Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

(η^5-Cyclopentadienyl){[3-(2,2-dicyanoethenyl)bicyclo[2.2.1]hepta-2,5-dien-2-yl]ethynyl}(triphenylphosphine)nickel(II)

John F. Gallagher,[a]* Peter Butler[b] and A. R. Manning[b]

[a]School of Chemical Sciences, Dublin City University, Dublin 9, Ireland, and [b]Department of Chemistry, University College Dublin, Belfield, Dublin 4, Ireland
Correspondence e-mail: john.gallagher@dcu.ie

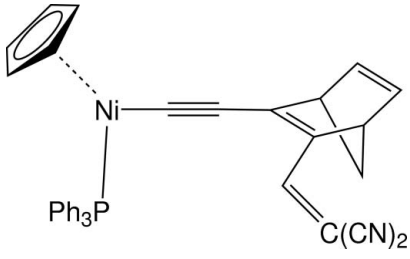
Received 18 January 2008; accepted 22 January 2008

Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.005 Å; disorder in main residue; R factor = 0.047; wR factor = 0.108; data-to-parameter ratio = 16.7.

The title compound, $[Ni(C_5H_5)(C_{13}H_7N_2)(C_{18}H_{15}P)]$ or (η^5-C_5H_5)(PPh_3)Ni—C≡C—C_7H_6—C(H)=$C(CN)_2$, contains an unusual disubstituted norbornadienyl (NBD) ligand containing ethynyl (–C≡C–) and dicyanovinyl [–C(H)=$C(CN)_2$] groups. Disorder is present in the NBD group with site occupancies of 0.636 (10) and 0.364 (10) for two distinct orientations. There are no strong hydrogen bonds and the primary interactions are weak C—H···π(arene) interactions.

Related literature

For related literature, see: Butler *et al.* (1998, 2005, 2007); Gallagher *et al.* (1998, 2002); McArdle (1995); Whittal *et al.* (1998*a*,*b*).



Experimental

Crystal data

$[Ni(C_5H_5)(C_{13}H_7N_2)(C_{18}H_{15}P)]$
M_r = 577.28
Triclinic, $P\overline{1}$
a = 10.7972 (16) Å
b = 11.8155 (14) Å
c = 12.1248 (14) Å
α = 73.169 (5)°
β = 78.153 (9)°
γ = 78.586 (9)°
V = 1433.1 (3) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.76 mm^{-1}
T = 296 (1) K
0.50 × 0.40 × 0.30 mm

Data collection

Bruker P4 diffractometer
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.716, T_{max} = 0.883
(expected range = 0.645–0.796)
7832 measured reflections
6787 independent reflections
4533 reflections with $I > 2\sigma(I)$
R_{int} = 0.029
3 standard reflections
every 197 reflections
intensity decay: 5%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.108
S = 1.01
6787 reflections
407 parameters
94 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.33 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C33—H33···$Cg1^{i}$	0.93	2.98	3.648 (4)	130

Symmetry code: (i) $-x, -y+2, -z$. $Cg1$ is the centroid of the cyclopentadienyl ring.

Data collection: *XSCANS* (Bruker, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PREP8* (Ferguson, 1998).

JFG thanks Dublin City University for the purchase of a Bruker P4 diffractometer and computer system in 1998.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH2592).

References

Bruker, (1996). *XSCANS*, Version 2.2. Bruker AXS Inc., Madison, Wisconsin, USA.
Butler, P., Gallagher, J. F., Lough, A. J. & Manning, A. R. (2007). *Acta Cryst.* E**63**, m1415.
Butler, P., Gallagher, J. F. & Manning, A. R. (1998). *Inorg. Chem. Commun.* **1**, 343–345.
Butler, P., Gallagher, J. F., Manning, A. R., Mueller-Bunz, H., McAdam, C. J., Simpson, J. & Robinson, B. H. (2005). *J. Organomet. Chem.* **690**, 4545–4556.
Ferguson, G. (1998). *PREP8*. University of Guelph, Canada.
Gallagher, J. F., Butler, P., Hudson, R. D. A. & Manning, A. R. (2002). *Dalton Trans.* pp. 75–82.
Gallagher, J. F., Butler, P. & Manning, A. R. (1998). *Acta Cryst.* C**54**, 342–345.
McArdle, P. (1995). *J. Appl. Cryst.* **28**, 65.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
Whittal, I. R., Humphrey, M. G. & Hockless, D. C. R. (1998*a*). *Aust. J. Chem.* **51**, 219–227.
Whittal, I. R., McDonagh, A. M., Humphrey, M. G. & Samoc, M. (1998*b*). *Adv. Organomet. Chem.* **42**, 291–362.

supplementary materials

Acta Cryst. (2008). E**64**, m411 [**doi:10.1107/S1600536808002328**]

(η^5-Cyclopentadienyl){[3-(2,2-dicyanoethenyl)bicyclo[2.2.1]hepta-2,5-dien-2-yl]ethynyl}(triphenylphosphine)nickel(II)

J. F. Gallagher, P. Butler and A. R. Manning

Comment

The acetylide linkage in Ni(η^5-C_5H_5)(PPh_3)-C≡C—*X* complexes allows facile electronic communication between the electron rich Ni(η^5-C_5H_5)(PPh_3) moiety and the *X* group (*X* = alkyl, arene) thus affecting the characteristic chemistry of both *X* and the acetylide linkage (Gallagher *et al.*, 2002). However, if *X* is an electron withdrawing group the molecule is a donor-π-acceptor (D-π-A) system which may have non-linear optical (NLO) properties (Whittal *et al.*, 1998*a*,b) although the phenyl derivative (*X* = C_6H_5) does not appear to be particularly effective.

We have demonstrated that polycylic hydrocarbons containing 1–5 aromatic rings can act as an electron-donor endgroup in D-π-A systems in the presence of suitable acceptors and have examined their behaviour when attached to the Ni(η^5-C_5H_5)(PPh_3) donor moiety (Butler *et al.*, 2005, 2007). The spectroscopic and electrochemical evidence suggests limited communication between either end of these Ni(η^5-C_5H_5)(PPh_3)-C≡C—*X* systems at least in the ground state and is not sufficient to influence significant changes in the geometric data from diffraction measurements. Herein, we present an unusual norbornadiene derivative (I) (η^5-C_5H_5)(PPh_3)Ni—C≡C-NBD-C(H)=C(CN)$_2$ (where NBD is a 2,3-substituted C_7H_6 group).

