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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KA1130). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Chloro(η^5-cyclopentadienyl)(triphenylphosphine)nickel(II)

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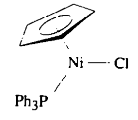
Abstract

The title compound, [NiCl(C_5H_5)($C_{18}H_{15}P$)], belongs to the class of two-legged piano-stool complexes, and has Ni—Cl and Ni—P distances of 2.176 (1) and 2.160 (1) Å, respectively.

Comment

We have been investigating the nonlinear optical responses of organometallic acetylides (Whittall *et al.*, 1994; Whittall, Humphrey, Hockless, Skelton & White, 1995). In the course of our studies employing *ZINDO* (Biosym Technologies, 1994) to compute molecular first hyperpolarizabilities, we have required accurate molecular geometries for acetylide complexes and their precursor chloro compounds. We report herein the structure determination of chloro(η^5-cyclopentadienyl)(triphenylphosphine)nickel(II), (I), which can be readily transformed into σ-arylacetylide derivatives by replacement of the chloro ligand (Bruce, Humphrey, Matisons, Roy & Swincer, 1984).



(I)

The title complex is readily obtained in excellent yield by ligand metathesis of [Ni(η-C_5H_5)$_2$] and [$NiCl_2(PPh_3)_2$] (Barnett, 1974), and can be crystallized from a toluene/hexane mixture. The Ni atom can be considered five-coordinate (with the cyclopentadienyl occupying three facially disposed sites). The complex is an example of a two-legged piano stool complex, of which many examples exist. The Ni—Cl [2.176 (1) Å], Ni—P [2.160 (1) Å] and Ni—C_5H_5 [2.081 (4)–2.154 (4) Å] distances fall within the range of expected values.

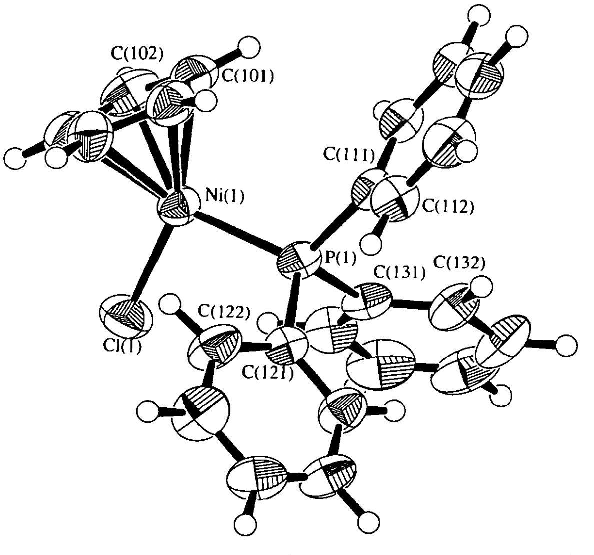


Fig. 1. The molecular structure of the title compound showing the labelling of the non-H atoms. Numbering of unlabelled atoms continues in sequence around each ring. Displacement ellipsoids are shown at the 50% probability level and H atoms are drawn as circles of arbitrary radii.

Experimental

The synthesis of the title compound was carried out by reaction of [Ni(η-C_5H_5)$_2$] and [$NiCl_2(PPh_3)_2$], following the literature route of Barnett (1974). The complex was recrystallized by addition of hexane to a toluene solution followed by cooling to 273 K.

Crystal data

[$NiCl(C_5H_5)(C_{18}H_{15}P)$]
$M_r = 421.54$
Orthorhombic
Pbca
$a = 17.578$ (3) Å
$b = 9.909$ (4) Å
$c = 22.945$ (4) Å
$V = 3996$ (2) Å^3
$Z = 8$
$D_x = 1.401$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 13.7$–15.8°
$\mu = 1.188$ mm^{-1}
$T = 296$ (1) K
Prism
0.32 × 0.24 × 0.12 mm
Red

Data collection

Rigaku AFC-6*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical using azimuthal (ψ) scans (North, Phillips & Mathews, 1968)
$T_{\min} = 0.81$, $T_{\max} = 1.00$
3990 measured reflections
3990 independent reflections

2092 observed reflections [$I > 3\sigma(I)$]
$\theta_{\max} = 25.04°$
$h = 0 \rightarrow 20$
$k = 0 \rightarrow 11$
$l = -27 \rightarrow 0$
3 standard reflections monitored every 150 reflections
intensity decay: none

Refinement

Refinement on *F*
$R = 0.0323$
$wR = 0.0210$
$S = 1.728$
2092 reflections
236 parameters
H-atom parameters not refined
$w = 4F_o^2/[\sigma^2(F_o^2) + (0.002F_o^2)^2]$
$(\Delta/\sigma)_{\max} = 0.01$

