

N(1)	0.7292 (4)	0.0278 (2)	0.5100 (2)	0.0554 (9)
N(2)	1.1049 (4)	−0.0924 (2)	0.8574 (2)	0.0637 (10)
N(3)	0.3874 (4)	0.1504 (3)	0.8441 (3)	0.0730 (12)
N(4)	0.8881 (4)	0.1682 (2)	0.8324 (2)	0.0501 (9)
C(1)	0.7468 (4)	0.0430 (3)	0.5943 (3)	0.0514 (10)
C(2)	0.6710 (6)	−0.0451 (3)	0.4768 (3)	0.0725 (14)
C(3)	0.7823 (8)	−0.1024 (4)	0.4668 (4)	0.104 (2)
C(4)	0.7700 (5)	0.0827 (3)	0.4456 (3)	0.0639 (13)
C(5)	0.6548 (6)	0.1367 (3)	0.4163 (4)	0.083 (2)
C(6)	1.0205 (5)	−0.0347 (3)	0.8377 (3)	0.0553 (11)
C(7)	1.2142 (6)	−0.1127 (4)	0.8029 (4)	0.080 (2)
C(8)†	1.3437 (16)	−0.0741 (8)	0.8287 (11)	0.100 (4)
C(8A)‡	1.356 (4)	−0.1165 (16)	0.851 (2)	0.114 (11)
C(9)	1.0784 (6)	−0.1468 (3)	0.9256 (3)	0.0712 (14)
C(10)	0.9760 (7)	−0.2076 (3)	0.8916 (4)	0.089 (2)
C(11)	0.5140 (5)	0.1319 (3)	0.8256 (3)	0.0644 (13)
C(12)	0.2970 (6)	0.1991 (3)	0.7830 (4)	0.082 (2)
C(13)	0.3225 (7)	0.2819 (4)	0.7992 (5)	0.101 (2)
C(14)	0.3356 (6)	0.1246 (4)	0.9248 (4)	0.097 (2)
C(15)	0.3617 (9)	0.1800 (5)	0.9965 (5)	0.127 (3)

† Occupancy of 0.65. ‡ Occupancy of 0.35.

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

Mo(1)—N(4)	1.765 (4)	Mo(1)—S(6)	2.5182 (14)
Mo(1)—S(2)	2.4817 (14)	Mo(1)—S(3)	2.5320 (13)
Mo(1)—S(4)	2.5016 (13)	Mo(1)—S(1)	2.6083 (14)
Mo(1)—S(5)	2.5152 (15)	S(7)—N(4)	1.568 (4)
S(5)—Mo(1)—S(6)	67.90 (5)	S(2)—Mo(1)—S(1)	69.29 (4)
S(4)—Mo(1)—S(3)	68.05 (4)	S(7)—N(4)—Mo(1)	174.8 (2)
N(4)—Mo(1)—S(1)	164.62 (11)		

One of the C atoms was disordered over two sites, C(8) and C(8A). Their occupancies and those of the attached H atoms were refined to 0.65 and 0.35, respectively.

Data collection: Nicolet R3 software. Cell refinement: Nicolet R3 software. Data reduction: *XDISK* (Siemens, 1991). Program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1986). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: *SHELXL93*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BM1082). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(4-Chlorobenzenethiolato-*S*)(η^5 -cyclopentadienyl)(triphenylphosphine-*P*)nickel(II)

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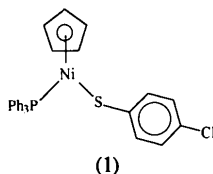
(Received 24 August 1995; accepted 7 May 1996)

Abstract

The Ni atom in [Ni(C₆H₄ClS)(C₅H₅)(C₁₈H₁₅P)] has a distorted trigonal geometry, with bond angles *Cp*—Ni—S 132.3 (1), *Cp*—Ni—P 135.3 (5) and P—Ni—S 92.4 (1)°, where *Cp* represents the centroid of the C₅H₅ ring. The bond distances *Cp*—Ni, Ni—S and Ni—P are 1.763 (1), 2.190 (1) and 2.144 (1) Å, respectively, which are close to distances found in similar compounds. A structural model with disordered cyclopentadienyl ligands was used.