Molecule (I) has a half sandwich structure at the Ni^{II} centre and contains the σ-bonded ethynyl-2-norbornadienyl(methylidene)propanedinitrile ligand, a η^5-C_5H_5 ring and triphenylphosphine bonded to the Ni^{II} atom. A view of the molecule with atomic numbering scheme is depicted (Fig. 1). The principal Ni-ligand dimensions include Ni1—P1 2.1417 (8) Å, Ni1—C1 1.839 (3) Å, Ni···*Cg* 1.7444 (16) Å (*Cg* is the cyclopentadienyl ring centroid), P1—Ni1—C1 87.86 (8)° and similar to geometric data in related derivatives (Gallagher *et al.*, 1998, 2002; Butler *et al.*, 1998, 2005). The acetylide –C≡C– and $_{sp}$C—C_{NBD} bond lengths are 1.214 (4) Å and 1.403 (4) Å and similar to the geometric data reported for the dicyanovinyl derivative (II) (η^5-C_5H_5)(PPh_3)Ni—C≡C—C(H)=C(C≡N)$_2$ (Gallagher *et al.*, 2002). The two C=C bond lengths of 1.371 (4) Å (C3=C4) and 1.358 (4) Å (C5=C6) can be explained by an increase of delocalization along the conjugated metallo-ligand chain and the increase in bond lengths often observed in strained ring systems *i.e.* the C3=C4 in the NBD ring system.

The Ni—C≡C—C chain bond angles deviate slightly from linearity with Ni—C≡C 173.6 (2)° and C≡C—C 171.8 (3)°: this is greater than the two corresponding 176.6 (2)°/177.8 (3)° angles reported for (II) but similar to related systems (Butler *et al.*, 1998) and this can be attributed mainly to crystal packing forces.

The η^5-C_5H_5 ring is orthogonal to the P1/Ni1/C1 plane, 88.84 (10)°. Of interest is the relative co-planarity of atoms in the 11-atom chain Ni1—C1≡C2—C3=C4—C5=C6(C≡N)$_2$, where the Ni1 and C8 atoms deviate by a maximum of 0.334 (2) Å and 0.269 (2) Å from the 11-atom plane (the next greatest deviation is C2 by 0.159 (3) Å). This highlights the relative co-planarity of atoms along this chain increasing the potential for conjugation effects.

The closest intramolecular contact to Ni1 involves H22 with H22···Ni1 2.94 Å and C22—H22···Ni1 119° (C22 is the closest PPh_3 *ortho*-C to Ni1 at 3.476 (3) Å). The three Ni1—P—C angles vary as 111.28 (9)°, 113.62 (9)° and 118.31 (8)°. There is a small asymmetry in the PPh_3 ligand with four P—C—C angles in the range 119.1 (2)° to 122.5 (2)° at C21 and C31. However, at C41 these P—C—C angles are 117.53 (2)° and 124.5 (2)°. The three P—C_{ipso}···C_{para} angles are 179.50 (16)°, 177.56 (15)°, 175.90 (16)° and reflecting the greater phenyl asymmetry at C41.

In the absence of strong hydrogen bond donors or acceptors, C—H···π(arene) interactions involving the PPh_3 arene rings arise (details in Table) (Fig. 2). The C33···{C11,···,C15} distances are in the range 3.618 (4) Å to 4.023 (4) Å and C—H···C angles (in *Cg*1) vary from 108° to 147°.

Experimental

Compound (I) was prepared according to literature methods (Butler *et al.*, 1998, 2005, 2007), (Gallagher *et al.*, 2002) and involves hydrolysis of an acetal precursor to an aldehyde and subsequent reaction with malonitrile $H_2C(C{\equiv}N)_2$ to give the dicyanovinyl derivative (title compound). Yield 95%. Crystals suitable for X-ray diffraction were grown from Et_2O/hexane. ^{1}H NMR (δ, 270 MHz, $CDCl_3$): 7.68 - 7.37 (m, 15H, PPh_3), 6.68 (s, 1H, –CH=), 6.63 and 6.29 (d, 2H, –C(H)=C(H)-), 5.26 (s, 5H, Cp), 4.31, 3.04 (s, 2H, bridgehead H), 1.78 (dd, $^1J_{HH}$ = 8 Hz, 2H, μ-CH_2). ^{13}C NMR (δ, 270 MHz, $CDCl_3$): 165.81 (s, Ni—C≡C), 148.59 and 147.43 (s, C_3 and C_4), 142.61 and 139.89 (s, $C_{52\ A/B}$ and $C_{53\ A/B}$), 132.95 (d, $^1J_{CP}$ = 50 Hz, Ni—C), 133.7 - 128.4 (m, PPh_3), 119.33 (s, $C(C{\equiv}N)_2$, 116.59 and 115.37 (s, C≡N), 93.27 (s, Cp), 67.7 (s, μ-CH_2), 57.85 and 47.22 (s, bridgehead C). IR ($\nu_{C\equiv C}$, cm^{-1}): 2150 (CH_2Cl_2); 2152 (KBr) and ($\nu_{C\equiv N}$, cm^{-1}): 2216 (CH_2Cl_2); 2216 (KBr). Microanalysis: calculated for $C_{36}H_{21}N_2PNi$: C, 74.9, H, 4.7, N 4.8; found: C, 74.6, H, 5.2, N 4.8.

Refinement

In the penultimate stages of refinement it was observed that there was disorder within the norbornadienyl (NBD) $–C_7H_6–$ moiety: this was resolved and successfully modelled into two partial occupancy A/B residues [C51A/B,···,C55A/B] involving the $–C_5H_6–$ bridgehead group as two A/B components with site occupancies of 0.636 (10):0.364 (10). The C3=C4 atoms were used as 'anchor' atoms for loose *DFIX* restraints: DELU/ISOR restraints were also used for the anisotropic displacement parameters (McArdle, 1995; Sheldrick, 2008). The orientational disorder is explained by swapping the NBD group $–CH_2$ and –CH=CH– atoms.

All H atoms attached to aromatic C atoms were treated as riding atoms using the *SHELXL97* (Sheldrick, 2008) defaults at 296 (1) K, with C—H distances of 0.93 Å (for aromatic H) and in the range 0.93 to 0.98 Å (for aliphatic C—H) and with $U_{iso}(H) = 1.2U_{eq}(C)$ for all H atoms.

Figures

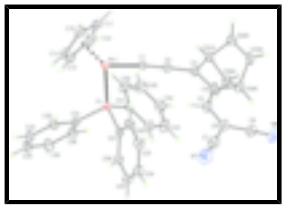


Fig. 1. A view of the major conformation of (I) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 20% probability level.

