

## [(8a,9,9a- $\eta$ )-9-( $\eta^5$ -Cyclopentadienyl)-9-nickelafluorenyl]( $\eta^5$ -pentamethylcyclopentadienyl)nickel(II)

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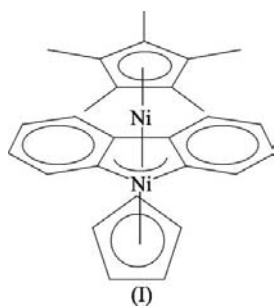
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The title compound, [Ni<sub>2</sub>(C<sub>5</sub>H<sub>5</sub>)(C<sub>10</sub>H<sub>15</sub>)(C<sub>12</sub>H<sub>8</sub>)] or [Ni(C<sub>10</sub>H<sub>15</sub>){Ni(C<sub>5</sub>H<sub>5</sub>)(C<sub>12</sub>H<sub>8</sub>)}], is a rare example (and the first obtained from nickelafluorenyllithium) of an analogue of nickelocene in which the central Ni atom is coordinated to one pentamethylcyclopentadienyl ring and one nickelafluorenyl ring. Both rings lie almost parallel to one another: the dihedral angle between the planes which include these rings is 4.4 (1)°. Slip parameter analysis indicates that the bonding mode of the central Ni atom to the nickelacyclic ring is between  $\eta^3$  and  $\eta^5$ . Two-dimensional layers of molecules are formed by C—H... $\pi$  interactions.

### Comment

Heterocyclic  $\pi$ -systems are useful in the synthesis of organometallic compounds because they can be used as multi-electron ligands. To examine the reactivity of the recently characterized nickelafluorenyllithium complex (Buchalski *et al.*, 2008), and to use it as a potential donor of the nickelafluorenyl group, we carried out the reaction of nickelafluorenyllithium with (acetylacetonato)(pentamethylcyclopentadienyl)nickel in diethyl ether. This reaction resulted in the formation of the title dinickel complex, (I), in 58% yield.



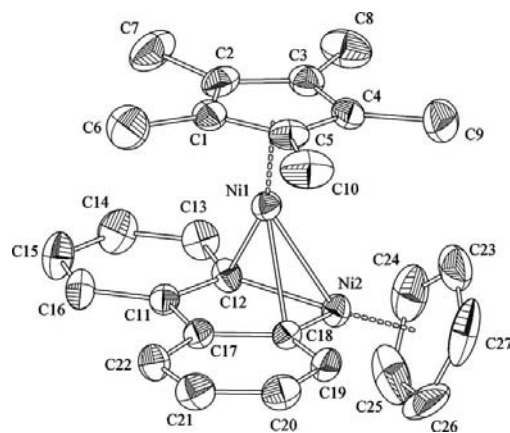
Complex (I) is an example of a heterometalocene in which the central Ni atom is bonded to two ligands, one cyclopentadienyl (Cp) and one heterocyclopentadienyl. To our

knowledge, this is the first example of the synthesis of a heterometalocene derivative possessing one metallacyclic ring in which a metallafluorenyllithium complex was used.

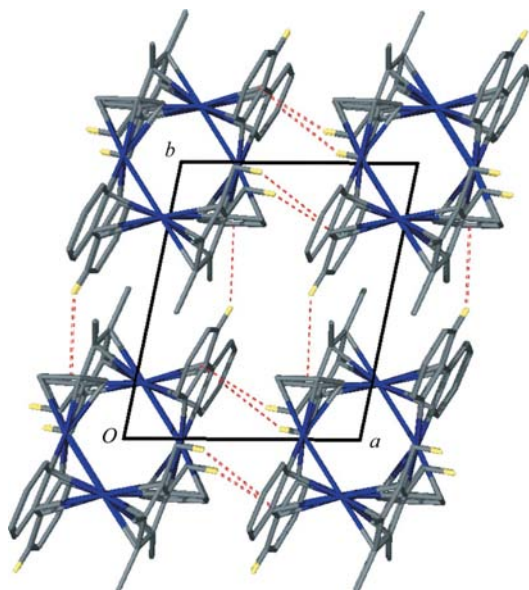
The molecular structure of complex (I) is shown in Fig. 1. The five-membered nickelacyclic ring of the nickelafluorenyl group is not absolutely planar; the Ni atom deviates by 0.308 Å from the plane defined by the four C atoms. To define the bonding mode of the apical Ni1 atom to the nickelafluorenyl ring, we have determined the degree of slip-fold distortion using previously reported parameters (Westcott *et al.*, 1990). The slip parameter  $\Delta_{M-C}$ , *i.e.* the difference between the average Ni1—C distances to atoms C12 and C18 and those to atoms C11 and C17, is *ca* 0.22 Å, which indicates that the bonding mode of atom Ni1 to the nickelacyclic ring is between  $\eta^3$  and  $\eta^5$ .