$\Delta\rho_{\max} = 0.32$ e Å^{-3}
$\Delta\rho_{\min} = -0.24$ e Å^{-3}
Extinction correction: Zachariasen (1967) type 2, Gaussian isotropic
Extinction coefficient: $1.5 (5) \times 10^{-8}$
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Ni(1)	0.08873 (3)	0.18880 (5)	0.19881 (2)	0.0457 (1)
Cl(1)	0.01996 (6)	0.0094 (1)	0.18396 (5)	0.0705 (4)
P(1)	0.04442 (5)	0.3028 (1)	0.12611 (4)	0.0431 (3)
C(101)	0.1393 (2)	0.3276 (4)	0.2564 (2)	0.062 (1)
C(102)	0.1172 (2)	0.2193 (5)	0.2892 (2)	0.068 (2)
C(103)	0.1539 (3)	0.1049 (5)	0.2662 (2)	0.071 (2)
C(104)	0.2043 (2)	0.1463 (5)	0.2229 (2)	0.065 (2)
C(105)	0.1928 (2)	0.2822 (4)	0.2142 (2)	0.060 (2)
C(111)	0.0867 (2)	0.4698 (4)	0.1174 (1)	0.043 (1)
C(112)	0.1326 (2)	0.5050 (4)	0.0703 (2)	0.056 (1)
C(113)	0.1631 (2)	0.6324 (5)	0.0667 (2)	0.070 (2)
C(114)	0.1495 (3)	0.7256 (5)	0.1092 (2)	0.076 (2)
C(115)	0.1049 (2)	0.6925 (5)	0.1566 (2)	0.067 (2)
C(116)	0.0734 (2)	0.5652 (4)	0.1607 (2)	0.052 (1)
C(121)	0.0618 (2)	0.2163 (4)	0.0576 (1)	0.042 (1)
C(122)	0.1224 (2)	0.1281 (5)	0.0541 (2)	0.066 (2)
C(123)	0.1378 (2)	0.0576 (5)	0.0028 (2)	0.076 (2)
C(124)	0.0923 (3)	0.0739 (5)	−0.0449 (2)	0.066 (2)
C(125)	0.0328 (2)	0.1610 (5)	−0.0420 (2)	0.067 (2)
C(126)	0.0170 (2)	0.2317 (4)	0.0087 (2)	0.058 (1)
C(131)	−0.0583 (2)	0.3415 (4)	0.1244 (1)	0.047 (1)
C(132)	−0.0861 (2)	0.4525 (4)	0.0943 (2)	0.059 (1)
C(133)	−0.1638 (3)	0.4758 (5)	0.0916 (2)	0.076 (2)
C(134)	−0.2130 (2)	0.3900 (6)	0.1186 (2)	0.083 (2)
C(135)	−0.1866 (3)	0.2813 (5)	0.1484 (2)	0.082 (2)
C(136)	−0.1091 (2)	0.2567 (4)	0.1522 (2)	0.062 (1)

Table 2. *Selected geometric parameters (Å, °)*

Ni(1)—Cl(1)	2.176 (1)	Ni(1)—C(105)	2.081 (4)
Ni(1)—P(1)	2.160 (1)	C(101)—C(102)	1.367 (5)
Ni(1)—C(101)	2.103 (4)	C(101)—C(105)	1.422 (5)
Ni(1)—C(102)	2.154 (4)	C(102)—C(103)	1.407 (6)
Ni(1)—C(103)	2.096 (4)	C(103)—C(104)	1.394 (5)
Ni(1)—C(104)	2.147 (4)	C(104)—C(105)	1.377 (5)
Cl(1)—Ni(1)—P(1)	96.08 (4)	P(1)—Ni(1)—C(101)	107.2 (1)
Cl(1)—Ni(1)—C(101)	150.1 (1)	P(1)—Ni(1)—C(102)	138.9 (1)
Cl(1)—Ni(1)—C(102)	113.2 (1)	P(1)—Ni(1)—C(103)	166.9 (1)
Cl(1)—Ni(1)—C(103)	95.5 (1)	P(1)—Ni(1)—C(104)	130.0 (1)
Cl(1)—Ni(1)—C(104)	113.9 (1)	P(1)—Ni(1)—C(105)	102.5 (1)
Cl(1)—Ni(1)—C(105)	151.4 (1)		

The θ-scan width used was $(0.80 + 1.3\tan\theta)°$ at a speed of 2.0° min^{-1} (in ω). The weak reflections were rescanned a maximum of four times and the counts accumulated to ensure good counting statistics. Stationary background counts were made on each side of the reflection with a 2:1 ratio of peak to background counting time. H atoms were included at calculated positions and held fixed with $U_{\rm iso} = 1.2U_{\rm eq}$(C).

