H atoms treated by a mixture of independent and constrained refinement

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

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 φ angles for the crystal; each 10 s exposure covered 0.3° in ω. The crystal-to-detector distance was 5.0 cm. Coverage of the unique set was over 97% complete to at least 26° in θ. 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 $1.2U_{eq}$ of the carrier atom.

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

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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(1,3-Butadiynyl-C^1)(η^5-cyclopentadienyl)(triphenylphosphine-P)nickel(II)

JOHN F. GALLAGHER,[a] PETER BUTLER[b] AND ANTHONY R. MANNING[b]

[a]*School of Chemical Sciences, Dublin City University, Dublin 9, Ireland, and* [b]*Department of Chemistry, University College Dublin, Dublin 4, Ireland. E-mail: gallagherjfg@dcu.ie*

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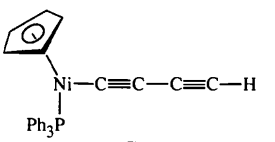
Abstract

The title compound, $[Ni(Cp)(PPh_3)(C{\equiv}C{-}C{\equiv}C{-}H)]$ or $[Ni(C_4H)(C_5H_5)(C_{18}H_{15}P)]$, 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 σ-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 π 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 σ-bonded 1,3-butadiynyl ligand.



(I)

Molecule (I) has a half-sandwich structure and contains the σ-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≡C bond length of 1.187 (3) Å is significantly shorter than the *M*—C≡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 π system in the *M*—C≡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}≡C_{sp}) and 1.38 (1) Å (C_{sp}—C_{sp}) (Orpen *et al.*, 1994). The angles in the Ni—C≡C—C≡CH group deviate slightly from linearity with Ni—C≡C 177.61 (14), and C≡C—C 177.94 (19) and 179.5 (2)°.

The intramolecular C32*B*—H32*B*···C1 and intermolecular C35*B*—H35*B*···C3^{i} interactions involve the 1,3-butadiynyl group [symmetry code: (i) $-x$, $1-y$, $2-z$; details in Table 2]. A C—H···π(arene) interaction is also present, C43—H43···*Cg*2^{ii}, where *Cg*2^{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···*Cg*45^{iii}, where *Cg*45^{iii} is the midpoint of C44—C45 and symmetry code (iii) is $(x, 1+y, z)$. Examination of the structure with *PLATON* (Spek, 1997*a*) showed that there are no solvent-accessible voids in the crystal lattice.

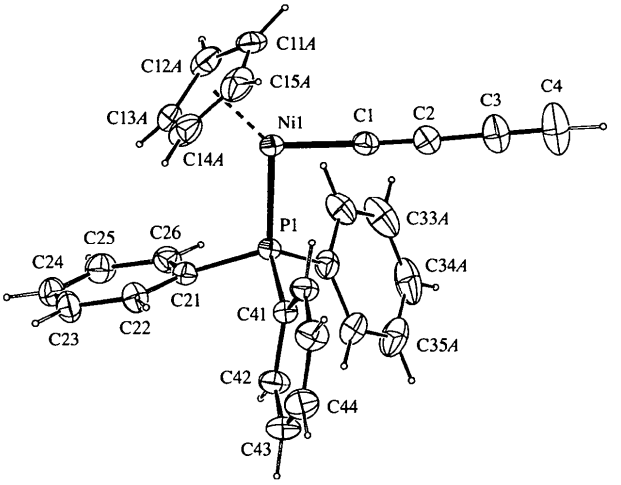


Fig. 1. A view of (I) with the atomic numbering scheme. Atom labels with the suffix '*A*' are for the major conformations of the cyclopentadienyl and phenyl rings. Displacement ellipsoids are drawn at the 30% probability level.

