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Bis[methylenebis(diphenylphosphine)-*P,P'*]nickel(II) diperchlorate

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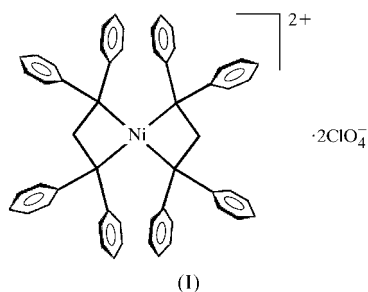
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The title compound, $[\text{Ni}(\text{Ph}_2\text{PCH}_2\text{PPh}_2)_2](\text{ClO}_4)_2$, was synthesized and its structure determined crystallographically. The Ni atom lies on an inversion centre and is at the center of a square formed by four P atoms which are necessarily coplanar. The Ni–P distances are 2.2188 (5) and 2.2322 (5) Å, and the P–Ni–P angle is 73.12 (3)°. The unique perchlorate anion is not coordinated to the Ni atom.

Comment

Much interest has been given to metal–phosphine complexes because they not only have special geometrical and electronic structures, but also serve as catalysts in industry. In order to understand the microstructures of these complexes and research their catalytical mechanisms to provide more information for the development of catalysts, we now report the crystal structure of the title compound, (I). The four P atoms and the Ni^{II} atom are coplanar. At the same time, the two diphenylphosphine groups are linked by a methylene group.



The Ni^{II} ion lies in the center of the square formed by atoms of P1, P2, P1' and P2'. The dihedral angles between the plane which these four P atoms are sited in and each of the eight benzene rings fall in the range 63–93°. It can be inferred that a negatively charged area is formed around the Ni^{II} ion, while the center of the positively charged Ni^{II} ion is completely exposed

and easily coordinated by some gas or solid molecules along the axis vertical to the plane formed by four P atoms. Perhaps that is the reason that the title complex has high catalytical activities. The Ni–P bond lengths are 2.2322 (5), 2.2322 (5), 2.2188 (5) and 2.2188 (5) Å; the average length is 2.2255 (5) Å, which is in the normal range of Ni–P bond lengths. The Ni atom lies on an inversion centre.

Experimental

A methanol solution of tris(*N*-methyl-1-benzimidazol- τ -yl)amine (TMBMA; 100 mg, 0.222 mmol) and a methylene chloride solution of methylenebis(diphenylphosphine) (44 mg, 0.111 mmol) were mixed at room temperature. With stirring, the methanol solution of Ni(ClO₄)₆·6H₂O (81 mg, 0.222 mmol) was added to the mixture. After stirred for 12 h, the precipitate was filtered, washed with methanol and ethanol in turn, then dried *in vacuo* to obtain a green–yellow powder. Green–yellow monocrystals suitable for X-ray determination were formed by slowly evaporating the acetonitrile solution for a period of one month at room temperature.

Crystal data

$[\text{Ni}(\text{C}_{25}\text{H}_{22}\text{P}_2)_2](\text{ClO}_4)_2$	$D_x = 1.413 \text{ Mg m}^{-3}$
$M_r = 1026.32$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 25 reflections
$a = 11.226 (2) \text{ \AA}$	$\theta = 14.19\text{--}14.79^\circ$
$b = 17.836 (2) \text{ \AA}$	$\mu = 0.699 \text{ mm}^{-1}$
$c = 12.932 (2) \text{ \AA}$	$T = 296 \text{ K}$
$\beta = 111.32 (1)^\circ$	Block, green–yellow
$V = 2412.0 (6) \text{ \AA}^3$	$0.38 \times 0.30 \times 0.17 \text{ mm}$
$Z = 2$	

Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{\text{int}} = 0.033$
$\omega/2\theta$ scans	$\theta_{\text{max}} = 25^\circ$
Absorption correction: ψ scans (North <i>et al.</i> , 1968)	$h = 0 \rightarrow 13$
$T_{\text{min}} = 0.773$, $T_{\text{max}} = 0.889$	$k = 0 \rightarrow 21$
4624 measured reflections	$l = -15 \rightarrow 15$
4431 independent reflections	3 standard reflections every 300 reflections
4340 reflections with $I > 3\sigma(I)$	intensity decay: 1.0%

Refinement

Refinement on F	All H-atom parameters refined
$R = 0.033$	$w = 1/[\sigma^2(F)]$
$wR = 0.044$	$(\Delta/\sigma)_{\text{max}} = 0.05$
$S = 1.22$	$\Delta\rho_{\text{max}} = 0.29 \text{ e \AA}^{-3}$
3262 reflections	$\Delta\rho_{\text{min}} = -0.25 \text{ e \AA}^{-3}$
323 parameters	

Table 1

Selected geometric parameters (Å, °).

Ni–P2	2.2188 (5)	P1–C1	1.832 (3)
Ni–P1	2.2322 (5)	P2–C31	1.803 (3)
P1–C21	1.802 (3)	P2–C41	1.805 (3)
P1–C11	1.815 (3)	P2–C1	1.834 (3)
P2–Ni–P1	73.12 (3)		

All H atoms were located in difference Fourier maps and refined with isotropic displacement parameters; the C–H range is 0.86 (3)–1.03 (4) Å.

Data collection: *CAD-4 Operations Manual* (Enraf–Nonius, 1977); cell refinement: *CAD-4 Operations Manual*; data reduction: *PROCESS* in *TEXSAN* (Molecular Structure Corporation, 1987); program(s) used to solve structure: *MITHRIL* (Gilmore, 1983); program(s) used to refine structure: *LS* in *TEXSAN*; software used to prepare material for publication: GCIF (local program).

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