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Bis(μ-diphenylthiophosphinito-*S*:*P*)bis[(η^5-cyclopentadienyl)nickel(II)]

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.036
wR factor = 0.092
Data-to-parameter ratio = 20.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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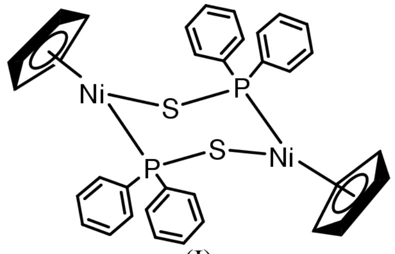
The title compound, $[(\eta^5\text{-}C_5H_5)Ni(S)PPh_2]_2$ or $[Ni_2(C_5H_5)_2(C_{12}H_{10}PS)_2]$, consists of two $(\eta^5\text{-}C_5H_5)Ni$ moieties bridged by the P and S atoms of two $[Ph_2P(S)]^-$ ligands, forming a non-planar Ni—S—P—Ni—S—P twist-boat heterocycle. The average Ni—P and Ni—S bond lengths are 2.1498 (6) and 2.1983 (5) Å, respectively.

Comment

Organometallic compounds play an increasingly important role as homogeneous catalysts and model systems for biologically active compounds. These very specific applications create a need for chemically robust systems, the properties of which can be varied by functionalization and derivatization (Cotton & Wilkinson, 1988). Recently, the coordination chemistry of tridentate oxygen ligands $[CpCo\{P(O)RR'\}]^-$ (Cp = C_5H_5, *R*, *R*′ = alkyl, aryl, *O*-alkyl, *O*-aryl) has been extensively investigated (Klaui, 1990); the corresponding ligands with sulfur donor atoms are less common. Klaui and co-workers have reported an interesting example for organometallic *S*,*S*′-ligands with π-donor properties, $[(\eta^5\text{-}C_5H_5)Ni\{P(S)(OCH_3)_2\}_2]^-$, which was obtained from the reaction of the intermediate dimer $[(\eta^5\text{-}C_5H_5)Ni(S)P(OCH_3)_2]_2$ with excess $HP(S)(OCH_3)_2$ in the presence of $Zn(OOCH_3)_2$ (Klaui *et al.*, 1983). Compared with the air-sensitive methoxy compound, the moderately soluble and air-stable phenyl compound is expected to be of more practical application. Thus, current research interest is directed towards the synthesis of the analogous phenyl *S*,*S*′-ligand $[(\eta^5\text{-}C_5H_5)Ni\{P(S)Ph_2\}]^-$. Herein, we report the crystal structure of an intermediate dimer $[(\eta^5\text{-}C_5H_5)Ni(S)PPh_2]_2$, (I), containing a six-membered twist-boat shape heterocycle.



(I)

The structure of (I) (Fig. 1) is very similar to that of $[(\eta^5\text{-}C_5H_5)Ni(S)P(CH_3)_2]_2$ (Lindner *et al.*, 1981). The two $[PhP(S)]^-$ ligands are coordinated to the Ni atoms of the two $(\eta^5\text{-}C_5H_5)Ni$ moieties, forming a six-membered heterocycle. This Ni—S—P—Ni—S—P heterocycle is obviously non-

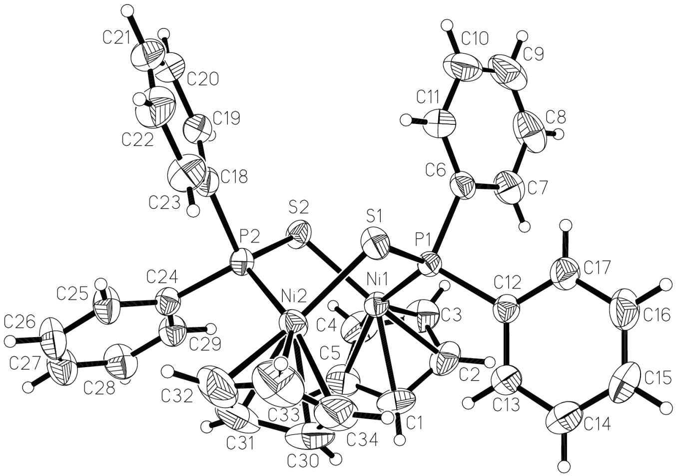


Figure 1

The structure of (I) showing 50% probability displacement ellipsoids and the atom-numbering scheme.

