLUTON* (Spek, 1997b). Software used to prepare material for publication: *NRCVAX96*, *SHELXL97* and *WordPerfect* macro *PRPCIF97* (Ferguson, 1997).

JFG thanks the Research and Postgraduate Committee of Dublin City University, the Royal Irish Academy and Forbairt for generous funding of a research visit to the University of Guelph (June–August, 1997), and especially Professor George Ferguson for use of his diffractometer and computer system.

Table 1. *Selected geometric parameters* (Å, °)

Ni1—P1	2.1410 (4)	P1—C41	1.8226 (14)
Ni1—C1	1.8383 (15)	C1—C2	1.212 (2)
P1—C21	1.8256 (14)	C2—C3	1.370 (2)
P1—C31A	1.8285 (15)	C3—C4	1.187 (3)
P1—C31B	1.8310 (17)	C4—H4	0.96 (3)

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AB1525). Services for accessing these data are described at the back of the journal. A view of the cyclopentadienyl and phenyl ring disorder has also been deposited.

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*Acta Cryst.* (1998). **C54**, 345–347

## Dichloro[ferrocene-1,1'-diylbis(diphenylphosphine-P)]mercury(II) Methanol Solvate

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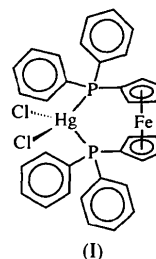
(Received 11 August 1997; accepted 29 October 1997)

### Abstract

The title complex,  $[\text{HgCl}_2\{\text{Fe}(\text{C}_{17}\text{H}_{14}\text{P})_2\}]\cdot\text{CH}_3\text{OH}$ , is monomeric with the Hg atom in a tetrahedral environment provided by the two  $\text{Cl}^-$  ions and two P atoms of the bis(diphenylphosphino)ferrocene ligand.

### Comment

The asymmetric unit contains one  $[\text{HgCl}_2(\text{dppf})]$ , (I), molecule, where dppf is 1,1'-bis(diphenylphosphino)ferrocene, and a disordered methanol solvate molecule. The Hg atom assumes essentially tetrahedral coordination, bonded to the two chelating P atoms of a single 1,1'-bis(diphenylphosphino)ferrocene ligand and to two terminal chloride ions (Fig. 1). The two cyclopentadienyl groups are inclined to each other at an angle of  $2.8(4)^\circ$  and are tilted away from the  $\text{Hg}^{\text{II}}$  ion. A survey of the other reported complexes of dppf in the Cambridge Structural Database (Allen *et al.*, 1993) shows that the cyclopentadiene rings can adopt eclipsed, staggered and intermediate conformations.



The geometry appears to be controlled, at least in part, by the size and geometry of the metal ion chelated by the 1,1'-bis(diphenylphosphino)ferrocene ligand. The

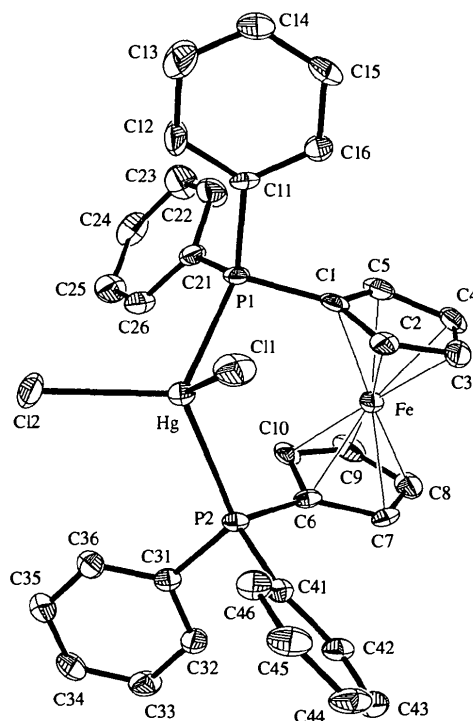


Fig. 1. Perspective view of the title molecule showing 50% probability displacement ellipsoids. H atoms and the disordered methanol have been omitted for clarity.