Fig. 2. A view of the NBD disorder in (I): the (cp)(PPh_3)Ni—C atoms are omitted for clarity. Displacement ellipsoids are drawn at the 20% probability level.

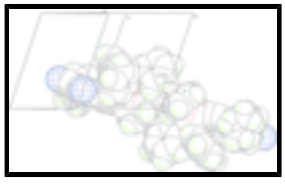


Fig. 3. A view of the principal C—H···π(arene) interaction and unit cell in (I) with atoms depicted as their van der Waals spheres. The atom labels C33—H33 and # (cp ring) signify the interaction listed in Table 1.

(η^5-Cyclopentadienyl){[3-(2,2-dicyanoethenyl)bicyclo[2.2.1]hepta-2,5- dien-2-yl]ethynyl}(triphenylphosphine)nickel(II)

Crystal data

$[Ni(C_5H_5)(C_{13}H_7N_2)(C_{18}H_{15}P)]$	$Z = 2$
$M_r = 577.28$	$F_{000} = 600$
Triclinic, $P\overline{1}$	$D_x = 1.338$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 10.7972$ (16) Å	Cell parameters from 40 reflections
$b = 11.8155$ (14) Å	$\theta = 3.6$–14.9^o
$c = 12.1248$ (14) Å	$\mu = 0.76$ mm^{-1}
$\alpha = 73.169$ (5)^o	$T = 296$ (1) K
$\beta = 78.153$ (9)^o	Block, green
$\gamma = 78.586$ (9)^o	0.50 × 0.40 × 0.30 mm
$V = 1433.1$ (3) Å^3	

Data collection

Bruker P4 diffractometer	$R_{int} = 0.029$
Radiation source: X-ray tube	$\theta_{max} = 28.0^o$
Monochromator: graphite	$\theta_{min} = 2.0^o$
$T = 296(1)$ K	$h = -1 \rightarrow 14$
ω scans	$k = -14 \rightarrow 15$
Absorption correction: ψ scan (North *et al.*, 1968)	$l = -15 \rightarrow 16$

T_{min} = 0.716, T_{max} = 0.883
7832 measured reflections
6787 independent reflections
4533 reflections with $I > 2\sigma(I)$

3 standard reflections
every 197 reflections
intensity decay: 5%

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.108$
$S = 1.01$
6787 reflections
407 parameters
94 restraints
Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0422P)^2 + 0.2761P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.33$ e Å^{-3}
$\Delta\rho_{min} = -0.25$ e Å^{-3}
Extinction correction: none

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Ni1	0.27893 (3)	0.93823 (3)	0.16592 (3)	0.04182 (11)	
P1	0.25181 (6)	0.75680 (6)	0.25072 (6)	0.03890 (16)	
C7	0.3069 (4)	0.8014 (3)	0.7760 (3)	0.0742 (10)	
N7	0.2068 (4)	0.8081 (4)	0.8281 (3)	0.1087 (13)	
C8	0.5323 (3)	0.7390 (3)	0.7788 (3)	0.0656 (9)	
N8	0.6099 (3)	0.6948 (3)	0.8358 (3)	0.0900 (10)	
C11	0.3133 (4)	1.0983 (3)	0.0448 (3)	0.0775 (11)	
C12	0.1960 (4)	1.1199 (3)	0.1177 (3)	0.0754 (10)	
C13	0.1155 (3)	1.0515 (3)	0.1036 (3)	0.0673 (9)	
C14	0.1824 (3)	0.9861 (3)	0.0235 (3)	0.0630 (9)	
C15	0.3020 (3)	1.0210 (3)	−0.0173 (3)	0.0713 (10)	
C21	0.1743 (2)	0.7343 (2)	0.4027 (2)	0.0411 (6)	
C22	0.1526 (3)	0.8261 (3)	0.4567 (2)	0.0525 (7)	
C23	0.0924 (3)	0.8097 (3)	0.5709 (3)	0.0641 (8)	
C24	0.0546 (3)	0.7015 (3)	0.6334 (3)	0.0654 (9)	
C25	0.0729 (3)	0.6103 (3)	0.5809 (3)	0.0628 (8)	
C26	0.1314 (3)	0.6267 (3)	0.4661 (2)	0.0538 (7)	
C31	0.1525 (2)	0.6869 (2)	0.1912 (2)	0.0404 (6)	
C32	0.0282 (3)	0.7414 (3)	0.1783 (2)	0.0510 (7)	
C33	−0.0502 (3)	0.6905 (3)	0.1360 (3)	0.0564 (8)	
C34	−0.0066 (3)	0.5840 (3)	0.1077 (3)	0.0621 (8)	
C35	0.1157 (3)	0.5280 (3)	0.1206 (3)	0.0638 (8)	
C36	0.1958 (3)	0.5797 (3)	0.1611 (2)	0.0537 (7)	
C41	0.4038 (2)	0.6565 (2)	0.2487 (2)	0.0416 (6)	
C42	0.4416 (3)	0.5703 (3)	0.3439 (3)	0.0588 (8)	