Comment

The use of [(η^5 -C₅H₅)Ru(PPh₃)₂Cl] as a starting material for entry into (cyclopentadienyl)ruthenium chemistry is very well documented (Bruce, Cifuentes, Snow & Tiekink, 1989; Davies, McNally & Smallbridge, 1990). The effectiveness of this complex as a starting material is aided by the substitutionally labile PPh₃ groups and also by the ability of the complex to react metathetically with replacement of the halide atom. We have been using the isoelectronic complex [(η^5 -C₅H₅)Ni(PPh₃)X] (X = Cl, Br, I) for a similar purpose. Our results so far indicate that the metathetical replacement of the halide in our starting compound leads to complexes of the type [(η^5 -C₅H₅)Ni(PPh₃)(*ER*)] (*E* = S, Se; *R* = alkyl, aryl) (Darkwa, Bothata & Koczon, 1993; Darkwa, 1994) and is similar to the analogous ruthenium reactions. In an attempt to study the effect of halide-substituted organosulfur ligands on the Ni—P bond in these compounds, we isolated [(η^5 -C₅H₅)Ni(PPh₃)(SC₆H₄Cl-4)], (1), whose structure is reported here.



If the centroid of the C₅H₅ ring (Cp) is considered to occupy a coordination site, then the geometry around nickel is distorted trigonal. In the structure studied, the cyclopentadienyl groups appear to be disordered over two orientations. The overall geometry around the Ni atom is comparable to that found in both [(η⁵-C₅H₅)Ni(PPh₃)(SC₆H₅)] [(2); Darkwa, Bothata & Koczon, 1993] and [(η⁵-C₅H₅)Ni(PPh₃)(SeC₆H₅)] [(3); Darkwa, 1994]. A comparison of selected geometric parameters for these nickel complexes is given in Table 2 in order to emphasize their similarities. There are no significant differences in the Ni—P and Ni—S bond distances, implying that the Cl substitution of the phenyl ring of the thiolato ligand in (1) has little effect on the electron density on the nickel. Hence, the Ni—P bond in particular is invariant in all three nickel compounds.

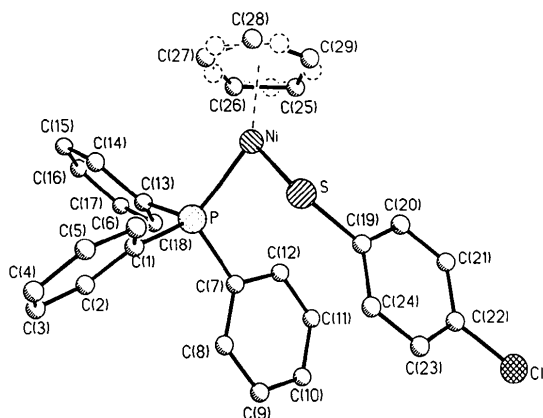


Fig. 1. The molecular structure of (1) with H atoms omitted for clarity.

Experimental

The title compound was prepared by adding excess Et₃N (2 ml) to a mixture of [(η⁵-C₅H₅)Ni(PPh₃)Br] (1.00 g, 2.15 mmol) and 4-chlorobenzenethiol (0.25 ml, 2.15 mmol) in toluene (75 ml) and stirring the resulting solution at room temperature for 1 h. After filtration to remove the Et₃NHCl by-product, the filtrate was evaporated to dryness. Green crystals suitable for X-ray structural study were isolated after cooling a CH₂Cl₂ solution of the product layered with hexane (2:1) to 258 K overnight (yield 0.70 g, 62%). Analysis calculated for C₂₉H₂₄ClNiPS: C 65.76, H 4.57%; found: C 65.88, H 4.67%. ¹H NMR (CDCl₃): δ 7.68–7.62 (*m*, 6H, PPh₃), 7.38–7.30 (*m*, 9H, PPh₃), 7.25 (*d*, 2H, *J*_{HH} = 8.50 Hz, SC₆H₄Cl-4), 6.82 (*d*, 2H, *J*_{HH} = 8.50 Hz, SC₆H₄Cl-4), 5.11 (*s*, 5H, C₅H₅). ¹³C{¹H} NMR: 133.6 (*d*, *J*_{CP} = 10.78 Hz), 130.2 (*d*, *J*_{CP} = 2.34 Hz), 128.2 (*d*, *J*_{CP} = 10.18 Hz) (PPh₃), 134.5 (*s*), 132.4 (*s*), 127.0 (*s*) (SC₆H₄Cl-4), 93.9 (*s*, C₅H₅). ³¹P{¹H} NMR: 35.83 (*s*, PPh₃).