planar; the conformation is a twist-boat form, indicated by the P—Ni—S [average 91.32 (2)°], Ni—P—S [average 116.62 (3)°] and Ni—S—P [average 102.92 (3)°] ring angles. The (η^5-C_5H_5)Ni moiety in (I) resembles those reported for [(η^5-C_5H_5)Ni(S)P(CH_3)$_2$]$_2$ (Lindner *et al.*, 1981) and [(η^5-C_5H_5)NiPPh$_2$]$_2$ (Coleman & Dahl, 1967); that is, the C atoms C2 and C4, and C31 and C32, which are closest to the Ni—S—P plane, form shorter Ni—C bonds [average 2.087 (2) Å] than the other C atoms [2.128 (2)–2.173 (2)°]. The trend in the ring bond distances is also compatible with the Ni—C interactions being relatively stronger at C2, C4, C31 and C32. The average Ni—P and Ni—S bond lengths are 2.1498 (6) and 2.1983 (5)°, respectively, in (I), which compare reasonably well with the corresponding distances in [{(η^5-C_5H_5)Ni(S)P(OCH_3)$_2$}$_2$Ni] (Klaui *et al.*, 1986) and [(η^5-C_5H_5)Ni(S)P(CH_3)$_2$]$_2$ (Lindner *et al.*, 1981). The mean P—S bond length of 2.0624 (7)° in (I) is normal, and also compares excellently with those in other related compounds (Churchill *et al.*, 1971; Lindner *et al.*, 1981; Klaui *et al.*, 1986).

Experimental

The title compound was prepared according to the literature method of Klaui *et al.* (1983). A mixture of (η^5-C_5H_5)$_2$Ni (189 mg, 1.0 mmol) and $Ph_2P(S)H$ (218 mg, 1.0 mmol) was dissolved in 20 ml toluene and refluxed for 2 h, during which time the solution color changed from green to brown. The solvent was pumped off and residue was washed with hexane and chilled Et_2O. Single crystals suitable for X-ray analysis were obtained by recrystallization from CH_2Cl_2/Et_2O.

Crystal data

[$Ni_2(C_5H_5)_2(C_{12}H_{10}PS)_2$]
M_r = 682.06
Monoclinic, $P2_1/c$
a = 9.4231 (2) Å
b = 14.5514 (2) Å
c = 22.2014 (4) Å
β = 94.560 (1)°
V = 3034.60 (9) Å^3
Z = 4
D_x = 1.493 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7990 reflections
θ = 2.7–28.4°
μ = 1.51 mm^{-1}
T = 293 (2) K
Block, black
0.48 × 0.42 × 0.38 mm

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{\min}$ = 0.532, $T_{\max}$ = 0.598
21 461 measured reflections
7506 independent reflections
6064 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.059
$\theta_{\max}$ = 28.3°
$h = -11 \rightarrow 12$
$k = -19 \rightarrow 18$
$l = -25 \rightarrow 29$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.092
S = 0.98
7506 reflections
361 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0384P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.001
$\Delta\rho_{\max}$ = 0.67 e Å^{-3}
$\Delta\rho_{\min}$ = −0.66 e Å^{-3}

Table 1

Selected geometric parameters (Å, °).

Ni1—C2	2.060 (2)	Ni2—P2	2.1440 (6)
Ni1—C4	2.119 (2)	Ni2—C30	2.153 (3)
Ni1—C3	2.129 (2)	Ni2—C33	2.155 (3)
Ni1—P1	2.1555 (6)	Ni2—S1	2.1986 (6)
Ni1—C1	2.157 (2)	P1—C6	1.825 (2)
Ni1—C5	2.173 (2)	P1—C12	1.832 (2)
Ni1—S2	2.1979 (5)	P1—S1	2.0648 (7)
Ni2—C31	2.064 (2)	P2—C18	1.830 (2)
Ni2—C32	2.106 (3)	P2—C24	1.845 (2)
Ni2—C34	2.128 (3)	P2—S2	2.0600 (7)
P1—Ni1—S2	92.01 (2)	S1—P1—Ni1	117.85 (3)
P2—Ni2—S1	90.62 (2)	S2—P2—Ni2	115.39 (3)

After checking their presence in the difference map, all H atoms were geometrically fixed and allowed to ride on their attached atoms with $U_{\rm iso} = 1.2U_{\rm eq}$ for the attached atoms.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 1990).

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