H atoms from the pentamethylcyclopentadienyl (Cp\*) group (H8 and H9) of one molecule form C—H... $\pi$  interactions with the arene rings (C11—C16 and C17—C22) on the fluorenyl group of an adjacent molecule, resulting in the formation of one-dimensional chains of molecules along the crystallographic *a* direction (Fig. 2). These chains are organized into two-dimensional layers perpendicular to the crystallographic *c* axis by another C—H... $\pi$  interaction formed by atoms H16 from the fluorenyl groups to the Cp rings of the parallel chains (Table 2).

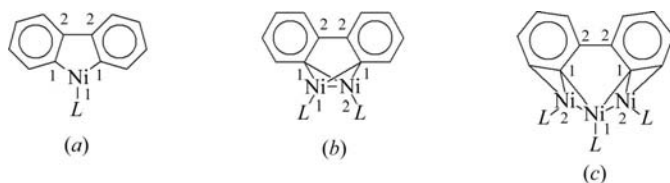
The structure of (I) may be compared with other compounds which contain a nickelafluorenyl ring. So far, only a few examples of such complexes have been reported, containing either one (Vicic & Jones, 1999; Schaub *et al.*, 2006; Keen *et al.*, 2007; Bennett *et al.*, 2003; Schaub & Radius, 2005), two (Buchalski *et al.*, 2006; Losi *et al.*, 2007) or three (Schaub *et al.*, 2006; Keen *et al.*, 2007; Bennet *et al.*, 1990) Ni atoms in the molecule (Fig. 3). The bond lengths between atoms Ni2 and C1 (as numbered in Fig. 3) in all compounds are between 1.90 and 2.00 Å. The C1—C2—C2—C1 torsion angles in all complexes are less than 8°, with the exception of two dinickel compounds in which these values are 25° (Keen *et al.*, 2007) and 30° (Keen & Johnson, 2006). In complex (I), the value of the


**Figure 1**

A view of the molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at 40% probability level and H atoms have been omitted for clarity.



**Figure 2**  
The C–H... $\pi$  interactions (dashed lines) of H atoms with the fluorenyl arene rings.



**Figure 3**  
Atom-numbering scheme of nickelaflorenyl complexes with (a) one, (b) two and (c) three Ni atoms in the molecule.

corresponding torsion angle (C12–C11–C17–C18) is  $0.2(4)^\circ$ .

The hinge angle, defined as the dihedral angle between the planes C1/C2/C2/C1 and C1/Ni2/C1 in most complexes, is less than  $4^\circ$ . The exceptions are complex (I) ( $12.5^\circ$ ) and its analogue ( $\eta^5$ -pentamethylcyclopentadienyl) $\{\eta^3$ -[9-( $\eta^5$ -pentamethylcyclopentadienyl)nickelaflorenyl]nickel (20.0 and  $15.4^\circ$ ; Buchalski *et al.*, 2006). In these compounds, the nickelaflorenyl rings are not flat: the Ni atoms deviate from the plane formed by the four C atoms. The reason for this may be the inductive effect of the methyl groups in the Cp\* ring, which increases the electron density of both Ni atoms. In complex (I), in which only the apical Ni atom is bonded to the Cp\* group, the value of the hinge angle is  $5$ – $7^\circ$  less than in the compound in which both Ni atoms are bonded to Cp\* groups.

## Experimental

All reactions were carried out under an atmosphere of dry argon or nitrogen using Schlenk tube techniques. Solvents were dried by conventional methods. NMR spectra were measured on a Varian Mercury 400BB instrument. Mass spectra were recorded on an AMD-604 spectrometer. EPR spectra were measured on a Bruker ESP 300 spectrometer in the X-band.