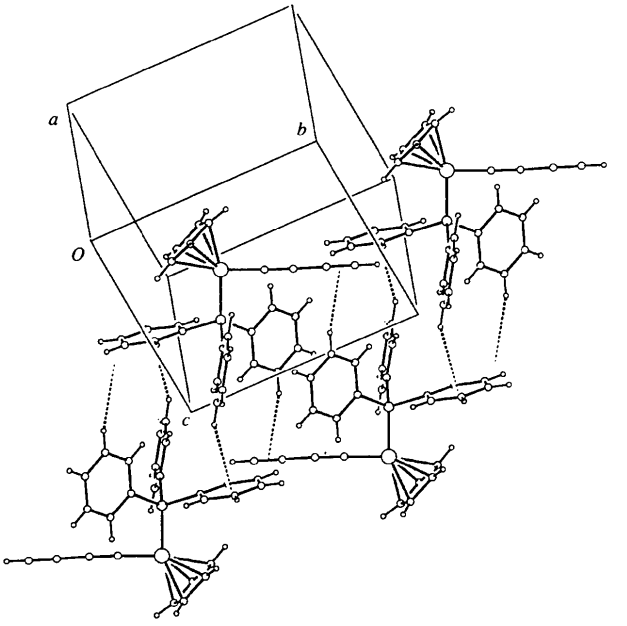


Fig. 2. A view of the intermolecular interactions in the crystal structure.

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 (*Cg*1) of the major conformation is 1.7343 (2) Å from Ni1; *Cg*1—Ni1—P1 and *Cg*1—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, C_4 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 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≡C—C≡C—Si chain, indicating π 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_2. The solvent was removed under reduced pressure and the residue dissolved in Et_2O and filtered. The preparation of a basic alumina column using a 1:1 benzene–hexane mixture and subsequent chromatography of the filtrate with Et_2O eluted a green band, (Cp)Ni(PPh_3)C≡C—C≡C—H (yield 76%). Crystals suitable for X-ray diffraction were grown from Et_2O–hexane. ^{1}H NMR (δ, 270 MHz, $CDCl_3$): 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). ^{13}C NMR (δ, 67.8 MHz, $CDCl_3$): 133.8 (*d*, $^2J_{CP}$ = 12 Hz, *o*-Ph), 133.5 (*d*, $^1J_{CP}$ = 49 Hz, *i*-Ph), 130.4 (*s*, *p*-Ph), 128.3 (*d*, $^3J_{CP}$ = 12 Hz, *m*-Ph), 99.5 (*s*, NiC$_2$—*C*), 93.1 (*s*, Cp), 85.9 (*d*, $^2J_{CP}$ = 44 Hz, Ni—C), 71.5 (*d*, $^3J_{CP}$ = 3 Hz, NiC≡*C*), 66.1 (*s*, ≡C—H). IR (ν $_{C\equiv C}$, cm^{-1}): 2138 (CH_2Cl_2); 2135 (KBr). Microanalysis: calculated for $C_{27}H_{21}NiP$: C 74.53, H 4.86%; found: C 74.12, H 4.79%.

Crystal data

[Ni(C4H)(C5H5)(C18H15P)]
M_r = 435.12
Triclinic
$P\overline{1}$
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^3
Z = 2
D_x = 1.319 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.7107 Å
Cell parameters from 25 reflections
θ = 9.65–21.16°
μ = 0.968 mm^{-1}
T = 294 (1) K
Plate
0.39 × 0.32 × 0.14 mm
Green

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_{min} = 0.773, T_{max} = 0.873
5005 measured reflections
5005 independent reflections