Data collection and cell refinement were carried out using *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). The structure was solved using heavy-atom Patterson methods (*PATTY* in *DIRDIF*; Beurskens *et al.*, 1992) and expanded using Fourier techniques (*DIRDIF*). All calculations were performed using *TEXSAN* (Molecular Structure Corporation, 1992).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: TA1050). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bis(*N*,*N*-*cyclo*-heptamethylenedithiocarbamato-*S*,*S*′)platinum(II),† a Platinum Dithiocarbamate Containing a Large Carbocyclic Ring

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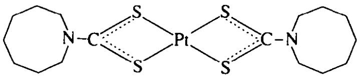
Abstract

The title compound, [Pt($C_8H_{14}NS_2$)$_2$], contains the largest carbocyclic dithiocarbamate ligand yet characterized. Typical Pt—S distances and S—Pt—S angles are observed, but there is a pronounced twist between the plane defined by Pt, S(1), S(2) and C(1) and that of N(1), C(2) and C(8), relative to open-chain analogues.

Comment

Metal complexes containing the α-dioximato ligand become more soluble in organic solvents by incorporation of a large carbocyclic ring in the ligand (Baxter, Heath, Raptis & Willis, 1992). Such a modification of a platinum bis(α-dioximato) complex, with incorporation of a C_8 backbone, led to the discovery of a novel unbridged platinum(III) dimer (Baxter, Heath, Raptis & Willis, 1992). We report here a similar modification of a dithiocarbamate ligand, resulting in an eight-membered ring, and present the crystal structure of the platinum(II) complex, (1). This is the first report of the structure of a platinum complex containing an *N*,*N*-*cyclo*-polymethylenedithiocarbamate ligand.



(1)

Structural characterizations of simple platinum(II) bisdithiocarbamates are scarce. We know of only one other study (Baker & Emett, 1992), where [Pt(S_2CNEt_2)$_2$] and [Pt($S_2CN(EtOH)_2$)$_2$] were reliably characterized. Early reports of the structure of bis(diethyldithiocarbamato)platinum(II) (Amanov, Kukina & Porai-Koshits, 1967, 1977) gave an *R* value of 0.14. Other studies (Ebihara *et al.*, 1990, 1992) involve structures where the S atoms form platinum-to-silver bridges. The Pt—S bond lengths and S—Pt—S angles found in this study are very similar to those reported by Baker & Emett (1992).

There is a significant twist of 12° between the plane defined by Pt, S(1), S(2) and C(1) and that of N(1), C(2) and C(8). This is larger than those discovered in [Pt(S_2CNEt_2)$_2$] (4°) and [Pt($S_2CN(EtOH)_2$)$_2$] (2°) (Baker & Emett, 1992). The larger twist in (1) may be attributed to crystal-packing effects since an examination of a molecular model reveals that there are no apparent steric barriers to a smaller dihedral angle.

The large carbocyclic ring does not impart any appreciable improvement in organosolubility over the diethyl analogue in conventional solvents such as dichloromethane, toluene, hexane and carbon tetrachloride. The packing diagram, showing the *bc* plane, indicates that there is a degree of interlocking of the

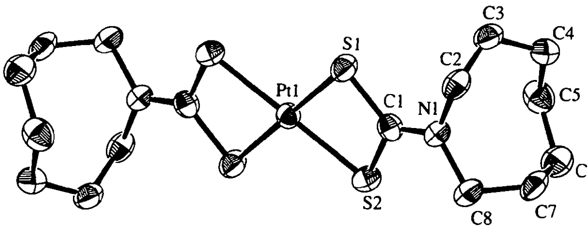


Fig. 1. The molecular structure of the title compound showing the labelling of all non-H atoms. Displacement ellipsoids are shown at the 50% probability level and H atoms are omitted for clarity.

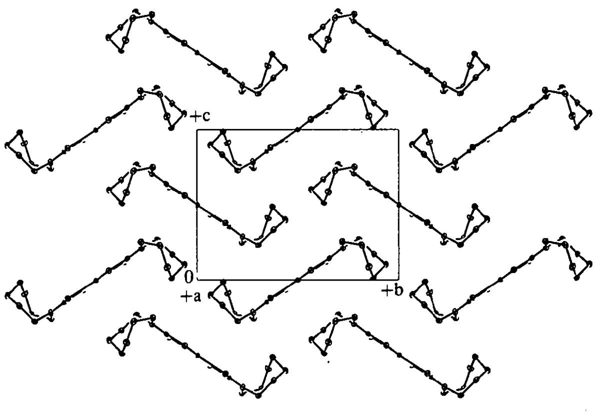


Fig. 2. Packing diagram viewed along the *bc* plane, with H atoms omitted, revealing an interlocking molecular network.

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† Alternative IUPAC nomenclature: bis(1-azocanecarbodithioato-*S*,*S*′)-platinum(II).