Crystal data

[Ni(C₆H₄ClS)(C₅H₅)-
(C₁₈H₁₅P)]

*M*_r = 529.7

Triclinic

*P*1

a = 9.743 (2) Å

b = 11.574 (2) Å

c = 12.184 (2) Å

α = 79.89 (2)°

β = 69.17 (2)°

γ = 81.32 (2)°

V = 1258.3 (4) Å³

Z = 2

*D*_x = 1.398 Mg m⁻³

Mo Kα radiation

λ = 0.71073 Å

Cell parameters from 64
reflections

θ = 12–15°

μ = 1.039 mm⁻¹

T = 276 K

Prism

0.50 × 0.40 × 0.40 mm

Black

Data collection

Siemens P4 diffractometer

ω scans

Absorption correction:

empirical via ψ scan of 10
reflections (North, Phillips
& Mathews, 1968)

*T*_{min} = 0.4614, *T*_{max} =
0.5469

6717 measured reflections

5731 independent reflections

5731 observed reflections

*R*_{int} = 0.0115

θ_{max} = 27.5°

h = -9 → 12

k = -14 → 14

l = -15 → 15

3 standard reflections
monitored every 100

reflections

intensity decay: none

Refinement

Refinement on *F*

R = 0.0696

wR = 0.0370

S = 1.37

5731 reflections

276 parameters

H atoms riding with fixed
isotropic *U*

w = 1/[σ²(*F*)]

(Δ/σ)_{max} = 0.001

Δρ_{max} = 0.63 e Å⁻³

Δρ_{min} = -0.55 e Å⁻³

Extinction correction: none

Atomic scattering factors

from *International Tables*

for *X-ray Crystallography*

(1974, Vol. IV, pp. 55, 99,
149)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Ni	0.1831 (1)	0.3677 (1)	0.2521 (1)	0.041 (1)
P	0.2833 (1)	0.2162 (1)	0.1633 (1)	0.035 (1)
S	0.1927 (1)	0.2748 (1)	0.4224 (1)	0.058 (1)
Cl	0.7895 (1)	0.2730 (1)	0.5102 (1)	0.092 (1)
C(1)	0.1862 (3)	0.0827 (2)	0.2111 (2)	0.037 (1)
C(2)	0.2260 (4)	-0.0068 (3)	0.1410 (3)	0.052 (1)
C(3)	0.1509 (4)	-0.1073 (3)	0.1765 (3)	0.060 (2)
C(4)	0.0341 (4)	-0.1172 (3)	0.2825 (3)	0.055 (1)
C(5)	-0.0068 (4)	-0.0283 (3)	0.3507 (3)	0.052 (1)
C(6)	0.0680 (3)	0.0712 (3)	0.3163 (3)	0.043 (1)
C(7)	0.4710 (3)	0.1728 (2)	0.1657 (2)	0.038 (1)
C(8)	0.5235 (4)	0.0580 (3)	0.1933 (3)	0.052 (1)
C(9)	0.6675 (4)	0.0335 (3)	0.1958 (3)	0.067 (2)
C(10)	0.7565 (4)	0.1218 (4)	0.1700 (3)	0.066 (2)
C(11)	0.7053 (4)	0.2350 (3)	0.1434 (3)	0.067 (2)
C(12)	0.5618 (4)	0.2620 (3)	0.1425 (3)	0.055 (1)
C(13)	0.3042 (3)	0.2419 (2)	0.0059 (2)	0.038 (1)
C(14)	0.1762 (4)	0.2508 (3)	-0.0240 (3)	0.051 (1)
C(15)	0.1831 (4)	0.2788 (3)	-0.1403 (3)	0.061 (2)
C(16)	0.3150 (5)	0.2997 (3)	-0.2284 (3)	0.070 (2)
C(17)	0.4416 (5)	0.2880 (3)	-0.2011 (3)	0.068 (2)
C(18)	0.4367 (4)	0.2601 (3)	-0.0843 (3)	0.054 (1)

$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \cdot a_i \cdot a_j$$

C(19)	0.3667 (3)	0.2776 (3)	0.4355 (3)	0.046 (1)
C(20)	0.4413 (4)	0.3766 (3)	0.4050 (3)	0.061 (2)
C(21)	0.5735 (4)	0.3754 (3)	0.4254 (3)	0.065 (2)
C(22)	0.6277 (4)	0.2734 (3)	0.4781 (3)	0.057 (2)
C(23)	0.5578 (5)	0.1748 (3)	0.5080 (3)	0.070 (2)
C(24)	0.4281 (4)	0.1758 (3)	0.4866 (3)	0.062 (2)
C(25)†	0.2293 (6)	0.5477 (6)	0.1891 (9)	0.062 (2)
C(26)†	0.1847 (6)	0.4996 (6)	0.1090 (9)	0.059 (2)
C(27)†	0.0388 (6)	0.4676 (6)	0.1693 (9)	0.065 (2)
C(28)†	−0.0067 (6)	0.4959 (6)	0.2865 (9)	0.073 (2)
C(29)†	0.1110 (6)	0.5454 (6)	0.2988 (9)	0.067 (3)
C(25′)†	0.2229 (5)	0.5351 (7)	0.1447 (8)	0.070 (2)
C(26′)†	0.1171 (5)	0.4826 (7)	0.1190 (8)	0.056 (2)
C(27′)†	−0.0073 (5)	0.4685 (7)	0.2240 (8)	0.057 (2)
C(28′)†	0.0216 (5)	0.5122 (7)	0.3147 (8)	0.061 (2)
C(29′)†	0.1639 (5)	0.5534 (7)	0.2657 (8)	0.058 (2)

† Site occupancy of 0.5.