C43	0.5589 (3)	0.4972 (3)	0.3331 (3)	0.0739 (10)	
C44	0.6380 (3)	0.5098 (3)	0.2283 (3)	0.0677 (9)	
C45	0.6005 (3)	0.5934 (3)	0.1337 (3)	0.0832 (12)	
C46	0.4849 (3)	0.6665 (3)	0.1434 (3)	0.0703 (10)	
C1	0.3981 (2)	0.9205 (2)	0.2607 (2)	0.0437 (6)	
C2	0.4765 (3)	0.8968 (2)	0.3259 (2)	0.0474 (6)	
C3	0.5745 (2)	0.8557 (3)	0.3944 (2)	0.0521 (7)	
C4	0.5668 (3)	0.8212 (3)	0.5134 (3)	0.0717 (10)	
C5	0.4523 (3)	0.8275 (3)	0.5920 (3)	0.0650 (9)	
C6	0.4332 (3)	0.7919 (3)	0.7104 (3)	0.0607 (8)	
C51A	0.7154 (7)	0.8267 (12)	0.3422 (11)	0.055 (3)	0.636 (10)
C52A	0.7821 (10)	0.9071 (9)	0.3796 (7)	0.067 (2)	0.636 (10)
C53A	0.7758 (7)	0.8686 (6)	0.4953 (7)	0.067 (2)	0.636 (10)
C55A	0.7544 (17)	0.7069 (12)	0.4307 (8)	0.055 (2)	0.636 (10)
C54A	0.7055 (5)	0.7614 (7)	0.5348 (6)	0.0548 (19)	0.636 (10)
C51B	0.7190 (9)	0.841 (2)	0.3499 (18)	0.055 (6)	0.364 (10)
C52B	0.754 (3)	0.709 (2)	0.4038 (14)	0.070 (6)	0.364 (10)
C53B	0.7446 (10)	0.6940 (10)	0.5189 (12)	0.065 (3)	0.364 (10)
C55B	0.7770 (16)	0.8884 (15)	0.4301 (11)	0.056 (4)	0.364 (10)
C54B	0.7028 (9)	0.8154 (11)	0.5398 (10)	0.064 (4)	0.364 (10)
H11	0.3866	1.1310	0.0395	0.093*	
H12	0.1772	1.1712	0.1663	0.090*	
H13	0.0312	1.0485	0.1404	0.081*	
H14	0.1513	0.9291	0.0017	0.076*	
H15	0.3630	0.9968	−0.0755	0.086*	
H22	0.1787	0.8994	0.4158	0.063*	
H23	0.0772	0.8724	0.6060	0.077*	
H24	0.0166	0.6905	0.7112	0.078*	
H25	0.0462	0.5375	0.6224	0.075*	
H26	0.1424	0.5648	0.4304	0.065*	
H32	−0.0026	0.8131	0.1986	0.061*	
H33	−0.1328	0.7286	0.1267	0.068*	
H34	−0.0599	0.5495	0.0798	0.074*	
H35	0.1448	0.4552	0.1021	0.077*	
H36	0.2791	0.5423	0.1681	0.064*	
H42	0.3886	0.5607	0.4159	0.071*	
H43	0.5838	0.4390	0.3980	0.089*	
H44	0.7170	0.4615	0.2220	0.081*	
H45	0.6533	0.6015	0.0617	0.100*	
H46	0.4607	0.7238	0.0776	0.084*	
H5	0.3790	0.8608	0.5582	0.078*	
H51A	0.7338	0.8274	0.2595	0.066*	0.636 (10)
H52A	0.8206	0.9716	0.3310	0.081*	0.636 (10)
H53A	0.8084	0.9013	0.5425	0.080*	0.636 (10)
H55A	0.7084	0.6438	0.4318	0.066*	0.636 (10)
H55B	0.8459	0.6800	0.4210	0.066*	0.636 (10)
H54A	0.7147	0.7083	0.6123	0.066*	0.636 (10)
H51B	0.7462	0.8700	0.2657	0.066*	0.364 (10)
H52B	0.7767	0.6490	0.3646	0.085*	0.364 (10)

H53B	0.7612	0.6224	0.5747	0.078*	0.364 (10)
H55C	0.8690	0.8656	0.4247	0.067*	0.364 (10)
H55D	0.7539	0.9740	0.4199	0.067*	0.364 (10)
H54B	0.7105	0.8256	0.6154	0.077*	0.364 (10)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.03662 (18)	0.0448 (2)	0.04238 (19)	−0.00811 (14)	−0.01386 (14)	−0.00215 (14)
P1	0.0332 (3)	0.0436 (4)	0.0394 (3)	−0.0066 (3)	−0.0086 (3)	−0.0073 (3)
C7	0.077 (3)	0.086 (3)	0.0514 (19)	0.006 (2)	−0.0049 (18)	−0.0218 (18)
N7	0.084 (3)	0.150 (4)	0.079 (2)	0.007 (2)	0.006 (2)	−0.039 (2)
C8	0.079 (2)	0.068 (2)	0.0507 (18)	−0.0046 (18)	−0.0169 (17)	−0.0155 (16)
N8	0.105 (3)	0.099 (2)	0.0661 (19)	0.004 (2)	−0.0413 (19)	−0.0155 (17)
C11	0.071 (2)	0.061 (2)	0.088 (3)	−0.0264 (18)	−0.039 (2)	0.0289 (19)
C12	0.096 (3)	0.0448 (18)	0.084 (3)	0.0104 (18)	−0.044 (2)	−0.0085 (17)
C13	0.0409 (16)	0.077 (2)	0.069 (2)	0.0022 (16)	−0.0194 (15)	0.0032 (18)
C14	0.067 (2)	0.065 (2)	0.0586 (19)	−0.0101 (17)	−0.0347 (17)	−0.0017 (16)
C15	0.067 (2)	0.084 (2)	0.0422 (17)	−0.0023 (19)	−0.0077 (16)	0.0097 (16)
C21	0.0331 (13)	0.0500 (15)	0.0407 (14)	−0.0073 (11)	−0.0073 (11)	−0.0105 (12)
C22	0.0447 (15)	0.0619 (18)	0.0533 (17)	−0.0163 (13)	0.0014 (13)	−0.0192 (14)
C23	0.0578 (19)	0.084 (2)	0.0586 (19)	−0.0153 (17)	0.0001 (15)	−0.0341 (18)
C24	0.0547 (19)	0.092 (3)	0.0448 (17)	−0.0148 (17)	−0.0003 (14)	−0.0126 (17)
C25	0.065 (2)	0.065 (2)	0.0507 (18)	−0.0206 (16)	−0.0039 (15)	0.0004 (15)
C26	0.0585 (18)	0.0542 (17)	0.0488 (16)	−0.0136 (14)	−0.0090 (14)	−0.0095 (13)
C31	0.0359 (13)	0.0494 (15)	0.0358 (13)	−0.0089 (11)	−0.0054 (10)	−0.0092 (11)
C32	0.0391 (14)	0.0566 (17)	0.0605 (18)	−0.0020 (12)	−0.0106 (13)	−0.0216 (14)
C33	0.0375 (15)	0.077 (2)	0.0587 (18)	−0.0057 (14)	−0.0137 (13)	−0.0209 (16)
C34	0.0533 (18)	0.091 (2)	0.0549 (18)	−0.0209 (17)	−0.0097 (14)	−0.0317 (17)
C35	0.062 (2)	0.072 (2)	0.072 (2)	−0.0083 (16)	−0.0144 (16)	−0.0401 (18)
C36	0.0434 (15)	0.0634 (19)	0.0574 (18)	−0.0028 (13)	−0.0097 (13)	−0.0228 (15)
C41	0.0357 (13)	0.0417 (14)	0.0466 (15)	−0.0057 (11)	−0.0092 (11)	−0.0084 (11)
C42	0.0584 (18)	0.070 (2)	0.0435 (16)	0.0057 (15)	−0.0153 (14)	−0.0132 (14)
C43	0.070 (2)	0.078 (2)	0.068 (2)	0.0182 (18)	−0.0344 (19)	−0.0136 (18)
C44	0.0469 (17)	0.062 (2)	0.091 (3)	0.0065 (15)	−0.0169 (18)	−0.0219 (19)
C45	0.0493 (19)	0.088 (3)	0.078 (2)	0.0088 (18)	0.0132 (17)	0.002 (2)
C46	0.0476 (17)	0.073 (2)	0.061 (2)	0.0035 (16)	0.0039 (15)	0.0104 (16)
C1	0.0410 (14)	0.0420 (14)	0.0462 (15)	−0.0084 (11)	−0.0094 (12)	−0.0051 (12)
C2	0.0438 (15)	0.0529 (16)	0.0435 (15)	−0.0095 (12)	−0.0107 (12)	−0.0050 (12)
C3	0.0402 (15)	0.0603 (18)	0.0513 (16)	−0.0047 (13)	−0.0125 (13)	−0.0055 (14)
C4	0.0404 (16)	0.111 (3)	0.0523 (18)	0.0029 (17)	−0.0173 (14)	−0.0063 (18)
C5	0.0476 (17)	0.088 (2)	0.0522 (18)	0.0031 (16)	−0.0150 (14)	−0.0107 (17)
C6	0.0596 (19)	0.067 (2)	0.0518 (18)	0.0048 (15)	−0.0122 (15)	−0.0176 (15)
C51A	0.045 (6)	0.068 (6)	0.049 (5)	−0.012 (4)	−0.009 (4)	−0.007 (4)
C52A	0.041 (3)	0.067 (4)	0.086 (6)	−0.011 (3)	−0.016 (5)	−0.001 (5)
C53A	0.048 (4)	0.076 (4)	0.090 (6)	−0.008 (3)	−0.037 (4)	−0.025 (4)
C55A	0.046 (4)	0.051 (4)	0.060 (5)	0.008 (3)	−0.018 (4)	−0.007 (3)
C54A	0.044 (3)	0.054 (5)	0.060 (3)	0.018 (3)	−0.024 (3)	−0.012 (3)