Nickelaflorenyllithium (0.762 g, 2.05 mmol; Buchalski *et al.*, 2008) and diethyl ether (40 ml) were placed in a Schlenk flask and cooled to 243 K. A solution of (acetylacetonato)(pentamethylcyclopentadienyl)nickel (0.612 g, 2.1 mmol; Smith & Andersen, 1996) in diethyl ether (30 ml) was added slowly. The reaction was stirred for 1 h at 243 K and then at room temperature overnight. When the reaction was complete, the solvent was removed and the residue was extracted with toluene (100 ml). The extract was filtered through alumina and then the solvent was evaporated. The residue was chromatographed on alumina (deactivated with 5% of water). One brown band was collected (hexane–toluene, 4:1 v/v). The solvent was removed and a brown solid, compound (I), was obtained (yield: 0.557 g, 1.19 mmol, 58%). Crystals appropriate for X-ray measurements were grown from a hexane–THF (250:1) solution. EIMS (70 eV, *m/e*, relative intensities,  $^{58}\text{Ni}$ ): 468 (96%,  $M^+$ ), 402 (100%,  $\text{C}_{22}\text{H}_{22}\text{Ni}_2^+$ ), 334 (29%,  $\text{C}_{17}\text{H}_{14}\text{Ni}_2^+$ ), 314 (21%,  $\text{C}_{15}\text{H}_{18}\text{Ni}_2^+$ ), 275 (31%,  $\text{C}_{17}\text{H}_{13}\text{Ni}^+$ ), 215 (27%,  $\text{C}_{17}\text{H}_{11}^+$ ), 152 (19%,  $\text{C}_{12}\text{H}_8^+$ ), 119 (7%,  $\text{C}_9\text{H}_{11}^+$ ); EIHRMS: observed = 468.09058, calculated for  $\text{C}_{27}\text{H}_{28}^{58}\text{Ni}_2$  = 468.08980. Magnetic susceptibility was determined by NMR measurements at 293 K by the Evans method (Crawford & Swanson, 1971; Evans, 1959) from differences in the chemical shifts of methyl group H atoms of toluene used as solvent and as external standard. The magnetic moment of (I) in toluene solution at 293 K is  $3.084 \mu_B$ , which indicates that the compound is paramagnetic with two unpaired electrons per molecule. There were no signals in any EPR spectrum of (I) at room temperature or at 77 K in the solid state or in benzene solution.

### Crystal data

$[\text{Ni}_2(\text{C}_5\text{H}_5)(\text{C}_{10}\text{H}_{15})(\text{C}_{12}\text{H}_8)]$	$\gamma = 78.244(2)^\circ$
$M_r = 469.91$	$V = 1076.93(6) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 2$
$a = 7.8022(2) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 9.3335(3) \text{ \AA}$	$\mu = 1.76 \text{ mm}^{-1}$
$c = 15.2091(6) \text{ \AA}$	$T = 100(2) \text{ K}$
$\alpha = 84.677(2)^\circ$	$0.26 \times 0.20 \times 0.14 \text{ mm}$
$\beta = 84.953(2)^\circ$	

### Data collection

Nonius KappaCCD diffractometer	10193 measured reflections
Absorption correction: empirical [using intensity measurements and spherical harmonic expansion of the absorption surface (Katayama, 1986; Blessing, 1995)]	3651 independent reflections
$T_{\min} = 0.621$ , $T_{\max} = 0.844$	2786 reflections with $I > 2\sigma(I)$
(expected range = 0.575–0.782)	$R_{\text{int}} = 0.033$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$	271 parameters
$wR(F^2) = 0.088$	H-atom parameters constrained
$S = 1.04$	$\Delta\rho_{\max} = 0.37 \text{ e \AA}^{-3}$
3651 reflections	$\Delta\rho_{\min} = -0.30 \text{ e \AA}^{-3}$

**Table 1**  
Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

Ni1–C18	2.150(3)	Ni2–C18	1.911(3)
Ni1–C12	2.176(3)	Ni2–C12	1.914(3)
Ni1–C17	2.374(3)	C11–C12	1.421(4)
Ni1–C11	2.384(3)	C11–C17	1.468(4)
Ni1–Ni2	2.3974(6)	C17–C18	1.428(4)
C18–Ni1–C12	72.6(1)	C18–Ni2–C12	84.1(1)

**Table 2**

$X-H \cdots Cg(\pi \text{ ring})$  interactions ( $H \cdots Cg < 3.0 \text{ \AA}$ ,  $\gamma < 30.0^\circ$ ).

$Cg2$  is the centroid of the C23–C27 ring,  $Cg3$  is the centroid of the C11–C16 ring and  $Cg4$  is the centroid of the C17–C22 ring.

$X-H \cdots CgJ$	$H \cdots Cg$	$H \cdots \text{Ring}$	$\gamma$	$X-H \cdots Cg$	$X \cdots Cg$	$X-H \cdots \pi$
C8–H8B $\cdots$ Cg3 <sup>i</sup>	2.76	2.671	14.33	157	3.661 (5)	69
C9–H9A $\cdots$ Cg4 <sup>i</sup>	2.77	2.716	11.54	149	3.628 (4)	67
C16–H16 $\cdots$ Cg2 <sup>ii</sup>	2.88	2.848	9.14	140	3.648 (4)	57

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

All H atoms were placed in geometric positions and treated as riding, with C–H = 0.95 Å and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{aromatic C})$  or  $1.5U_{\text{eq}}(\text{methyl C})$ .

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3150). Services for accessing these data are described at the back of the journal.

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