4085 reflections with $I > 2\sigma(I)$
θ_{max} = 27.4°
h = −12 → 12
k = 0 → 13
l = −14 → 15
3 standard reflections
frequency: 120 min
intensity variation: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.024
$wR(F^2)$ = 0.066
S = 1.047
5005 reflections
342 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.037P)^2 + 0.1432P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.248 e Å^{-3}
$\Delta\rho_{min}$ = −0.220 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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—C31*A*	1.8285 (15)	C3—C4	1.187 (3)
P1—C31*B*	1.8310 (17)	C4—H4	0.96 (3)
Ni1—P1—C21	112.47 (5)	P1—Ni1—C1	93.47 (5)
Ni1—P1—C31*A*	114.31 (16)	Ni1—C1—C2	177.61 (14)
Ni1—P1—C31*B*	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, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C32*B*—H32*B*···C1	0.93	2.58	3.198 (7)	124
C35*B*—H35*B*···C3^i	0.93	2.69	3.586 (7)	162
C43—H43···*Cg*2^{ii}†	0.93	2.81	3.685 (2)	156
C4—H4···*Cg*45^{iii}†	0.96	3.04	3.94	158

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

† *Cg*2 is the centroid of the C21–C26 ring and *Cg*45 is the midpoint of the C44—C45 bond.

H atoms were allowed for as 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 $R[F^2 > 2\sigma(F^2)]$ 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 *SHELXL*97 (Sheldrick, 1997*b*) calculations. The relevant part of the *SHELXL*97 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 (C31*B*–C36*B*). 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: *SET*4 and *CELDIM* in *CAD-4-PC Software*. Data reduction: *DATRD*2 in *NRCVAX*96 (Gabe *et al.*, 1989). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*a*). Program(s) used to refine structure: *NRCVAX*96 and *SHELXL*97. Molecular graphics: *NRCVAX*96, *ORTEP*II (Johnson, 1976), *PLATON* (Spek, 1997*a*) and *PLUTON* (Spek, 1997*b*). Software used to prepare material for publication: *NRCVAX*96, *SHELXL*97 and *WordPerfect* macro *PRPCIF*97 (Ferguson, 1997).

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

JOHN MCGINLEY,[a] VICKIE MCKEE[b] AND CHRISTINE J. MCKENZIE[a]

[a]*Department of Chemistry, Odense University, DK-5230 Odense, Denmark, and* [b]*School of Chemistry, The Queen's University, Belfast BT9 5AG, Northern Ireland. E-mail: v.mckee@qub.ac.uk*

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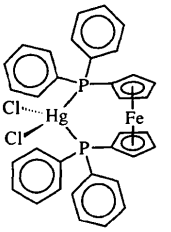
Abstract

The title complex, $[HgCl_2\{Fe(C_{17}H_{14}P)_2\}].CH_3OH$, is monomeric with the Hg atom in a tetrahedral environment provided by the two Cl^- ions and two P atoms of the bis(diphenylphosphino)ferrocene ligand.

Comment

The asymmetric unit contains one $[HgCl_2(dppf)]$, (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)° and are tilted away from the Hg^{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.



(I)

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

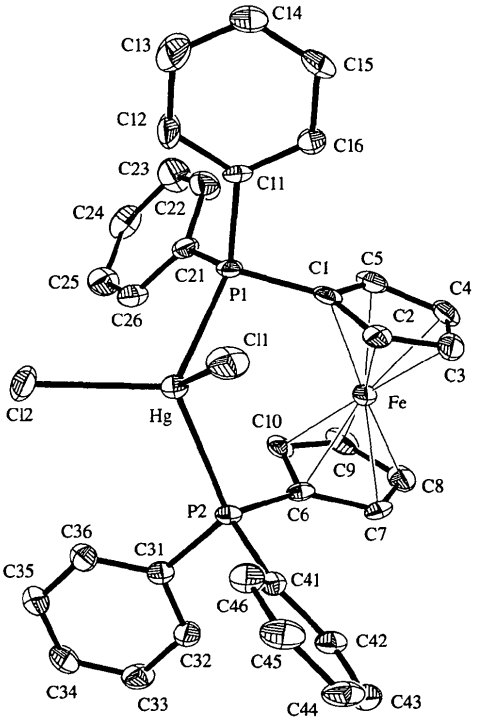


Fig. 1. Perspective view of the title molecule showing 50% probability displacement ellipsoids. H atoms and the disordered methanol have been omitted for clarity.