C51B	0.035 (9)	0.061 (9)	0.060 (9)	0.009 (7)	−0.014 (7)	−0.010 (7)
C52B	0.059 (9)	0.070 (10)	0.081 (10)	−0.008 (7)	−0.010 (9)	−0.019 (8)
C53B	0.047 (6)	0.061 (6)	0.077 (7)	−0.005 (5)	−0.023 (5)	0.005 (6)
C55B	0.048 (6)	0.070 (8)	0.057 (9)	−0.019 (5)	−0.024 (8)	−0.007 (8)
C54B	0.068 (8)	0.061 (8)	0.056 (6)	0.014 (7)	−0.017 (5)	−0.016 (6)

Geometric parameters (Å, °)

Ni1—C1	1.839 (3)	C23—H23	0.9300
Ni1—C11	2.078 (3)	C24—C25	1.366 (5)
Ni1—C12	2.116 (3)	C24—H24	0.9300
Ni1—C13	2.122 (3)	C25—C26	1.380 (4)
Ni1—C14	2.081 (3)	C25—H25	0.9300
Ni1—C15	2.136 (3)	C26—H26	0.9300
Ni1—P1	2.1417 (8)	C31—C36	1.385 (4)
P1—C21	1.827 (3)	C31—C32	1.388 (3)
P1—C31	1.835 (3)	C32—C33	1.378 (4)
P1—C41	1.824 (3)	C32—H32	0.9300
C1—C2	1.214 (3)	C33—C34	1.368 (4)
C2—C3	1.403 (4)	C33—H33	0.9300
C3—C4	1.371 (4)	C34—C35	1.373 (4)
C3—C51A	1.535 (7)	C34—H34	0.9300
C3—C51B	1.535 (9)	C35—C36	1.385 (4)
C4—C5	1.400 (4)	C35—H35	0.9300
C4—C54B	1.550 (9)	C36—H36	0.9300
C4—C54A	1.563 (6)	C41—C42	1.373 (4)
C5—C6	1.358 (4)	C41—C46	1.380 (4)
C5—H5	0.9300	C42—C43	1.390 (4)
C7—N7	1.135 (5)	C42—H42	0.9300
C7—C6	1.432 (5)	C43—C44	1.364 (5)
C8—N8	1.144 (4)	C43—H43	0.9300
C8—C6	1.423 (4)	C44—C45	1.354 (5)
C11—C15	1.377 (5)	C44—H44	0.9300
C11—C12	1.412 (5)	C45—C46	1.375 (4)
C11—H11	0.9300	C45—H45	0.9300
C12—C13	1.363 (5)	C46—H46	0.9300
C12—H12	0.9300	C51A—C52A	1.510 (8)
C13—C14	1.410 (5)	C51A—C55A	1.550 (7)
C13—H13	0.9300	C52A—C53A	1.335 (7)
C14—C15	1.382 (5)	C53A—C54A	1.514 (7)
C14—H14	0.9300	C55A—C54A	1.532 (8)
C15—H15	0.9300	C51B—C52B	1.510 (10)
C21—C22	1.381 (4)	C51B—C55B	1.536 (9)
C21—C26	1.394 (4)	C52B—C53B	1.340 (9)
C22—C23	1.379 (4)	C53B—C54B	1.493 (9)
C22—H22	0.9300	C55B—C54B	1.525 (9)
C23—C24	1.377 (5)		
C1—Ni1—C11	100.90 (12)	C25—C26—H26	119.4
C1—Ni1—C14	163.39 (12)	C21—C26—H26	119.4