Table 2. Selected geometric parameters (Å, °) in (1) and a comparison with those of related compounds (2) and (3)

	(1)	(2)	(3)
Cp—Ni*	1.763 (1)	1.748 (4)	1.748 (4)
Ni—P	2.144 (1)	2.139 (1)	2.136 (1)
Ni—S	2.190 (1)	2.192 (1)	
Cp—Ni—S	132.3 (1)	133.0 (4)	
Cp—Ni—Se			132.3 (2)
Cp—Ni—P	135.3 (5)	136.4 (5)	136.4 (5)
P—Ni—S	92.4 (1)	90.5 (1)	
P—Ni—Se			91.4 (1)
Other selected geometric parameters in (1)			
Ni—C(25)	2.146 (6)	Ni—C(26)	2.103 (9)
Ni—C(27)	2.107 (8)	Ni—C(28)	2.153 (5)
Ni—C(29)	2.177 (7)	Ni—C(25′)	2.142 (7)
Ni—C(26′)	2.130 (8)	Ni—C(27′)	2.139 (6)
Ni—C(28′)	2.157 (7)	Ni—C(29′)	2.159 (8)
P—C(1)	1.832 (3)	P—C(7)	1.831 (3)
P—C(13)	1.831 (3)	S—C(19)	1.764 (4)
Cl—C(22)	1.753 (4)		
Ni—P—C(7)	112.0 (1)	Ni—P—C(13)	113.0 (1)
C(1)—P—C(7)	107.0 (1)	Ni—S—C(19)	111.5 (1)
C(1)—P—C(13)	100.6 (1)	C(7)—P—C(13)	104.5 (1)
Ni—P—C(1)	118.3 (1)		

* Cp represents the centroid of the cyclopentadienyl group.

In the refinement, the five C atoms of each cyclopentadienyl group were treated as a rigid body, with isotropic atomic displacement parameters and no H atoms attached.

Data collection: *SHELXTL-Plus* (Sheldrick, 1990). Cell refinement: *SHELXTL-Plus*. Data reduction: *SHELXTL-Plus*. Program(s) used to solve structure: *SHELXTL-Plus*. Program(s) used to refine structure: *SHELXTL-Plus*. Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: *SHELXTL-Plus*.

This work was supported by a grant to JD from the International Foundation for Science (grant No. F/1954-1).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HA1150). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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An Mo₂(CO)₄ (Mo≡Mo) Fragment Stabilized by a Tripod Ligand

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Abstract

Tetracarbonyl-1 κ^2 C;2 κ^2 C-bis[3,4(η^5)-cyclopentadienyl]-hexakis- μ -dimethylphosphito-1:3 κ^6 O:P;2:4 κ^6 O:P-dicobaltdimolybdenum(I)(Mo—Mo), [Mo(CO)₂{Co(C₅H₅)(C₂H₆O₃P)₃}]₂, a binuclear metal complex of type L₂Mo₂(CO)₄ (L is a tripod ligand), shows central Mo≡Mo triple bond lengths of 2.467 (1) and 2.468 (1) Å in the two independent molecules. The structure agrees very well with that of a related tungsten complex. The coordination of the central Mo atoms is distorted octahedral with acute Mo—Mo—C angles. All twelve Mo—O—P—Co fragments are synperiplanar, with Co—P bond lengths ranging from 2.152 (2) to 2.171 (1) Å.

Comment

The (η^5 -cyclopentadienyl)tris(dimethylphosphito)cobaltate(1−) anion, which is itself a half-sandwich complex, has a strong tendency to act as an O,O,O-tripod ligand using its three P=O groups and forms stable complexes with many metal ions (Kläui, 1990). Its structure has been studied thoroughly, for example, by crystal structure analysis of its Na and Cs salts (Kläui, Matt, Balegroune & Grandjean, 1991; Englert, Kläui & Weber-Schuster, 1992). We have determined the structure of a binuclear Mo complex, (I), in which two LMo(CO)₂ fragments [L = Co(C₅H₅)(C₂H₆O₃P)₃] are connected by an Mo≡Mo triple bond.