C11—Ni1—C14	64.40 (14)	C36—C31—C32	118.4 (2)
C1—Ni1—C12	109.61 (13)	C36—C31—P1	122.5 (2)
C11—Ni1—C12	39.34 (14)	C32—C31—P1	119.1 (2)
C14—Ni1—C12	64.61 (14)	C33—C32—C31	120.8 (3)
C1—Ni1—C13	143.35 (14)	C33—C32—H32	119.6
C11—Ni1—C13	64.26 (13)	C31—C32—H32	119.6
C14—Ni1—C13	39.18 (13)	C34—C33—C32	120.1 (3)
C12—Ni1—C13	37.52 (13)	C34—C33—H33	119.9
C1—Ni1—C15	125.25 (13)	C32—C33—H33	119.9
C11—Ni1—C15	38.10 (14)	C33—C34—C35	120.0 (3)
C14—Ni1—C15	38.24 (13)	C33—C34—H34	120.0
C12—Ni1—C15	64.59 (15)	C35—C34—H34	120.0
C13—Ni1—C15	64.33 (13)	C34—C35—C36	120.1 (3)
C1—Ni1—P1	87.86 (8)	C34—C35—H35	119.9
C11—Ni1—P1	165.01 (13)	C36—C35—H35	119.9
C14—Ni1—P1	104.95 (10)	C35—C36—C31	120.4 (3)
C12—Ni1—P1	147.85 (12)	C35—C36—H36	119.8
C13—Ni1—P1	114.96 (10)	C31—C36—H36	119.8
C15—Ni1—P1	127.08 (12)	C42—C41—C46	117.9 (3)
C41—P1—C21	107.44 (12)	C42—C41—P1	124.5 (2)
C41—P1—C31	103.20 (12)	C46—C41—P1	117.5 (2)
C21—P1—C31	101.86 (11)	C41—C42—C43	120.2 (3)
C41—P1—Ni1	111.28 (9)	C41—C42—H42	119.9
C21—P1—Ni1	113.62 (9)	C43—C42—H42	119.9
C31—P1—Ni1	118.31 (8)	C44—C43—C42	120.8 (3)
N7—C7—C6	179.5 (4)	C44—C43—H43	119.6
N8—C8—C6	178.3 (4)	C42—C43—H43	119.6
C15—C11—C12	109.1 (3)	C45—C44—C43	119.4 (3)
C15—C11—Ni1	73.25 (19)	C45—C44—H44	120.3
C12—C11—Ni1	71.79 (19)	C43—C44—H44	120.3
C15—C11—H11	125.5	C44—C45—C46	120.4 (3)
C12—C11—H11	125.5	C44—C45—H45	119.8
Ni1—C11—H11	121.2	C46—C45—H45	119.8
C13—C12—C11	107.2 (3)	C45—C46—C41	121.4 (3)
C13—C12—Ni1	71.49 (19)	C45—C46—H46	119.3
C11—C12—Ni1	68.86 (18)	C41—C46—H46	119.3
C13—C12—H12	126.4	C2—C1—Ni1	173.6 (2)
C11—C12—H12	126.4	C1—C2—C3	171.8 (3)
Ni1—C12—H12	124.9	C4—C3—C2	129.7 (3)
C12—C13—C14	108.0 (3)	C4—C3—C51A	107.3 (5)
C12—C13—Ni1	70.99 (18)	C2—C3—C51A	122.6 (5)
C14—C13—Ni1	68.82 (16)	C4—C3—C51B	103.7 (8)
C12—C13—H13	126.0	C2—C3—C51B	126.6 (8)
C14—C13—H13	126.0	C3—C4—C5	124.3 (3)
Ni1—C13—H13	125.7	C3—C4—C54B	106.7 (5)
C15—C14—C13	108.5 (3)	C5—C4—C54B	126.2 (5)
C15—C14—Ni1	73.05 (18)	C3—C4—C54A	104.6 (3)
C13—C14—Ni1	72.00 (17)	C5—C4—C54A	130.6 (3)
C15—C14—H14	125.7	C6—C5—C4	129.2 (3)

C13—C14—H14	125.7	C6—C5—H5	115.4
Ni1—C14—H14	121.0	C4—C5—H5	115.4
C11—C15—C14	106.9 (3)	C5—C6—C8	124.3 (3)
C11—C15—Ni1	68.65 (18)	C5—C6—C7	120.9 (3)
C14—C15—Ni1	68.71 (17)	C8—C6—C7	114.7 (3)
C11—C15—H15	126.6	C52A—C51A—C3	103.7 (8)
C14—C15—H15	126.6	C52A—C51A—C55A	99.1 (10)
Ni1—C15—H15	127.6	C3—C51A—C55A	100.3 (9)
C22—C21—C26	118.1 (2)	C52A—C51A—H51A	117.0
C22—C21—P1	120.3 (2)	C53A—C52A—C51A	107.5 (9)
C26—C21—P1	121.5 (2)	C52A—C53A—C54A	106.7 (7)
C23—C22—C21	120.3 (3)	C54A—C55A—C51A	92.3 (8)
C23—C22—H22	119.8	C53A—C54A—C55A	99.9 (8)
C21—C22—H22	119.8	C53A—C54A—C4	101.6 (5)
C24—C23—C22	120.8 (3)	C55A—C54A—C4	102.2 (7)
C24—C23—H23	119.6	C52B—C51B—C3	99.6 (17)
C22—C23—H23	119.6	C52B—C51B—C55B	98.2 (18)
C25—C24—C23	119.8 (3)	C3—C51B—C55B	105.0 (11)
C25—C24—H24	120.1	C53B—C52B—C51B	107.1 (19)
C23—C24—H24	120.1	C52B—C53B—C54B	106.5 (15)
C24—C25—C26	119.7 (3)	C54B—C55B—C51B	92.3 (12)
C24—C25—H25	120.1	C53B—C54B—C55B	99.2 (11)
C26—C25—H25	120.1	C53B—C54B—C4	92.1 (8)
C25—C26—C21	121.2 (3)	C55B—C54B—C4	107.0 (9)
C1—Ni1—P1—C41	−52.45 (12)	C41—P1—C21—C26	−66.4 (2)
C11—Ni1—P1—C41	73.8 (4)	C31—P1—C21—C26	41.7 (2)
C14—Ni1—P1—C41	116.83 (14)	Ni1—P1—C21—C26	170.08 (19)
C12—Ni1—P1—C41	−177.3 (2)	C26—C21—C22—C23	1.3 (4)
C13—Ni1—P1—C41	157.32 (14)	P1—C21—C22—C23	179.0 (2)
C15—Ni1—P1—C41	81.63 (15)	C21—C22—C23—C24	0.9 (5)
C1—Ni1—P1—C21	68.98 (12)	C22—C23—C24—C25	−2.1 (5)
C11—Ni1—P1—C21	−164.7 (4)	C23—C24—C25—C26	1.2 (5)
C14—Ni1—P1—C21	−121.74 (14)	C24—C25—C26—C21	1.1 (5)
C12—Ni1—P1—C21	−55.9 (2)	C22—C21—C26—C25	−2.3 (4)
C13—Ni1—P1—C21	−81.26 (14)	P1—C21—C26—C25	−180.0 (2)
C15—Ni1—P1—C21	−156.95 (14)	C41—P1—C31—C36	2.6 (3)
C1—Ni1—P1—C31	−171.65 (13)	C21—P1—C31—C36	−108.7 (2)
C11—Ni1—P1—C31	−45.4 (4)	Ni1—P1—C31—C36	125.9 (2)
C14—Ni1—P1—C31	−2.38 (14)	C41—P1—C31—C32	−179.1 (2)
C12—Ni1—P1—C31	63.5 (2)	C21—P1—C31—C32	69.6 (2)
C13—Ni1—P1—C31	38.11 (15)	Ni1—P1—C31—C32	−55.8 (2)
C15—Ni1—P1—C31	−37.58 (15)	C36—C31—C32—C33	−0.4 (4)
C1—Ni1—C11—C15	135.0 (2)	P1—C31—C32—C33	−178.7 (2)
C14—Ni1—C11—C15	−36.8 (2)	C31—C32—C33—C34	1.0 (5)
C12—Ni1—C11—C15	−117.3 (3)	C32—C33—C34—C35	−0.5 (5)
C13—Ni1—C11—C15	−80.5 (2)	C33—C34—C35—C36	−0.7 (5)
P1—Ni1—C11—C15	10.1 (5)	C34—C35—C36—C31	1.3 (5)
C1—Ni1—C11—C12	−107.7 (2)	C32—C31—C36—C35	−0.8 (4)
C14—Ni1—C11—C12	80.5 (2)	P1—C31—C36—C35	177.5 (2)

C13—Ni1—C11—C12	36.8 (2)	C21—P1—C41—C42	7.7 (3)
C15—Ni1—C11—C12	117.3 (3)	C31—P1—C41—C42	−99.5 (3)
P1—Ni1—C11—C12	127.4 (4)	Ni1—P1—C41—C42	132.6 (2)
C15—C11—C12—C13	2.6 (4)	C21—P1—C41—C46	−173.8 (2)
Ni1—C11—C12—C13	−61.6 (2)	C31—P1—C41—C46	79.0 (3)
C15—C11—C12—Ni1	64.2 (2)	Ni1—P1—C41—C46	−48.9 (3)
C1—Ni1—C12—C13	−159.1 (2)	C46—C41—C42—C43	0.8 (5)
C11—Ni1—C12—C13	117.7 (3)	P1—C41—C42—C43	179.3 (2)
C14—Ni1—C12—C13	37.8 (2)	C41—C42—C43—C44	0.0 (5)
C15—Ni1—C12—C13	80.3 (2)	C42—C43—C44—C45	−1.0 (6)
P1—Ni1—C12—C13	−39.6 (3)	C43—C44—C45—C46	1.2 (6)
C1—Ni1—C12—C11	83.2 (2)	C44—C45—C46—C41	−0.4 (6)
C14—Ni1—C12—C11	−79.9 (2)	C42—C41—C46—C45	−0.6 (5)
C13—Ni1—C12—C11	−117.7 (3)	C2—C3—C4—C5	−3.8 (6)
C15—Ni1—C12—C11	−37.4 (2)	C51A—C3—C4—C5	−176.5 (6)
P1—Ni1—C12—C11	−157.29 (19)	C51B—C3—C4—C5	175.5 (9)
C11—C12—C13—C14	0.8 (4)	C2—C3—C4—C54B	−166.0 (6)
Ni1—C12—C13—C14	−59.1 (2)	C51A—C3—C4—C54B	21.2 (8)
C11—C12—C13—Ni1	59.9 (2)	C51B—C3—C4—C54B	13.3 (10)
C1—Ni1—C13—C12	34.2 (3)	C2—C3—C4—C54A	168.9 (4)
C11—Ni1—C13—C12	−38.6 (2)	C51A—C3—C4—C54A	−3.8 (7)
C14—Ni1—C13—C12	−118.9 (3)	C51B—C3—C4—C54A	−11.8 (10)
C15—Ni1—C13—C12	−81.0 (2)	C3—C4—C5—C6	177.3 (4)
P1—Ni1—C13—C12	158.0 (2)	C54B—C4—C5—C6	−24.0 (8)
C1—Ni1—C13—C14	153.1 (2)	C54A—C4—C5—C6	6.6 (8)
C11—Ni1—C13—C14	80.3 (2)	C4—C5—C6—C8	0.0 (6)
C12—Ni1—C13—C14	118.9 (3)	C4—C5—C6—C7	−177.4 (4)
C15—Ni1—C13—C14	37.9 (2)	C4—C3—C51A—C52A	−64.5 (9)
P1—Ni1—C13—C14	−83.1 (2)	C2—C3—C51A—C52A	122.1 (7)
C12—C13—C14—C15	−3.9 (3)	C4—C3—C51A—C55A	37.6 (8)
Ni1—C13—C14—C15	−64.4 (2)	C2—C3—C51A—C55A	−135.8 (7)
C12—C13—C14—Ni1	60.5 (2)	C3—C51A—C52A—C53A	67.7 (11)
C1—Ni1—C14—C15	7.4 (6)	C55A—C51A—C52A—C53A	−35.4 (11)
C11—Ni1—C14—C15	36.7 (2)	C51A—C52A—C53A—C54A	0.5 (11)
C12—Ni1—C14—C15	80.5 (2)	C52A—C51A—C55A—C54A	52.8 (10)
C13—Ni1—C14—C15	116.7 (3)	C3—C51A—C55A—C54A	−53.0 (10)
P1—Ni1—C14—C15	−132.0 (2)	C52A—C53A—C54A—C55A	35.2 (10)
C1—Ni1—C14—C13	−109.2 (5)	C52A—C53A—C54A—C4	−69.6 (9)
C11—Ni1—C14—C13	−80.0 (2)	C51A—C55A—C54A—C53A	−52.8 (9)
C12—Ni1—C14—C13	−36.2 (2)	C51A—C55A—C54A—C4	51.4 (10)
C15—Ni1—C14—C13	−116.7 (3)	C3—C4—C54A—C53A	71.0 (6)
P1—Ni1—C14—C13	111.32 (19)	C5—C4—C54A—C53A	−116.9 (6)
C12—C11—C15—C14	−5.0 (3)	C3—C4—C54A—C55A	−31.8 (8)
Ni1—C11—C15—C14	58.3 (2)	C5—C4—C54A—C55A	140.2 (8)
C12—C11—C15—Ni1	−63.3 (2)	C4—C3—C51B—C52B	59.8 (12)
C13—C14—C15—C11	5.5 (3)	C2—C3—C51B—C52B	−120.9 (13)
Ni1—C14—C15—C11	−58.2 (2)	C4—C3—C51B—C55B	−41.5 (15)
C13—C14—C15—Ni1	63.7 (2)	C2—C3—C51B—C55B	137.8 (10)
C1—Ni1—C15—C11	−58.3 (3)	C3—C51B—C52B—C53B	−72 (2)

C14—Ni1—C15—C11	119.1 (3)	C55B—C51B—C52B—C53B	35 (2)
C12—Ni1—C15—C11	38.6 (2)	C51B—C52B—C53B—C54B	1(3)
C13—Ni1—C15—C11	80.3 (2)	C52B—C51B—C55B—C54B	−53.8 (15)
P1—Ni1—C15—C11	−176.74 (18)	C3—C51B—C55B—C54B	48.5 (15)
C1—Ni1—C15—C14	−177.4 (2)	C52B—C53B—C54B—C55B	−36.9 (19)
C11—Ni1—C15—C14	−119.1 (3)	C52B—C53B—C54B—C4	70.7 (18)
C12—Ni1—C15—C14	−80.5 (2)	C51B—C55B—C54B—C53B	55.0 (12)
C13—Ni1—C15—C14	−38.8 (2)	C51B—C55B—C54B—C4	−40.0 (12)
P1—Ni1—C15—C14	64.1 (2)	C3—C4—C54B—C53B	−81.7 (8)
C41—P1—C21—C22	116.0 (2)	C5—C4—C54B—C53B	116.5 (7)
C31—P1—C21—C22	−135.9 (2)	C3—C4—C54B—C55B	18.6 (11)
Ni1—P1—C21—C22	−7.6 (2)	C5—C4—C54B—C55B	−143.2 (9)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C33—H33···Cg1^{i}	0.93	2.98	3.648 (4)	130

Symmetry codes: (i) −*x*, −*y*+2, −*z*.

Fig. 1

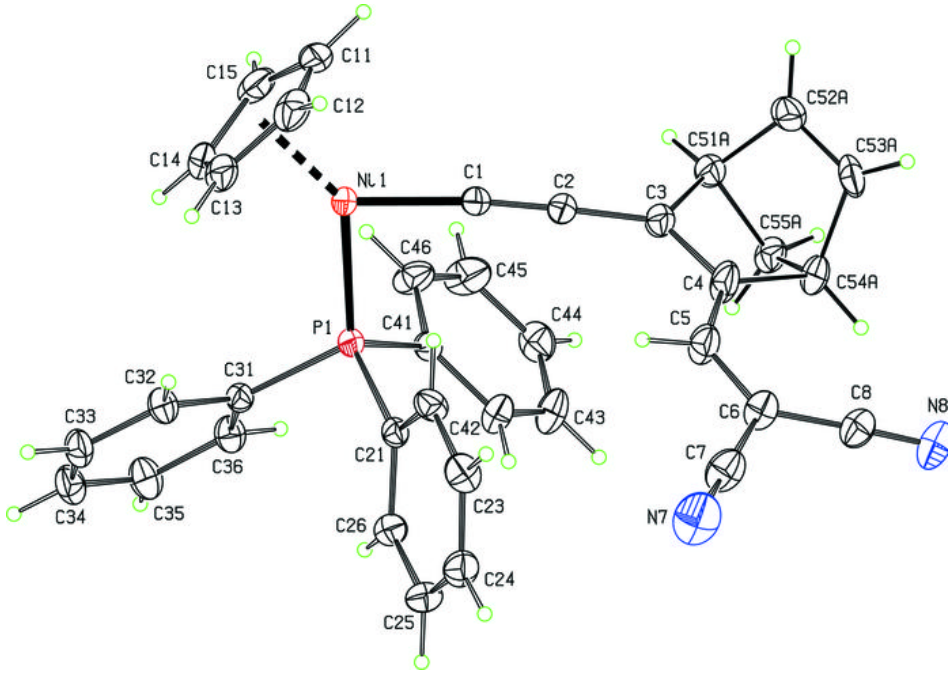

C11
C15
C12
C14
C13
NL1
C1
C2
C3
C52A
C51A
C53A
C55A
C54A
C4
C5
C6
C8
N8
C7
N7
C46
C45
C44
C41
P1
C31
C32
C33
C36
C34
C35
C21
C42
C43
C23
C26
C24
C25

Fig. 2

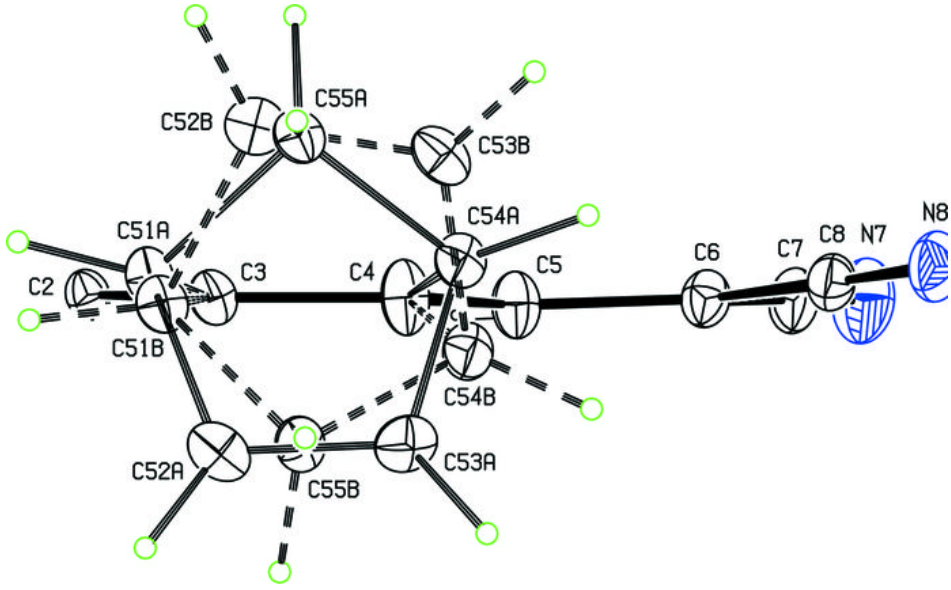

C55A
C52B
C53B
C54A
C51A
C2
C3
C4
C5
C6
C7
C8
N7
N8
C51B
C54B
C52A
C55B
C53A

Fig. 3